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COMPLEXES OF THE TRANSITION METALS WITH PHOSPHINES, ARSINES, AND STIBINES

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I. Introduction*

Just over a century ago Hofmann (263) prepared complexes of platinum and gold containing triethyl-phosphine, -arsine, and -stibine. In 1870

* Abbreviations used: X = Cl, Br, I (or sometimes other anions); M = metal; E = P, As, or Sb; R = alkyl or aryl; L = neutral ligand; dias = *o*-phenylenebisdimethyl-arsine; diphosphine = ditertiary phosphine; am = amine; en = ethylenediamine; Me = methyl; Et = ethyl; Pr = propyl; Bu = butyl; Pe = pentyl; All = allyl; Am = amyl; Cy = cyclohexyl; Bz = benzyl; Ph = phenyl.

Cahours and Gal (60-62) reported complexes of palladium, platinum, and gold with tertiary phosphines and arsines, which may be correctly formulated from their analyses. This was the start of a field of chemistry which has since expanded enormously, especially during the last decade. Complexes have now been prepared from salts of most transition metals and many other types of complex (e.g., derivatives of metal carbonyls) have also been obtained.

Tertiary phosphines, arsines, and stibines show many properties as ligands which distinguish them from amines. They have a marked tendency to form nonionic complexes readily soluble in organic solvents, in contrast to the saltlike complexes formed by ammonia and amines. The relative coordinating affinities of ligand atoms from Group V have been considered by Ahrlund and associates (9). A modified form of their classification of the transition elements is given in Fig. 1. To the right of the dividing line

Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Hf	Ta	W	Re	Os	Ir	Pt	Au

FIG. 1. Classification of the transition elements.

we have elements of class (b), which in their normal oxidation states form complexes in which the coordinating affinities of the donor atom lie in the sequence $N < P > As > Sb > Bi$. All these metals form stable phosphine complexes, and some form somewhat less stable arsine complexes and much less stable stibine complexes. To the left are the elements of class (a) character, where the sequence tends to change to $N > P > As > Sb > Bi$. The boundary is, however, not a sharp one and this classification is necessarily approximate. More definite is the tendency to form the most stable phosphine complexes along the diagonal toward platinum and gold.

Quantitative work in support of the above classification is difficult but nevertheless requires extension. One comparison shows the affinities of a set of ligands toward $Ag(I)$ ions to be in the order phosphine $>$ arsine $>$ amine (10). It is relevant also that the ligand field strength of tripropylphosphine is higher than that of tripropylamine or piperidine in a series of $Pt(II)$ complexes (80).

The fact that stable phosphine complexes are derived mainly from salts of elements to the right of the transition series is due to the character of the ligand. Phosphines act as σ -bond donors and π -bond acceptors, the vacant $3d$ orbitals of the phosphorus being capable of interaction with filled nonbonding d orbitals of a transition metal. In many cases the acceptor

character may be at least as important as the donor character. For example, stable complexes may be obtained from PF_3 , where much reduced donor properties are more than compensated by the increased electron affinity of the vacant d orbitals of the phosphorus. Because of the extent of the π -bonding, PF_3 shows even greater similarity to carbon monoxide than the tertiary phosphines as ligands (131). The high ligand-field strength of tertiary phosphines ensures a large energy difference between the low energy and high energy d orbitals of the metal. Generally the most stable complexes are those in which the metal has its low energy orbitals completely occupied by electrons, and its high energy orbitals vacant. Further, the energy difference should be sufficient to prohibit promotion of electrons from the low energy to the high energy orbitals.

Group IV (d^0) and Group V (d^1) elements can have little or no ligand-field stabilization energy, and the ligand-metal bonds have almost entirely σ character. Coordination with elements such as these, having empty non-bonding d orbitals, will therefore depend more upon the basicity of the ligand, and until recently it was thought that ligands more electronegative than those with Group VB ligand atoms were necessary. It has now been found that in many instances complex formation takes place, provided that a reaction medium with minimum donor capacity is used. This is an important observation to be remembered in any attempted preparation of complexes.

The stabilizing effect of phosphine ligands has been utilized in the preparation of a wide range of stable hydrido- and organometallic compounds where, due to the high ligand-field strengths of hydrogen and organic groups (93), the ligand-field stabilization energy is even further enhanced. Another application, particularly marked when using chelating diphosphine or diarsine ligands, lies in the stabilization of a large number of oxidation states for many transition metals. With the lower oxidation states the reducing properties of the ligands are an advantage, but in higher oxidation states of the metals any tendency toward dissociation will result in decomposition, since such complexes contain both an oxidizing and a reducing agent. Stable phosphine complexes have been used in kinetic studies (36), which are required to test current theories on reaction mechanisms of metal complexes and on metal-ligand bonding. This important question of the nature of the metal-ligand bond has also been studied in various other ways involving the examination of complexes having phosphine or arsine ligands.

All the above functions of the ligands will be evident from the present survey in which the transition metals are considered according to their position in the Periodic Table.

II. Group IV

A. TITANIUM

Titanous salts do not readily form complexes with phosphines and arsines due to the high polarizing power of Ti(III). The complexes $[\text{TiCl}_3(\text{Et}_2\text{PC}_2\text{H}_4\text{PEt}_2)]$ (97) and $[\text{TiX}_3 \cdot \text{dias} \cdot \text{H}_2\text{O}]$ ($\text{X} = \text{Cl}, \text{Br}$; dias = *o*-phenylenebisdimethyl-arsine) (421) have been described, although it has been suggested (138) that the last are in fact complexes of Ti(IV).

Complexes of Ti(IV) are somewhat more stable, but nevertheless are decomposed by air or water. With monodentate ligands, the red complexes $[\text{TiCl}_4(\text{PR}_3)_2]$ ($\text{R} = \text{Et}$ or Ph) (97) and $[\text{TiCl}_3\text{MePPh}_3]$ (38) have been prepared. Investigation of further complexes of the latter type, with determination of their configuration, would be of considerable interest. Using the bidentate ligands tertiary diarsine or diphosphine, the complexes $[\text{TiX}_4\text{dias}]$ (138, 139) and $[\text{TiCl}_4(\text{diphosphine})]$ (97) are readily prepared in an inert solvent. The 1:1 dias complexes react with further ligand to form $[\text{TiX}_4(\text{dias})_2]$. A preliminary report on the crystal structure of $[\text{TiCl}_4(\text{dias})_2]$ shows it to be an eight-coordinate dodecahedral complex with the atoms forming two interpenetrating tetrahedra (138). This is the first example of a coordination number eight for a first-row transition element.

Attempted preparation of a complex of Ti(0) by reduction of $[\text{TiCl}_4(\text{Me}_2\text{PC}_2\text{H}_4\text{PMe}_2)]$ in the presence of excess of the diphosphine was unsuccessful (125).

B. ZIRCONIUM AND HAFNIUM

ZrCl_4 and HfCl_4 complex with dias in acetone medium to give $[\text{ZrCl}_4(\text{dias})_2]$ and $[\text{HfCl}_4(\text{dias})_2]$, both isostructural with the titanium analogue (138, 139).

The scarcity of complexes of Group IV metals with monophosphine or monoarsine ligands may not be significant, since preparative conditions, particularly in respect to reaction medium, are obviously extremely critical.

III. Group V

Very little work has been published on vanadium halide complexes, presumably due to difficulties in preparing characterizable products. Issleib and Bohn (275) report that triphenyl-phosphine coordinates with VCl_3 to give compounds of varying atomic ratios, possibly including the dimeric $[\text{VCl}_3\text{PPh}_3]_2$. Triethyl- and tripropyl-phosphines, on the other hand, form the red complexes $[\text{VCl}_3(\text{PR}_3)_2]$, which have a magnetic moment corresponding to two unpaired spins. In carbon tetrachloride solution,

dias coordinates with VCl_4 to give the orange complex $[\text{VCl}_4(\text{dias})_2]$. A magnetic moment of 1.8 B.M. is in keeping with this formulation, and the complex has been shown to be isostructural with the analogous complexes of Group IV metals (138, 139).

Several interesting complexes of V(0) have recently been reported. Vanadium hexacarbonyl reacts with triphenyl-phosphine to give the orange complex $[\text{V}(\text{CO})_4(\text{PPh}_3)_2]$, which like the parent carbonyl is paramagnetic ($\mu = 1.78$ B.M.) (253, 442). This complex is unstable in air; the analogous arsine and stibine complexes are even less stable and are pyrophoric. When the reaction of triphenyl-phosphine is carried out in ether the product is $[\text{V}(\text{Et}_2\text{O})_6][\text{V}(\text{CO})_5\text{PPh}_3]_2$ (253). Reduction of $[\text{V}(\text{CO})_4(\text{PPh}_3)_2]$ with sodium amalgam gives not the expected $[\text{V}(\text{CO})_4(\text{PPh}_3)_2]^-$, but the $[\text{V}(\text{CO})_5\text{PPh}_3]^-$ anion. This redistribution of ligands is assumed to be due to steric factors. Nitric oxide displaces one triphenyl-phosphine molecule from $[\text{V}(\text{CO})_4(\text{PPh}_3)_2]$ to give the diamagnetic $[\text{V}(\text{CO})_4(\text{NO})\text{PPh}_3]$ (443). This reaction suggests that the four carbonyls exist as a stable planar entity with the other two ligands in *trans* positions. The simplicity of the infrared spectra of the two complexes also supports this configuration.

The complex $[\text{V}(\text{Me}_2\text{PC}_2\text{H}_4\text{PMe}_2)_3]$ is prepared by reduction of VCl_3 in the presence of the diphosphine (123, 125). A magnetic moment corresponding to one unpaired electron confirms the analogy to $[\text{V}(\text{CO})_6]$.

No complexes of niobium and tantalum are known.

IV. Group VI

A. CHROMIUM

1. Halide Complexes

Chromous chloride with trialkyl-phosphines gives complexes of the type $[\text{CrCl}_2\text{PR}_3]$. Issleib and Fröhlich (279) suggest that the triethyl-phosphine complex is polymeric and that the unstable complex $[\text{CrCl}_2(\text{PEt}_3)_2]$ is first formed in solution. Complexes of methyl-phosphine and dimethyl-phosphine are less stable than those of trimethyl-phosphine (44).

Chromic chloride with trialkyl-phosphines forms the dimeric chloro-bridged complexes $[\text{CrCl}_3(\text{PR}_3)_2]_2$. Triphenyl-phosphine or tricyclohexyl-phosphine does not react with chromic chloride in a solvent, but by using the molten phosphine the violet complexes $[\text{CrCl}_3\text{PR}_3]$ are obtained (279). With diethyl-phosphine the monomeric octahedral complex $[\text{CrCl}_3(\text{PHEt}_2)_3]$ is formed (278). Similarly, phenyl-phosphine forms $[\text{CrCl}_3(\text{PH}_2\text{Ph})_3]$ (287) although, in contrast, diphenyl-phosphine gives no complex with chromic chloride (286).

Reaction of trialkyl-phosphines with $\text{K}_3[\text{Cr}(\text{SCN})_6]$ produces $[\text{R}_3\text{PH}]$ -

$[\text{Cr}(\text{SCN})_4(\text{PR}_3)_2]$, analogous to Reinecke's salt obtained with ammonia (284).

With the bidentate ligand dias, no chromous complexes have been isolated (59, 385). Chromic halides readily form the complexes $[\text{CrX}_2(\text{dias})_2]$ - $[\text{CrX}_4\text{dias}]$ in nonaqueous solvent, and solvated monomeric complexes are also known, e.g., $[\text{CrCl}_3(\text{dias})\text{H}_2\text{O}]$ (385).

Chromic chloride is reduced, by sodium naphthalenide in tetrahydrofuran in the presence of tetramethylethane-diphosphine, to give the zero-valent complex $[\text{Cr}(\text{Me}_2\text{PC}_2\text{H}_4\text{PMe}_2)_3]$ (123, 125).

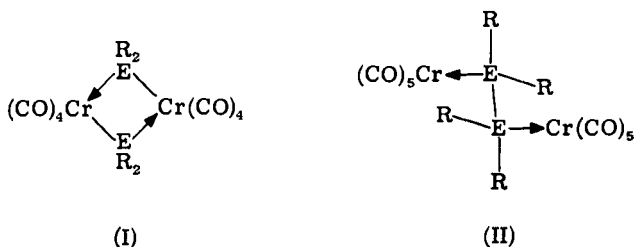
2. Carbonyl Complexes

Chromium hexacarbonyl, on heating at reflux in diglyme with triphenyl-phosphine, -arsine, or-stibine, forms a monosubstituted complex $[\text{Cr}(\text{CO})_5(\text{EPh}_3)]$ (339). Some disubstitution also takes place (311), but $[\text{Cr}(\text{CO})_4(\text{PPh}_3)_2]$ is best formed directly at 140–160° in a sealed tube (252) or via $[\text{Cr}(\text{CO})_5\text{NH}_3]$ under milder conditions (42). A single strong carbonyl absorption in the infrared spectrum of the disubstituted derivative suggests the phosphines to be in *trans* positions. The complex $[\text{Cr}(\text{CO})_4(\text{PEt}_2\text{Ph})_2]$ (124), however, has a *cis*-phosphorus configuration as indicated by a dipole moment of ca. 6 Debye units, although there is evidence of some isomerization in solution.

Suitable intermediates for the preparation of trisubstituted derivatives are complexes of the type $[\text{Cr}(\pi\text{-toluene})(\text{CO})_3]$, from which $[\text{Cr}(\text{CO})_3(\text{AsMe}_2\text{Ph})_3]$ is readily obtained (361). A mixture of products is obtained by partial displacement of the ammonia from $[\text{Cr}(\text{CO})_3(\text{NH}_3)_3]$ by triphenyl-phosphine (227).

With the chelating ligands dias (280, 282) and ditertiary phosphines (95), replacement of two carbonyl groups to give $[\text{Cr}(\text{CO})_4(\text{chelate})]$ is effected at ca. 150°. Under more vigorous conditions (200–240°) four carbonyl groups are expelled, resulting in formation of $[\text{Cr}(\text{CO})_2(\text{chelate})_2]$. The complexes $[\text{Cr}(\text{CO})_2(\text{diphosphine})_2]$ are more readily prepared from π -mesitylene chromium tricarbonyl and exhibit *cis-trans* isomerism. Zingales and Canziani (459) report that $[\text{Cr}_2(\text{CO})_6(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_3]$ is also formed in a reaction of this type.

The diphosphines and diarsines, $\text{R}_2\text{E}\cdot\text{ER}_2$ (E = P or As, R = alkyl or aryl), form two products on reaction with chromium hexacarbonyl. High temperatures (240–260°) favor the formation of highly colored (orange to red) phosphido- and arsenido-bridged carbonyls of structure (I); metal-metal bonding is probable since the complexes are diamagnetic. Less vigorous conditions often result in the formation of complexes of structure (II), which in contrast are weakly colored (115).



B. MOLYBDENUM AND TUNGSTEN

Due to the polymeric and consequently unreactive nature of molybdenum and tungsten halides, halide complexes are not readily prepared. The complexes $[\text{Mo}^{\text{VI}}\text{X}_2(\text{dias})_2]$ have been obtained, starting from $[\text{Mo}^{\text{VI}}\text{Cl}_6]^{3-}$, and are isomorphous with the corresponding iron, technetium, and rhenium complexes (304).

It may be mentioned here that uranium tetrachloride and tetrabromide readily form complexes of the type $[\text{UX}_4(\text{PET}_3)_2]$ (12).

Carbonyl complexes are formed in a similar way to those of chromium, but they are generally more stable. Examples of mono-, di-, and trisubstituted derivatives have been prepared (see Table I). *Cis*- and *trans*- $[\text{Mo}(\text{CO})_4(\text{PET}_3)_2]$ have been isolated and characterized by their infrared spectra (398); $[\text{W}(\text{CO})_4(\text{PET}_3)_2]$ is more prone to isomerization, but a preliminary crystallographic study of the *trans* complex confirms the octahedral configuration (265). Trisubstituted derivatives of the type *cis*- $[\text{Mo}(\text{CO})_3(\text{PR}_3)_3]$ have been prepared by direct substitution (399), and a general method of preparation for the complexes $[\text{Mo}(\text{CO})_3\text{L}_3]$ is by treatment of $[\text{Mo}(\text{CO})_3(\text{cycloheptatriene})]$ with the phosphine, arsine, or stibine ligand (1). Another precursor which has been used is $[\text{Mo}_2(\text{CO})_6(\text{OH})_3\text{H}_3]$ (234).

The complexes $[\text{M}(\text{CO})_4(\text{chelate})]$ and $[\text{M}(\text{CO})_2(\text{chelate})_2]$, where $\text{M} = \text{Mo}$ or W , and chelate = dias (362, 364), $\text{Ph}_2\text{AsC}_2\text{H}_4\text{AsPh}_2$ (460), or ditertiary phosphine (124), are similar to their chromium analogues, but the bisdiphosphine complexes differ by existing only in the *cis* form. Again as with chromium, phosphido- and arsenido-bridged carbonyls (115) and diphosphine and diarsine binuclear derivatives may be obtained (115, 459, 460). The increasing difficulty found in replacing consecutive pairs of carbonyl groups by bidentate ligands and the tendency to form binuclear complexes under certain conditions are due to the increased strength of the metal-carbonyl bonds in the *trans* positions (419).

The action of halogens on the dias-molybdenum carbonyl complexes yields carbonyl halide derivatives (365). Of particular interest is the seven-

TABLE I
SUBSTITUTION PRODUCTS OF Cr, Mo, AND W CARBONYLS
WITH MONODENTATE LIGANDS

Complex	Reference	Color	M.p. (°C)	Dipole moment (D)
[Cr(CO) ₅ PPh ₃]	339	Pale yellow	127-128	—
[Cr(CO) ₅ AsPh ₃]	339	Yellow	135	—
[Cr(CO) ₅ SbPh ₃]	339	Yellow	147-149	—
[Cr(CO) ₅ PBu ₃]	311	Chartreuse	Liquid	—
[Mo(CO) ₅ PPh ₃]	339	White	138-139	—
[Mo(CO) ₅ PEt ₃]	398	—	Liquid	—
[Mo(CO) ₅ AsEt ₃]	51	—	Liquid	—
[W(CO) ₅ PPh ₃]	339	Pale yellow	146-147	—
<i>trans</i> -[Cr(CO) ₄ (PPh ₃) ₂]	252, 311	Yellow	251-252	—
<i>cis</i> -[Cr(CO) ₄ (PEt ₂ Ph) ₂]	124	Pale yellow	95	ca. 5.90
<i>trans</i> -[Mo(CO) ₄ (PPh ₃) ₂]	252	Yellow	273-275 d ^a	—
<i>cis</i> -[Mo(CO) ₄ (PEt ₂ Ph) ₂]	124	Buff	99	6.95
<i>cis</i> -[Mo(CO) ₄ (PEt ₃) ₂]	398	White	73	—
<i>trans</i> -[Mo(CO) ₄ (PEt ₃) ₂]	398	Yellow	58	—
<i>cis</i> -[Mo(CO) ₄ (AsEt ₃) ₂]	51	Pale yellow	—	—
<i>cis</i> -[Mo(CO) ₄ (AsPh ₃) ₂]	51	Yellow	—	—
<i>cis</i> -[W(CO) ₄ (PEt ₃) ₂]	265, 398	—	—	—
<i>trans</i> -[W(CO) ₄ (PEt ₃) ₂]				
<i>cis</i> -[W(CO) ₄ (PEt ₂ Ph) ₂]	124	Pale yellow	104	7.25
<i>trans</i> -[W(CO) ₄ (PPh ₃) ₂]	252	Yellow	292-294 d	—
[Cr(CO) ₃ (PPh ₃) ₃]	361	—	175-177	—
[Cr(CO) ₃ (AsMe ₂ Ph) ₃]	361	Yellow	98-100	—
<i>cis</i> -[Mo(CO) ₃ (PPh ₃) ₃]	1	Yellow	160 d	—
<i>cis</i> -[Mo(CO) ₃ (AsPh ₃) ₃]	1	Yellow	170 d	—
<i>cis</i> -[Mo(CO) ₃ (SbPh ₃) ₃]	1	Yellow	220 d	—
<i>cis</i> -[Mo(CO) ₃ (PR ₃) ₃]	399	—	—	—

^a Symbol d = decomposed.

coordinate complex [MoBr₂(CO)₃dias], which may be further oxidized to the Mo(IV) complex [MoBr₄dias].

Although total substitution of Group VI carbonyls by direct action of phosphines or arsines cannot be effected, products of the formula [M(diphosphine)₃] have been obtained by other methods. For example, [Mo(Me₂PC₂H₄PMc₂)₃] results from treatment of di- π -benzenemolybdenum with the diphosphine (122), and [W(Me₂PC₂H₄PMc₂)₃] is prepared similarly to the chromium analogue (123, 125).

Complexes of the chromium group thus provide excellent exemplification of the general trends of the A subgroups. That is to say: (1) the difference between first and second members is very much greater than

between second and third; (2) on descending the series, compounds of the higher valency states are more stable; (3) on descending, the tendency to ionization of compounds of lower valency states is much smaller.

V. Group VII

A. MANGANESE

1. Halide Complexes

Most known complexes of manganese(II) have a polar metal-ligand bond involving ligands of high electronegativity. Phosphine and arsine complexes are therefore not expected to be very stable, particularly in the presence of donor solvents. There are many recorded examples of unsuccessful attempts to prepare complexes. The manganous ion does not coordinate with dias in water, alcohol, or acetone, although complexes are formed in dioxane (59, 386). The magnetic moments of the octahedral products, $[\text{MnX}_2(\text{dias})_2]$, show the presence of five unpaired electrons. Manganous halides complex with triphenyl-phosphine or -arsine in tetrahydrofuran to give $[\text{MnX}_2(\text{EPh}_3)_2]$, which are spin-free and presumably tetrahedral (359); MnI_2 also forms this type of product on reaction with molten triphenyl-phosphine. In acetone solution manganous halides form $[\text{MnX}_4][\text{PPh}_3\text{H}]_2$ and $[\text{MnX}_4][\text{AsPh}_4]_2$ (360).

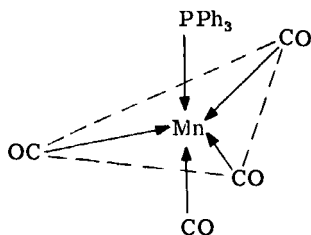
Manganic salts are readily reduced by phosphines and arsines, but manganic acetate in the presence of perchloric acid and hydrogen chloride has been induced to form the spin-free complex $[\text{MnCl}_2(\text{dias})\text{H}_2\text{O}]\text{ClO}_4$ (386).

2. Carbonyl Complexes

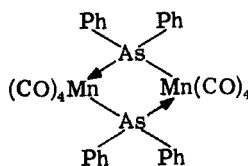
Triphenyl-phosphine and dimanganese decacarbonyl react with expulsion of carbon monoxide and formation of $[\text{Mn}(\text{CO})_4\text{PPh}_3]$ (26, 239, 259). This complex is monomeric and paramagnetic ($\mu_{\text{eff}} = 1.84$ B.M.) and infrared evidence suggests a trigonal bipyramid structure (III). Triethyl-phosphine and triphenyl-arsine and -stibine give analogous complexes (239), but at a slightly higher temperature (139° vs. 120°) triphenyl-arsine gives the very stable diamagnetic complex $[\text{MnAsPh}_2(\text{CO})_4]_2$ with the probable bridged structure (IV) (298). Tricyclohexyl-phosphine is apparently the only ligand of this type giving the expected dimeric product, $[\text{Mn}(\text{CO})_4\text{PCy}_3]_2$ (236). The phosphorus analogue of (IV) is obtained by reaction of diphenylchloro-phosphine with $\text{Na}[\text{Mn}(\text{CO})_5]$ (200). Another product in the same class is $[\text{Mn}_2(\text{CO})_8\text{P}(\text{CF}_3)_2\text{I}]$ (175) with phosphorus and iodine bridging atoms.

Dimanganese decacarbonyl and dias form $[\text{Mn}(\text{CO})_3\text{dias}]_2$ at 130° ,

which on further heating splits to the monomeric $[\text{Mn}(\text{CO})_5\text{dias}]$ (177, 383). The ditertiary phosphine $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ behaves differently than dias, since the product is $[\text{Mn}_2(\text{CO})_8(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]$ (240). This may mean that the diphosphine is not chelating; a comparison with other diphosphines would be of interest. The carbon monoxide of π -cyclopentadienylmanganese tricarbonyl may be displaced by triphenyl-phosphine (420).



(III)



(IV)

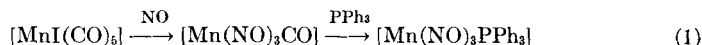
The complexes $[\text{Mn}(\text{CO})_4\text{PR}_3]$ are reduced by sodium in tetrahydrofuran to the carbonyl manganates (-1), $\text{Na}[\text{Mn}(\text{CO})_4\text{PR}_3]$. These provide useful intermediates for the preparation of alkyl, acyl, and hydrido derivatives. For example, $\text{Na}[\text{Mn}(\text{CO})_4\text{PPh}_3]$ yields $[\text{MnMe}(\text{CO})_4\text{PPh}_3]$, $[\text{Mn}(\text{COMe})(\text{CO})_4\text{PPh}_3]$, $[\text{Mn}(\text{SnPh}_3)(\text{CO})_4\text{PPh}_3]$, or $[\text{MnH}(\text{CO})_4\text{PPh}_3]$ on treatment with methyl iodide, acetyl chloride, triphenylstannic chloride, or phosphoric acid, respectively (197, 235, 236).

3. Carbonyl Halide Complexes

The carbonyl halides $[\text{MnX}(\text{CO})_5]$ and $[\text{MnX}(\text{CO})_4]_2$ form complexes of the type $[\text{MnX}(\text{CO})_3\text{L}_2]$ (where $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{or SbPh}_3$) (2, 254). Replacement with triphenyl-phosphine is more facile than with triphenylarsine or -stibine, even though there is little difference in double bonding due to the ligands, as judged by carbonyl frequencies (260). The monosubstituted products $[\text{MnX}(\text{CO})_4\text{L}]$ may be obtained (13, 230) under different conditions. Complexes of the type $[\text{MnCl}(\text{CO})_4\text{PR}_3]$ are also formed by the action of carbon tetrachloride on $[\text{MnH}(\text{CO})_4\text{PR}_3]$ or by oxidation of $[\text{Mn}(\text{CO})_4\text{PR}_3]$ with chlorine (236). The dias-substituted carbonyls, mentioned earlier, are both oxidized with bromine to give $[\text{MnBr}_2(\text{CO})_2\text{dias}]$, but iodine behaves differently and a diamagnetic manganese(I) complex, $[\text{MnI}(\text{CO})_3\text{dias}]$, is produced (383). Complexes of the type $[\text{MnX}(\text{CO})_3\text{chelate}]$ (chelate = dias or diphosphine) may also be obtained directly (390).

4. Nitrosyl Complexes

Both $[\text{Mn}(\text{CO})_4\text{PPh}_3]$ and $[\text{MnI}(\text{CO})_4\text{PPh}_3]$ on treatment with nitric oxide yield the dark green $[\text{Mn}(\text{NO})_3\text{PPh}_3]$ (230). An intermediate product of the reaction, $[\text{Mn}(\text{CO})_3(\text{NO})\text{PPh}_3]$, can also be isolated (299). The trinitrosyl complex may alternatively be prepared by the following scheme (23):



Reduction of $[\text{MnBr}(\text{NO})_2(\text{PPh}_3)_2]$ with sodium borohydride produces $[\text{MnH}(\text{NO})_2(\text{PPh}_3)_2]$ (257).

B. TECHNETIUM

Due to the limited availability of compounds of this element, comparatively little complex chemistry has yet been investigated. Fergusson and Nyholm (180, 181), using remarkably small quantities of material, have prepared Tc(III) complexes, $[\text{TcX}_2(\text{dias})_2]\text{X}$, which may be reversibly reduced to the Tc(II) complexes $[\text{TcX}_2(\text{dias})_2]$ and oxidized to the Tc(V) complex $[\text{TcCl}_4(\text{dias})]\text{Cl}$. The Tc(II) complexes differ from their manganese analogues in being spin-paired.

C. RHENIUM

1. Halide Complexes

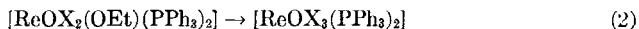
Some confusion exists in the literature on this subject because of the failure to recognize oxygen in complexes obtained when using a perrhenate or rhenium heptoxide as starting material.

a. Re(II). The complexes formed by reacting together perrhenic acid, triphenyl-phosphine, hydrazine, and a hydrohalic acid were originally formulated $[\text{ReX}_2(\text{PPh}_3)_2]$ (187). They have since been reformulated as $[\text{Re}^{\text{VO}}(\text{OEt})\text{X}_2(\text{PPh}_3)_2]$ (103, 308) or $[\text{Re}^{\text{V}}\text{NX}_2(\text{PPh}_3)_2]$ (81, 82), the constitution varying according to the precise reaction conditions. The so-called $[\text{ReI}_2(\text{PPh}_3)_2]$ further coordinates with isocyanides (186).

The complexes thought to be $[\text{ReX}_2(\text{PPh}_3)_2]$ have been reduced with NaBH_4 (any oxygen present originally may thus have been removed) to $[\text{ReH}_3(\text{PPh}_3)_2(\text{EtOH})_2]$, which with triphenyl-phosphine yields $[\text{ReH}_3(\text{PPh}_3)_4]$ (188, 320).

Like their technetium analogues, the complexes $[\text{ReX}_2(\text{dias})_2]$ are produced by reduction of $[\text{ReX}_2(\text{dias})_2]\text{X}$ (160). Complexes of Re(II) with diphosphine (103) and tri- and tetra-arsine (340) ligands have also been described.

b. Re(III). Rhenium trihalides have been reported to coordinate with one, two, and three molecules of tertiary phosphine. $[\text{ReCl}_3\text{PPh}_3]$ (147, 148, 187) and $[\text{ReCl}_3(\text{PEt}_2\text{Ph})]$ (103) are of uncertain structure. The supposed oxidation of $[\text{ReX}_2(\text{PPh}_3)_2]$ to $[\text{ReX}_3(\text{PPh}_3)_2]$ (187) is really the reaction:

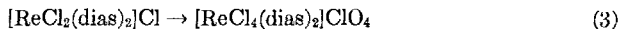


These rhenium(V) oxytrihalide complexes are also readily formed from perrhenic acid (103, 308). A further correction in this field lies in the formulation of the product from $[\text{ReCl}_3(\text{PPh}_3)]$ on treatment with triphenylphosphine and chlorine as $[\text{ReCl}_3(\text{OPPh}_3)_2]$ (308), and not $[\text{ReCl}_3(\text{PPh}_3)_2]$ (147). The complex $[\text{ReCl}_3\text{PPh}_3]$ reacts with acetylenes and olefins to give products of the type $[\text{ReCl}(\text{acetylene})_2\text{PPh}_3]$ (146).

The only six-coordinate Re(III) complex with monodentate ligands is $[\text{ReCl}_3(\text{PEt}_2\text{Ph})_3]$ (103). Octahedral complexes of the types $[\text{ReCl}_2(\text{dias})_2]\text{Cl}$ (179) and $[\text{ReX}_2(\text{dias})_2](\text{ClO}_4)$ (160) are readily obtained and a five-coordinate complex $[\text{ReCl}_3(\text{dias})]$ has been mentioned (380).

c. Re(IV). Rhenium tetraiodide has given the paramagnetic derivative $[\text{ReI}_4(\text{PPh}_3)_2]$ (147, 148). Complexes of the type $[\text{ReX}_4(\text{PPh}_3)_2]$ ($\mu = 3.84$ B.M.) are also obtained from $[\text{ReH}_3(\text{PPh}_3)_4]$ by treating with a halogen or a hydrohalide (188, 320).

d. Re(V). Complexes of the type $[\text{ReOX}_3(\text{PPh}_3)_2]$ have already been mentioned; the green isomer of $[\text{ReOCl}_3(\text{PEt}_2\text{Ph})_2]$ has been shown to have a *trans* octahedral configuration (174). The dias- Re(III) complexes may be oxidized to Re(V) complexes (179), e.g.,



Rhenium(V), in combination with tertiary phosphines as ligands, has a strong tendency to form multiple bonds to nitrogen. The formation of $[\text{ReNX}_2(\text{PPh}_3)_2]$ was described in Section V,C,1,a; tertiary phosphines containing aliphatic groups show a tendency to form six-coordinate rather than five-coordinate nitrides, e.g., $[\text{ReNCl}_2(\text{PEt}_2\text{Ph})_3]$ (81). Related imido complexes of the type $[\text{ReCl}_3(\text{NPh})(\text{PEt}_2\text{Ph})_2]$ are obtained by the reaction of an arylamine on the complexes $[\text{ReOX}_3(\text{PR}_3)_2]$ (81, 104).

2. Carbonyl Complexes

Prolonged treatment of $[\text{Re}_2(\text{CO})_{10}]$ with triphenylphosphine gives $[\text{Re}(\text{CO})_4\text{PPh}_3]_2$ (240). Rhenium carbonyl halides give the complexes $[\text{ReX}(\text{CO})_3\text{L}_2]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3$) (2) in the same way as the manganese compounds. One of these complexes had earlier been formulated as $[\text{Re}(\text{CO})_4(\text{PPh}_3)_2]\text{Cl}$ (255), but this seems unlikely to be correct since the reported value of conductivity was very low. Carbonyl halide complexes

have also been obtained by treatment of halide complexes with carbon monoxide under pressure. Even where the starting materials are incorrectly formulated, the reducing conditions (especially in the presence of copper) should eliminate any oxygen present, although there are a surprising number of products of different types. With increasingly vigorous conditions the so-called $[\text{ReX}_2(\text{PR}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}$) yields successively products formulated as $[\text{ReX}_2(\text{CO})(\text{PR}_3)_2]$, $[\text{ReX}(\text{CO})_2(\text{PR}_3)_2]$, and $[\text{ReX}(\text{CO})_3(\text{PR}_3)_2]$. In contrast $[\text{ReI}_2(\text{PPh}_3)_2]$ forms $[\text{ReI}(\text{CO})(\text{PPh}_3)_2]$ (185, 187).

VI. Group VIIIA

A. IRON

1. Halide Complexes

a. Fe(II). Jensen (291) showed that ferrous chloride did not complex with PET_3 , in contrast to cobalt(II) and nickel(II) chlorides which readily coordinate, in ethanol solution. Complexes of the type $[\text{FeX}_2(\text{PR}_3)_2]$ have since been prepared, but they tend to dissociate in solution and are particularly unstable in hydroxylic solvents. The series of colorless complexes $[\text{FeCl}_2(\text{phosphine})_2]$, where phosphine = PET_3 , PET_2Ph , PETPh_2 , and PPh_3 , prepared in benzene under nitrogen, have a spin-free tetrahedral configuration ($\mu_{\text{eff}} = \text{ca. } 5 \text{ B.M.}$), and the complexes containing the last two ligands are the most stable (49). A series of yellow complexes $[\text{FeX}_2(\text{PPh}_3)_2]$, prepared in ether or by fusion, may differ in having an octahedral bridged structure in the solid state (357).

The two known complexes of secondary phosphines with ferrous chloride provide an interesting contrast; $[\text{FeCl}_2(\text{PHCy}_2)_2]$ is colorless and tetrahedral like the tertiary phosphine complexes, but $[\text{FeCl}_2(\text{PHEt}_2)]$ is red and probably square-planar (278). Phenyl-phosphine forms the saltlike complexes $[\text{Fe}(\text{PH}_2\text{Ph})_4]\text{X}_2$ (287).

Chelating bidentate ligands form diamagnetic complexes of the type $[\text{FeX}_2(\text{dias})_2]$ (363, 370) and $[\text{FeCl}_2(\text{diphosphine})_2]$ (96) with a *trans* octahedral configuration. The structures of the complexes $[\text{FeBr}_2\{\text{Cy}_2\text{P}(\text{CH}_2)_n\text{PCy}_2\}]$ (280) have not been defined.

b. Fe(III). Ferric chloride with methyldiphenyl- or dimethyltolyl-arsine gives complexes which dissociate so readily in solution that their constitution is not certain (367); $2\text{FeCl}_3 \cdot 4\text{arsine}$ may be formulated $[\text{FeCl}_3(\text{arsine})_2]_2$ or $[\text{FeCl}_2(\text{arsine})_4][\text{FeCl}_4]$. In ethyl acetate, triphenyl-phosphine and -arsine give complexes of probable formula $[\text{FeCl}_3(\text{EPh}_3)_2]_2$, but with triphenyl-phosphine and ferric chloride in methanol the solvent is involved in reaction to form $[\text{PMePh}_3][\text{FeCl}_4]$ (358). Tricyclohexyl-phosphine behaves rather differently in forming $[\text{FeCl}_3(\text{PCy}_3)]$ (276).

Complexes of the type $[\text{FeX}_2(\text{chelate})_2][\text{FeX}_4]$ have been prepared, where chelate = dias (370) or a diphosphine (96). Ferric bromide also yields the complex $[\text{FeBr}_2(\text{dias})]\text{Br}$. Polydentate tertiary arsine ligands give the complexes $[\text{Fe}(\text{CNS})_3(\text{triarsine})]$ (21) and $[\text{FeCl}_2(\text{tetraarsine})][\text{FeCl}_4]$ (20).

c. *Fe(IV)*. This unusual valency state is exemplified by the complex $[\text{Fe}^{\text{IV}}\text{Cl}_2(\text{dias})_2][\text{Fe}^{\text{III}}\text{Cl}_4]_2$, prepared by oxidation of the ferric chloride-dias complex (382).

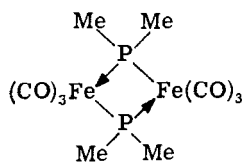
2. Carbonyl Complexes

Products of substitution from iron pentacarbonyl and triphenyl-phosphine and -stibine were first described by Reppe and Schweckendiek (30, 403), who mention $[\text{Fe}(\text{CO})_4\text{PPh}_3]$ and $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]$ as potential catalysts. The infrared spectra of these two complexes are entirely compatible with a trigonal bipyramidal structure (157), and both complexes are protonated in sulfuric acid (162). Other disubstituted products include $[\text{Fe}(\text{CO})_3(\text{SbCl}_3)_2]$ (449) and $[\text{Fe}(\text{CO})_3\text{dias}]$ (362, 363). Direct substitution of more than two carbon monoxide molecules by monodentate phosphine, arsine, or stibine ligands is not known, although $[\text{Fe}(\text{CO})(\text{dias})_2]$ may be prepared by using vigorous conditions. The use of $[\text{Fe}_3(\text{CO})_{12}]$ as starting material is preferred for the preparation of certain derivatives (162).

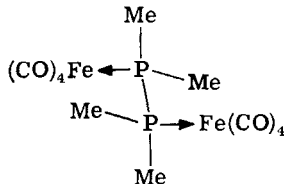
The trisubstituted derivative $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_3]$ is obtained, together with $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]$, on treatment of $[\text{Fe}(\text{CO})_3(\text{cycloheptatriene})]$ with triphenyl-phosphine (337). Other substituted carbonyl complexes include $[\text{Fe}(\text{CO})_2\text{PPh}_3(\text{tetracyclone})]$ (438), $[\text{FeI}(\text{C}_3\text{F}_7)(\text{CO})_3\text{PPh}_3]$ (397), and hydrocarbon derivatives (439).

Pentaphenyl-phosphole(L) forms the two compounds $[\text{Fe}(\text{CO})_4\text{L}]$ and $[\text{Fe}(\text{CO})_3\text{L}]$ in which L behaves, respectively, as a monodentate phosphine or a bidentate diene ligand (52). Another diene-carbonyl complex, $[\text{Fe}(\text{CO})_2(\text{cyclopentadiene})\text{PPh}_3]$, illustrates the stabilizing influence of the phosphine ligand (161).

Tetramethyl-diphosphine can be reacted with iron pentacarbonyl to yield either a phosphido-bridged (V) or a diphosphine-bridged (VI) product



(V)

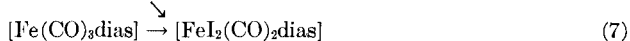
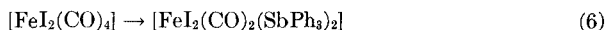


(VI)

(115). Tetraphenyl-diphosphine probably behaves similarly (33). There is an obvious parallel here with the reactions of Group VI metal carbonyls. The complex $[\text{FeI}(\text{CO})_3\text{P}(\text{CF}_3)_2]_2$ (175) may have a structure similar to (V), with iodine occupying the sixth coordination position rather than the metal-metal bonding probable in (V).

3. Carbonyl Halide Complexes

The three possible ways of preparing carbonyl halide complexes of Fe(II) have all been effected (49, 253, 363):



Treatment of $[\text{Fe}(\text{CO})_3\text{dias}]$ with a limited quantity of iodine produces a complex of Fe(I), $[\text{FeI}(\text{CO})_2\text{dias}]$ (363).

4. Nitrosyl Complexes

Although triphenyl-phosphine will displace both CO molecules from $[\text{Fe}(\text{NO})_2(\text{CO})_2]$ to form $[\text{Fe}(\text{NO})_2(\text{PPh}_3)_2]$ (402), triphenyl-arsine and -stibine may form only monosubstitution products (318, 341). Iron nitrosyl halides react with triphenyl-phosphine, giving complexes of the type $[\text{FeX}(\text{NO})_2\text{PPh}_3]$ (248).

5. Other Complexes

A study of iron complexes has provided three outstanding examples of the stabilizing effect of phosphine ligands.

The organometallic complex *trans*- $[\text{Fe}(\text{C}_6\text{Cl}_5)_2(\text{PEt}_2\text{Ph})_2]$ (112) is moderately stable; it dissociates less readily to give the free phosphine than the corresponding halide complex $[\text{FeCl}_2(\text{PEt}_2\text{Ph})_2]$. The stability of the hydrides *trans*- $[\text{FeHX}(\text{diphosphine})_2]$ and *trans*- $[\text{FeH}_2(\text{diphosphine})_2]$ (89, 96) is attributed to the large ligand-field splitting effects of the phosphine ligands and hydride ion. The only four-coordinate planar Fe(0) compound known is $[\text{Fe}(\text{Me}_2\text{PC}_2\text{H}_4\text{PMe}_2)_2]$ (125), prepared by reduction of *trans*- $[\text{FeCl}_2(\text{Me}_2\text{PC}_2\text{H}_4\text{PMe}_2)_2]$ with sodium naphthalenide ($\text{NaC}_{10}\text{H}_8$).

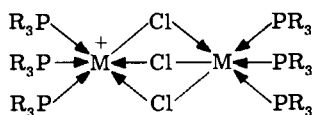
B. RUTHENIUM AND OSMIUM

1. Complexes Derived from Halides

Ruthenium(III) halides differ from ferric chloride in forming monomeric complexes with diphenylmethyl-arsine. These complexes, $[\text{RuX}_3\text{-}$

(AsMePh₂)₃], are reduced with hypophosphorous acid to the Ru(II) complexes [RuX₂(AsMePh₂)₄]. Ruthenium(IV) halides are first reduced to Ru(III) by the same tertiary arsine (166). Similarly, K₂OsX₆ yields the Os(III) complexes [OsX₃(arsine)₃], which may be reduced, for example, to [OsCl₂(AsMePh₂)₄] (172).

From this earlier work with tertiary arsines it might be expected that similar simple octahedral complexes would be formed with tertiary phosphines. However, although products of this type have been prepared, e.g., [OsCl₃(PEt₂Ph)₃] (111), complexes of the type [M^{II}₂Cl₃(phosphine)₆]Cl (M = Ru or Os) of cation structure (VII) (94) are often obtained directly.



(VII)

Vaska and Sloane treated ruthenium and osmium halides with triphenylphosphine and -arsine in high boiling alcohols to obtain stable products, which were originally incorrectly formulated as [RuCl(EPh₃)₃] (434) and [OsX(EPh₃)₃] (428) (E = P or As). This proposed univalency for the metals was difficult to reconcile with the properties of the complexes, particularly their diamagnetism. The explanation was found by Chatt and Shaw, who showed that the alcohol was involved in the reactions and that "reductive carbonylation" was taking place with production of [MHX(CO)(PPh₃)₃] (111). This has been confirmed by Vaska and Diluzio (431). Further examples of the involvement of an alcoholic solvent are provided by the preparation of [RuHCl(CO)(PEt₂Ph)₃] (110, 269), [RuCl₂(CO)(PEt₂Ph)₃] (110), and [RuCl₂(CO)₂(PEt₂Ph)₂] (111) from [Ru₂Cl₃(PEt₂Ph)₆]Cl. Participation of alcohols in these reactions is obviously a subject for further work, especially since Vaska has now shown the wide variety of products obtainable from the interaction of ruthenium and osmium halides with triphenylphosphine, -arsine, and -stibine, depending upon the reaction conditions and the particular alcohol used (cf. Tables II and III).

No carbonylation has been observed in preparation of complexes containing chelating ligands. [MX₂(dias)₂] where M = Ru (387) or Os (388) are stable complexes readily oxidized to [MX₂(dias)₂]X, having one unpaired spin. Further oxidation of the Os(III) complex yields [OsX₂(dias)₂](ClO₄)₂, but the corresponding Ru(IV) complex has not been obtained. α-Picolyl-dimethyl-arsine forms analogous Ru(II) and Ru(III) complexes (196), and the complexes [RuX₂(tetraarsine)] have been described (214). The com-

TABLE II
RUTHENIUM COMPLEXES

Complex	Reference	Color	M.p. (°C)	Preparation
$[\text{RuX}_2(\text{AsMePh}_2)_4]$	166	—	—	$[\text{RuX}_3(\text{AsMePh}_2)_3] + \text{H}_3\text{PO}_2$
$[\text{RuCl}_2(\text{CO})(\text{PEt}_2\text{Ph})_3]$	110	Colorless	250 d	$[\text{RuHCl}(\text{CO})(\text{PEt}_2\text{Ph})_3] + \text{HCl}$
$[\text{RuCl}_2(\text{CO})(\text{AsPh}_3)_3]$	430	Yellow	178 d	$\text{RuCl}_3 + \text{AsPh}_3 + \text{MeOC}_2\text{H}_4\text{OH} (124^\circ)$
$[\text{RuCl}_2(\text{CO})_2(\text{PEt}_2\text{Ph})_2]$	111	—	144–146	$[\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]\text{Cl} + \text{C}_3\text{H}_5\text{OH} + \text{KOH}$
$[\text{RuCl}_2(\text{CO})_2(\text{PEt}_3)_2]$	111	—	104–110	$[\text{Ru}_2\text{Cl}_3(\text{PEt}_3)_6]\text{Cl} + \text{C}_3\text{H}_5\text{OH} + \text{KOH}$
$[\text{RuI}_2(\text{CO})_2(\text{AsMePh}_2)_2]$	272	Orange-yellow	105	$[\text{Ru}(\text{CO})_2\text{I}_2]_n + \text{AsMePh}_2$
$[\text{RuI}_2(\text{CO})_2(\text{PPh}_3)_2]$	246	—	—	$[\text{Ru}(\text{CO})_2\text{I}_2]_n + \text{PPh}_3$
$[\text{RuHCl}(\text{CO})(\text{PEt}_2\text{Ph})_3]$	110	Colorless	102–103	$[\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]\text{Cl} + \text{C}_2\text{H}_4\text{OH} + \text{KOH}$
$[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$	111, 431	—	—	$\text{RuCl}_3 + \text{PPh}_3 + \text{MeOC}_2\text{H}_4\text{OH} (124^\circ)$
$[\text{RuX}_3(\text{AsMePh}_2)_3]$	166	—	—	$\text{RuX}_3 + \text{AsMePh}_2$
$[\text{RuCl}_3(\text{PPh}_3)_2 \cdot \text{MeOH}]$	430	Green	140 d	$\text{RuCl}_3 + \text{PPh}_3 + \text{MeOH} (25^\circ)$
$[\text{RuBr}_3(\text{AsPh}_3) \cdot \text{MeOH}]$	430	Dark red	174 d	$(\text{NH}_4)_2\text{RuBr}_5 + \text{AsPh}_3 + \text{MeOH} (25^\circ)$
$[\text{RuBr}_3(\text{CO})(\text{PPh}_3)_2]$	430	Red	204 d	$(\text{NH}_4)_2\text{RuBr}_5 + \text{PPh}_3 + \text{MeOH} (25^\circ)$

TABLE III
OSMIUM COMPLEXES

Complex	Reference	Color	M.p. (°C)	Preparation
$[\text{OsBr}_2(\text{PPh}_3)_3]$	430	Green	232 d	$(\text{NH}_4)_2\text{OsBr}_6 + \text{PPh}_3 + \text{MeOC}_2\text{H}_4\text{OH}$ (25°)
$[\text{OsCl}_2(\text{AsMePh}_2)_4]$	172	Yellow	113	$[\text{OsCl}_3(\text{AsMePh}_2)_3] + \text{H}_3\text{PO}_2$
$[\text{OsBr}_2(\text{SbPh}_3)_4]$	430	Orange	248 d	$(\text{NH}_4)_2\text{OsBr}_6 + \text{SbPh}_3 + \text{MeOC}_2\text{H}_4\text{OH}$ (124°)
$[\text{OsHCl}(\text{CO})(\text{PEt}_2\text{Ph})_3]$	111	—	—	$[\text{OsCl}_3(\text{PEt}_2\text{Ph})_3] + \text{EtOH} + \text{KOH}$
$[\text{OsHCl}(\text{CO})(\text{PPh}_3)_3]$	431	Colorless	—	$(\text{NH}_4)_2\text{OsCl}_6 + \text{PPh}_3 + \text{MeOC}_2\text{H}_4\text{OH}$ (120°)
$[\text{OsHBr}(\text{CO})(\text{PPh}_3)_3]$	430, 431	White	276 d	$(\text{NH}_4)_2\text{OsBr}_6 + \text{PPh}_3 + \text{MeOC}_2\text{H}_4\text{OH}$ (120°) or EtOH (25°)
$[\text{OsBr}_3(\text{AsMe}_2\text{Ph})_3]$	172	Red	163	$\text{K}_2\text{OsBr}_6 + \text{AsMe}_2\text{Ph} + \text{HBr}$
$[\text{OsBr}_3(\text{AsMePh}_2)_3]$	172	Red	205	$\text{K}_2\text{OsBr}_6 + \text{AsMePh}_2 + \text{HBr}$
$[\text{OsCl}_3(\text{PEt}_2\text{Ph})_3]$	111	Red	210 d	$(\text{NH}_4)_2\text{OsCl}_6 + \text{PEt}_2\text{Ph}$
$[\text{OsBr}_3(\text{AsPh}_3)_3]$	430	Purple	270 d	$(\text{NH}_4)_2\text{OsBr}_6 + \text{AsPh}_3 + \text{EtOH}$ (25°)
$[\text{OsBr}_3(\text{SbPh}_3)_3]$	430	Purple	215 d	$(\text{NH}_4)_2\text{OsBr}_6 + \text{SbPh}_3 + \text{MeOC}_2\text{H}_4\text{OH}$ (25°)
$[\text{OsCl}_3(\text{CO})(\text{PPh}_3)_2]$	430	Brown	235 d	$(\text{NH}_4)_2\text{OsCl}_6 + \text{PPh}_3 + \text{triethylene glycol}$ (270°)
$[\text{OsBr}_3(\text{CO})(\text{PPh}_3)_2]$	430	Purple	230 d	$(\text{NH}_4)_2\text{OsBr}_6 + \text{PPh}_3 + \text{triethylene glycol}$ (270°)
$[\text{OsBr}_4(\text{AsPh}_3)_2]$	430	Purple	245 d	$(\text{NH}_4)_2\text{OsBr}_6 + \text{AsPh}_3 + \text{MeOH}$ (64°)

plexes $[\text{MCl}_2(\text{diphosphine})_2]$ have a *trans* configuration when prepared directly. The *cis* isomers (dipole moment = 8–11 D) are obtained by reaction of the diphosphine with the complexes $[\text{M}_2\text{Cl}_3(\text{PR}_3)_6]\text{Cl}$ (94).

Hydrides of the types *trans*- $[\text{MHX}(\text{diphosphine})_2]$ and *trans*- $[\text{MH}_2(\text{diphosphine})_2]$ are prepared by reduction of *cis*- $[\text{MX}_2(\text{diphosphine})_2]$ with LiAlH_4 (92, 95). The derivatives *trans*- $[\text{RuClR}(\text{diphosphine})_2]$ (R = alkyl or aryl) are obtained from the *trans*-dichloro complex by reaction with, for example, aluminum alkyls (92). The complexes $[\text{MHR}(\text{diphosphine})_2]$ are the first examples of compounds with both a hydrogen atom and an organic group attached to a transition metal by σ -bonds (98).

A study of the visible and ultraviolet spectra of the compounds *trans*- $[\text{RuXY}(\text{diphosphine})_2]$ (X = Y = Cl, Br, I, or CN; X = H, Me, Ph, and Y = Cl), thus available, showed that the ligand field strengths of hydrogen and the organic groups are large and of the same order as that of cyanide ion (93).

2. Complexes Derived from Carbonyls

Comparatively little work has been done on substitution reactions of ruthenium and osmium carbonyls or carbonyl halides. Polymeric ruthenium carbonyl iodide, $[\text{RuI}_2(\text{CO})_2]_n$, reacts readily with AsMePh_2 (272), PCy_3 , PPh_3 , AsPh_3 , and SbPh_3 (245, 246), forming $[\text{RuI}_2(\text{CO})_2\text{L}_2]$.

VII. Group VIII B

A. COBALT

1. Halide Complexes with Monodentate Ligands

a. Co(II). Jensen (291) showed how readily cobalt(II) chloride and triethyl-phosphine, in alcoholic solution, form the blue complex $[\text{CoCl}_2(\text{PEt}_3)_2]$. A dipole moment of 8.7 D for this complex suggested that it had either a tetrahedral or a *cis*-planar structure, unlike the corresponding nickel complex which has a *trans*-planar structure. Many further complexes of the type $[\text{CoX}_2(\text{phosphine})_2]$ have since been prepared (see Table IV), and the magnetic moments of a representative selection show this class of compound to be tetrahedral. Square-planar d^7 complexes would have only one unpaired electron compared with three unpaired electrons associated with the metal of a tetrahedral d^7 complex. High actual values of about 4.5 B.M. are due to the considerable orbital contribution to the magnetic moment. Analogous tertiary arsine complexes are much less stable and only a few examples are known. $[\text{CoI}_2(\text{AsPh}_3)_2]$ (195) is isomorphous with the corresponding nickel complex, and $[\text{CoCl}_2(\text{AsEt}_3)_2]$ loses arsine to form $[\text{CoCl}_2(\text{AsEt}_3)]$, a halogen-bridged dimer or polymer (216).

TABLE IV
 PHOSPHINE COMPLEXES OF COBALT(II)

Complex	Reference	Color	M.p. (°C)	Magnetic moment (B.M.)	Dipole moment (D)
[CoCl ₂ (PMe ₃) ₂]	50	Green	(unstable)	—	—
[CoCl ₂ (PEt ₃) ₂]	291	Blue	101–102	4.39	8.7
[CoBr ₂ (PEt ₃) ₂]	112	Blue-green	134–136 d	4.76	—
[CoI ₂ (PEt ₃) ₂]	49	Green	128–135	4.74 (216)	—
[CoCl ₂ (PPr ₃ ⁿ) ₂]	291	Blue	ca. 80	—	—
[CoCl ₂ (PBu ₃ ⁿ) ₂]	291	Blue	oil	—	—
[CoBr ₂ (PCy ₃) ₂]	153	blue	199	4.61	—
[CoI ₂ (PCy ₃) ₂]	153, 276	Green	221–223 d	4.63	—
[CoCl ₂ (PPh ₃) ₂]	54, 112	Blue	247–251 d	4.3	—
[CoBr ₂ (PPh ₃) ₂]	112	Blue-green	234–239	4.57	7.6
[CoI ₂ (PPh ₃) ₂]	54, 112	Dark brown	209–214 d	4.6	9.6
	281	Green	—	4.4	8.08
[Co(SCN) ₂ (PPh ₃) ₂]	156, 408	Green	140	4.46	—
[CoBr ₂ (PEt ₃ Ph) ₂]	112	Blue-green	80–82	4.5	—
[CoI ₂ (PEt ₃ Ph) ₂]	50	Green	90–94	—	—
[CoBr ₂ (PEtFh) ₂]	112	Green-blue	186–196 d	—	—
[CoX ₂ (PMe ₃ C ₆ H ₄ NMe ₂) ₂]	66	Blue	—	—	—
[CoCl ₂ (PHEt ₂) ₄]	278	Green	78–82 d	—	—
[CoBr ₂ (PHEt ₂) ₄]	278	Green	108–112 d	1.97	5.63
[CoBr ₂ (PHCy ₂) ₂]	278	Light blue	112–114 d	4.85	7.89
[CoBr ₂ (PHPh ₂) ₃]	286	Brown	163–165 d	2.01	—
[CoCl ₂ (PH ₂ Et) ₂]	215	—	—	4.3	—
[CoCl ₂ (PH ₂ Ph) ₂]	287	Black	—	—	—
[CoBr ₂ (PH ₂ Ph) ₂]	287	Black	153–157	2.5	—
[CoI ₂ (PH ₂ Ph) ₄]	287	Yellow	—	1.83	6.5

The tetraphenyl-diphosphine in the complex [CoBr₂(Ph₂PPPh₂)₂] (282) may be behaving as a monodentate ligand, in which case the properties of the complex suggest a *cis*-planar structure. This unusual configuration could be due to peculiar steric conditions imposed by the ligand.

Tetrahedral anions of the type [CoX₃PPh₃][−] are contained in complexes such as [NEt₄][CoBr₃PPh₃] (153).

Primary and secondary phosphines behave differently than tertiary phosphines (as is often the case) and give different types of complex. [CoX₂(PHEt₂)₄] (278) and [CoBr₂(PHPh₂)₃] (286) both have magnetic moments corresponding to the one unpaired electron expected from their formulation. The black complexes [CoX₂(FH₂Ph)₂] (X = Cl, Br) (287) differ considerably in color from the four-coordinate tertiary phosphine complexes, and by virtue of a magnetic moment of 2.5 B.M. have been assigned a planar structure. Phenyl-phosphine behaves differently with

CoI_2 and the product, $[\text{CoI}_2(\text{PH}_2\text{Ph})_4]$, on further heating in ethanol is transformed into the phosphido compound $[\text{CoI}(\text{PPh})(\text{PH}_2\text{Ph})_3]$.

b. *Co(III)*. Although Jensen (cited in 447) has briefly mentioned the complex $[\text{CoCl}_3(\text{PEt}_3)_2]$, there is apparently no other record of this type of complex. This is not unexpected, since *Co(II)* complexes with monodentate ligands are readily oxidized to the phosphine oxide complex rather than the *Co(III)* complex.

2. Reactions of *Co(II)* Complexes

Complexes of the type $[\text{CoR}_2(\text{PEt}_2\text{Ph})_2]$ ($\text{R} = o$ -substituted aryl, e.g., mesityl), obtained by reaction of the appropriate Grignard reagent with $[\text{CoBr}_2(\text{PEt}_2\text{Ph})_2]$ (106, 112), have a *trans*-planar configuration (393) and are members of the series $[\text{MR}_2(\text{phosphine})_2]$ where $\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Pd}$, or Pt .

Hydrido complexes of the type $[\text{CoHX}(\text{phosphine})_2]$ would be expected to be extremely unstable. Their existence is, however, possible, since the system $[\text{CoCl}_2(\text{PPh}_3)_2] \cdot \text{NaBH}_4$ has similar catalytic behavior in the polymerization of acetylene to an analogous system containing nickel which, in turn, is known to contain a metal-hydride species (201).

Reactions of halide complexes with carbon monoxide and nitric oxide are described below (subheadings 4 and 5).

3. Complexes with Polydentate Ligands

a. *Co(II)* and *Co(III)*. With bidentate ligands, at least four types of *Co(II)* complex are formed:

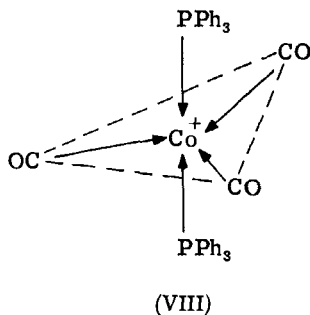
- (1) $[\text{CoX}_2(\text{chelate})_2]$, where chelate = dias (374) or a ditertiary phosphine (90, 453), are ionized in solution and tend to be hydrolyzed by water;
- (2) $[\text{CoX}_2(\text{chelate})]$, chelate = Cy_2PPCy_2 (283);
- (3) $[\text{Co}(\text{chelate})_2][\text{CoX}_4]$, chelate = dimethyl-*o*-methylthiophenylarsine (133);
- (4) $[\text{Co}(\text{dias})_3](\text{ClO}_4)_2$ (59).

In contrast to the monophosphine complexes, chelate complexes are readily oxidized to *Co(III)* complexes, e.g., $[\text{CoX}_2(\text{dias})_2]\text{X}$ (165, 374). Tri- and tetradentate ligands also form stable *Co(III)* complexes, e.g., $[\text{CoI}_3(\text{triarsine})]$ (21) and $[\text{CoI}_2(\text{tetraarsine})]\text{I}$ (20).

b. *Co(0)*. Several d^9 complexes of the type $[\text{Co}(\text{diphosphine})_2]$ have recently been prepared; $[\text{Co}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2]$ (90) and $[\text{Co}(\text{Me}_2\text{PC}_2\text{H}_4\text{PMe}_2)_2]$ (125) are obtained by reduction of halide complexes. They are isomorphous with the corresponding d^{10} *Ni(0)* complexes and thus have tetrahedral structures.

4. Carbonyl Complexes

Triphenyl-phosphine displaces carbon monoxide from dicobalt octacarbonyl; Reppe and Schweckendiek (403) first formulated the product as $[\text{Co}(\text{CO})_3\text{PPh}_3]_2$, but Hieber (256) showed the compound to be ionic and it was later given the formula $[\text{Co}(\text{CO})_3(\text{PPh}_3)_2][\text{Co}(\text{CO})_4]$ (238, 406). A trigonal bipyramidal structure (VIII) has been proposed for the cation



(436). The nonionic, dimeric product can, however, be prepared in a non-polar solvent (238). Both types of product have been prepared using other ligands, e.g., PEt_3 (240, 406), AsPh_3 , and SbPh_3 (240), but PCl_3 and PCl_2Ph did not give characterizable products (405). The salt $[\text{Co}(\text{CO})_3(\text{PPh}_3)_2][\text{Co}(\text{CO})_4]$ can be oxidized to $[\text{Co}(\text{CO})_3(\text{PPh}_3)_2][\text{CoCl}_4]$ (184). The cation tricarbonylbis(triphenyl-phosphine)cobalt(I) is also produced by reacting $[\text{CoI}_2(\text{PPh}_3)_2]$ with carbon monoxide under vigorous conditions (407). In contrast, $[\text{CoX}_2(\text{PEt})_2]$ reacts with carbon monoxide at atmospheric pressure to form $[\text{CoX}_2(\text{CO})(\text{PEt})_2]$ (49).

Tetracarbonyl cobaltates of mercury, and other metals, also lose carbon monoxide on treatment with triphenyl-phosphine and similar ligands with formation, for example, of $\text{Hg}[\text{Co}(\text{CO})_3\text{PPh}_3]_2$ (231-233).

It has recently been shown that the anion $[\text{Co}(\text{CO})_3\text{PPh}_3]^-$ is halogenated, using *N*-bromosuccinimide or trifluoromethyl iodide, to give Co(I) derivatives $[\text{CoX}(\text{CO})_3\text{PPh}_3]$ ($\text{X} = \text{Br}, \text{I}$). Phenylation of the bromide gives the stable $[\text{CoPh}(\text{CO})_3\text{PPh}_3]$ (250).

Heck and Breslow (222-225), in their work on reactions of cobalt carbonyl and its substitution products, have prepared stable triphenyl-phosphine complexes, e.g., $[\text{Co}(\text{COMe})(\text{CO})_3\text{PPh}_3]$, from unstable alkyl and acyl cobalt carbonyl derivatives. Hieber and Lindner (229, 249, 251) have prepared similarly stabilized derivatives and also $[\text{CoH}(\text{CO})_3\text{PPh}_3]$, which decomposes at 20° compared with -20° for $[\text{CoH}(\text{CO})_4]$.

There is a surprising lack of information concerning the action of polydentate ligands on dicobalt octacarbonyl. Tetraphenyl-diphosphine is reported to form the binuclear complex $[\text{Ph}_2\text{PPh}_2\{\text{Co}(\text{CO})_3\}_2]$ (33).

5. Nitrosyl Complexes

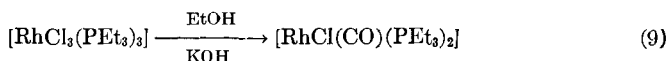
One carbon monoxide molecule is replaced from tricarbonyl-nitrosyl cobalt by triaryl-phosphine, -arsine, or -stibine with formation of $[\text{Co}(\text{CO})_2(\text{NO})\text{L}]$; with triphenyl-phosphine the disubstituted product $[\text{Co}(\text{CO})(\text{NO})(\text{PPh}_3)_2]$ can also be obtained (318, 402). The trisubstituted derivative in this series, $[\text{Co}(\text{NO})(\text{PPh}_3)_3]$, is obtained by reduction of $[\text{CoCl}(\text{NO})_2]_2$ in the presence of the phosphine. Direct action of PPh_3 on the dinitrosyl cobalt halides splits the halogen bridge with formation of $[\text{CoX}(\text{NO})_2\text{PPh}_3]$ (241, 243). Another type of diamagnetic nitrosyl complex, which like the latter contains the metal with an inert-gas configuration, is $[\text{CoX}_2(\text{NO})(\text{PEt}_3)_2]$, obtained by addition of NO to the phosphine-cobalt halide complex (49).

B. RHODIUM

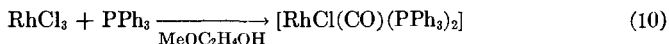
1. Halide Complexes

Rhodium(III) halides with methyldiphenyl-arsine form the complexes $[\text{RhX}_3(\text{AsMePh}_2)_3]$ (168, 303). In the presence of hypophosphorous acid these complexes are reduced to derivatives containing two halogens. These products were originally formulated as complexes of rhodium(II), $[\text{RhX}_2(\text{AsMePh}_2)_3]_2$ (167), but, when later found to be diamagnetic, were considered to be mixed salts of Rh(I) and Rh(III), e.g., $[\text{Rh}^{\text{I}}(\text{AsMePh}_2)_4] \cdot [\text{Rh}^{\text{III}}\text{Cl}_4(\text{AsMePh}_2)_2]$ (380). More recent work has shown the presence of a metal hydride ($\nu_{\text{Rh-H}}$ ca. 2075 cm^{-1}) and the reduction products are correctly formulated $[\text{RhHX}_2(\text{AsMePh}_2)_3]$ (303). With dimethyldiphenyl-arsine, rhodium(III) halides, in the presence of hypophosphorous and hydrohalogen acids, are reported to form $[\text{RhX}_2(\text{AsMe}_2\text{Ph})_4]$ (169). A further study of magnetic and other properties of these complexes is necessary for confirmation of their structure.

Tertiary phosphine complexes of the type $[\text{RhX}_3(\text{phosphine})_3]$ can be prepared and are particularly interesting in their reaction with alcohols, which forms carbonyl derivatives of Rh(I) (110, 111, 269):



and similarly



This represents, of course, a further example of the "reductive carbonylation" reaction related to that described earlier for ruthenium and osmium (see Section VI,B,1).

The chelating diarsine reacts with rhodium(III) halides to form the salts $[\text{RhX}_2(\text{dias})_2]\text{X}$ (371). With an alternative chelating ligand, dimethyl-*o*-methylthiophenyl-arsine (As-S), complexes with the same type of cation are obtained, $[\text{RhX}_2(\text{As-S})_2][\text{RhX}_4(\text{As-S})]$ (135). Analogous halide complexes containing tertiary diphosphines should be preparable but have not yet been described. A complex of unknown composition, but possibly a hydride, is obtained from rhodium metal and *o*-phenylenebisdiethylphosphine in the presence of hydrogen (90).

2. Carbonyl Complexes

The four-coordinate complexes $[\text{RhX}(\text{CO})\text{L}_2]$ provide a striking example of the stabilization of the univalent state of the metal. This might have been anticipated to some extent, since the rhodium is isoelectronic with Pd(II) in, for example, such stable complexes as $[\text{PdX}_2\text{L}_2]$. Before their preparation by "reductive carbonylation" complexes of the type $[\text{RhCl}(\text{CO})\text{L}_2]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3$) had been obtained from rhodium chlorocarbonyl. With triphenyl-stibine, Vallarino (426) obtained the analogous $[\text{RhCl}(\text{CO})\text{-(SbPh}_3)_2]$, although Hieber and co-workers (245, 247) report the preparation of a dicarbonyl, $[\text{RhCl}(\text{CO})_2(\text{SbPh}_3)_3]$, by this reaction. These complexes are all diamagnetic (237) and the dipole moments of about 3 Debye units for the four-coordinate complexes suggest a *trans* arrangement of the tertiary phosphine or related ligands.

The complexes $[\text{RhCl}(\text{CO})\text{L}_2]$ are remarkable for the difficulty with which Cl or CO is replaced or displaced by other ligands, although exchange with C^{14}O and Cl^{36} anion occurs immeasurably quickly (198). Oxidation of the Rh(I) complexes with halogens produces the very stable Rh(III) complexes $[\text{RhX}_3(\text{CO})\text{L}_2]$ ($\text{X} = \text{Cl}, \text{I}$) (427).

3. Nitrosyl Complexes

Dinitrosyl rhodium(I) chloride reacts with triphenyl-phosphine and related ligands to give $[\text{Rh}(\text{NO})\text{L}_3]$ and $[\text{RhCl}_2(\text{NO})\text{L}_2]$ (242, 244). Five-coordinate nitrosyl complexes of Co(II) analogous to the latter have been prepared, but not from $[\text{CoCl}(\text{NO})_2]_2$.

4. Organic Complexes

Alkyl or aryl derivatives of rhodium stabilized by tertiary phosphine ligands are very difficult to prepare compared with those of other Group VIII metals. The aryl derivatives which have been prepared are typi-

fied by $[\text{RhBr}(\text{1-naphthyl})_2(\text{PPr}_3)_2]$, obtained in very small yield from $[\text{RhBr}_3(\text{PPr}_3)_3]$ (116).

Complexes of the type $[\text{RhCl}(\text{diene})\text{PPh}_3]$, where diene = cyclo-octa-1,5-diene (121) or norbornadiene (43), have been obtained from $[\text{Rh}_2\text{Cl}_2(\text{diene})_2]$ by a bridge-splitting reaction.

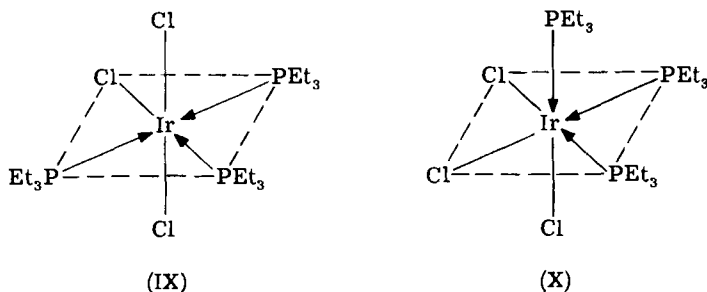
C. IRIDIUM

1. Halide Complexes

The Ir(III) complexes with tertiary arsines and phosphines are analogous to those of Rh(III). $[\text{IrCl}_3(\text{AsMePh}_2)_3]$ (171) has been isolated in two isomeric forms and the complexes originally thought to be $[\text{IrX}_2(\text{AsMePh}_2)_3]_2$ (170) have been reformulated as hydrides, e.g., $[\text{IrHBr}_2(\text{AsMePh}_2)_3]$ (303). The existence of complexes of the type $[\text{IrBr}_2(\text{AsMe}_2\text{Ph})_4]$ (170) has not been confirmed.

Dimethyl-*o*-methylthiophenyl-arsine with ammonium chloroiridate forms $[\text{IrCl}_3(\text{As-S})_2]$ (135), which is a seven-coordinate complex only if the ligand is fully chelated. The absence of information about iridium complexes with other chelating ligands is possibly indicative of difficulties in obtaining characterizable products.

The complexes $[\text{IrX}_3(\text{phosphine})_3]$ are readily prepared from chloroiridic acid and exist in two isomeric forms, e.g., structures (IX) and (X) (79).



They react with alcohols to give hydride complexes and are presumably intermediate products in the reaction of various iridium halides with a tertiary phosphine and an alcohol to give hydride and carbonyl complexes. Compared with rhodium, many more types of products are obtained by the "alcohol reaction" mainly because of the increased stability of iridium hydride complexes.

2. Hydride Complexes

Three types of complex, $[\text{IrHX}_2(\text{phosphine})_3]$, $[\text{IrH}_2\text{X}(\text{phosphine})_3]$, and $[\text{IrH}_3(\text{phosphine})_3]$, have been prepared (110, 111, 217, 429):

VIII. Group VIII C

A. NICKEL

1. *Ni(II) Complexes*

a. *Halide Complexes with Monodentate Ligands.* Jensen (290) prepared the red to brown complexes $[\text{NiX}_2(\text{PR}_3)_2]$ ($\text{R} = \text{Et}, n\text{-Pr}, n\text{-Bu}$) and showed them to have a dipole moment of approximately zero. He therefore suggested a *trans*-square-planar configuration, which has since been confirmed by an X-ray examination of $[\text{NiBr}_2(\text{PEt}_3)_2]$ (191, 410). The corresponding arsine and stibine complexes are much less stable and, of this class, only $[\text{NiI}_2(\text{AsEt}_3)_2]$ has been isolated. Nickel nitrate behaves differently than the halides, since the derived complex $[\text{Ni}(\text{NO}_3)_2(\text{PEt}_2)_2]$ is green and has a high dipole moment. Jensen suggested a *cis*-square-planar structure, but the magnetic moment of 3.1 B.M., later determined (18), led to suggestions of a tetrahedral configuration, although with a bidentate NO_3^- ligand an octahedral structure is possible (17). Preliminary X-ray examination of $[\text{Ni}(\text{NO}_3)_2(\text{PEt}_3)_2]$ favors a tetrahedral structure (191, 410).

Triphenyl-phosphine does not complex quite so easily as the trialkyl-phosphines; Jensen (290) failed to obtain a product from reaction in ethanol, although other solvents, e.g., butanol (454) and acetic acid (435), have since been used successfully. Molten triphenyl-phosphine may alternatively be used (266). The complexes $[\text{NiX}_2(\text{PPh}_3)_2]$ are paramagnetic with magnetic moments corresponding to two unpaired electrons; the problem of their stereochemistry has only recently been resolved by an X-ray examination of $[\text{NiCl}_2(\text{PPh}_3)_2]$, showing it to be monomeric with a tetrahedral configuration (435). Other related complexes, e.g., $[\text{NiX}_2(\text{PBuPh}_2)_2]$ (158), are similarly paramagnetic and presumably tetrahedral in the solid state, although in these and other examples the reduced magnetic moments of solutions compared with solids suggest an equilibrium between diamagnetic and paramagnetic forms in solution. With special combinations of ligands, as for example in $[\text{NiX}_2(\text{PBzPh}_2)_2]$ (55) or $[\text{NiBr}_2(\text{PEtPh}_2)_2]$ (220), the two isomers (diamagnetic and paramagnetic) have actually been isolated. The reason for the formation of paramagnetic complexes must be associated with the force of the field generated by the ligands, and the formation of a tetrahedral, rather than an octahedral, complex is probably due mainly to the steric requirements of the particular combination of ligands involved. These factors have been fully discussed by Venanzi and co-workers (55).

Many other tertiary phosphines have given four-coordinate complexes (see Table V), but very few arsine complexes and no stibine complexes have been reported. Stable complexes are thus formed with ligands of

TABLE V
TERTIARY PHOSPHINE AND ARSINE COMPLEXES OF NICKEL(II)

Complex	Reference	Color	M.p. (or decomp.) (°C)	Magnetic moment (B.M.)	Dipole moment (D)	Remarks
[NiX ₂ (PMe ₃) ₂]	40	Red to brown	—	Diamag.	—	And X = SCN, NO ₃
[NiCl ₂ (PEt ₃) ₂]	290	Dark red	112–113	Diamag. (18)	—	Spectra (158)
[NiBr ₂ (PEt ₃) ₂]	290	Dark red	106–107	—	~0	Spectra (158)
[NiI ₂ (PEt ₃) ₂]	290	Dark brown	91–92	—	—	Spectra (158)
[Ni(SCN) ₂ (PEt ₃) ₂]	158	Yellow	141–142	Diamag.	—	—
[Ni(NO ₂) ₂ (PEt ₃) ₂]	49	Orange	163–169	—	1.5	—
[Ni(NO ₃) ₂ (PEt ₃) ₂]	290	Green	131–132	3.1 (18)	8.85	Spectra (17, 189)
[NiI ₂ (AsEt ₃) ₂]	290	Dark brown	54–55	—	—	—
[NiCl ₂ (PPr ₃ ⁿ) ₂]	290	Dark red	92–93	Diamag.	~0	—
[NiX ₂ (PPr ₃ ⁱ) ₂]	192	Red	—	—	—	UV spectra
[NiCl ₂ (PBu ₃ ⁿ) ₂]	290	Dark red	48–49	—	—	—
[NiX ₂ (PBu ₃ ⁿ) ₂]	192	Red	—	—	—	UV spectra
[NiCl ₂ (PCy ₃) ₂]	424, 425	Red	227	Diamag.	0	—
[NiBr ₂ (PCy ₃) ₂]	276, 424	Olive green	204 d	Diamag.	1.9	UV spectra
[NiI ₂ (PCy ₃) ₂]	152	Green	214	—	—	—
[Ni(SCN) ₂ (PCy ₃) ₂]	424	Orange-yellow	230	Diamag.	0	UV spectra
[NiX ₂ (PBz ₃) ₂]	55	—	—	Diamag.	1.35–3.7	—
[NiCl ₂ (PPh ₃) ₂]	435, 454	Blue	247–250	3.07	—	—
[NiBr ₂ (PPh ₃) ₂]	435	Green	222–225	2.97	5.9	—
[NiI ₂ (PPh ₃) ₂]	435, 454	Brown	225	2.92	8.5	—
[Ni(SCN) ₂ (PPh ₃) ₂]	435	Red	217–218	3.04	<3	—
[Ni(NO ₃) ₂ (PPh ₃) ₂]	435	Green	224–227	3.04	—	—
[NiX ₂ (PMe ₂ Ph) ₂]	66	Red	—	—	—	—

$[\text{NiCl}_2(\text{PET}_2\text{Ph})_2]$	290	Dark red	112-113	—	> 0	—	
$[\text{NiBr}_2(\text{PET}_2\text{Ph})_2]$	109	Dark red	114-116	—	—	—	
$[\text{Ni}(\text{NO}_3)_2(\text{PET}_2\text{Ph})_2]$	49	Green	100-105	—	—	—	
$[\text{NiCl}_2(\text{PEtPh}_2)_2]$	220	Dark red	146-151	Diamag.	3.2	—	
$[\text{NiBr}_2(\text{PEtPh}_2)_2]$	109, 220	Dark green	173-175	3.2	5.9	—	
		Brown (isomers)	160-175	Diamag.	—	—	
$[\text{NiI}_2(\text{PEtPh}_2)_2]$	220	Brown-red	127-138	3.1	7.5	—	
$[\text{Ni}(\text{NO}_3)_2(\text{PEtPh}_2)_2]$	49	Green	155-157	—	—	—	
$[\text{NiX}_2(\text{PBu}_2\text{Ph})_2]$	158	—	—	Diamag.	1.3-3.1	And X = NO ₃ , SCN	
$[\text{NiX}_2(\text{PBuPh}_2)_2]$	158	—	—	ca. 3.3	3.3-6.8	And X = NO ₃ , SCN	
$[\text{NiX}_2\{\text{P}(p\text{-anisyl})_3\}_2]$	54	Brown	—	ca. 3.25	7.4-9.2	And X = NO ₃ , SCN	
$[\text{NiX}_2\{\text{P}(p\text{-tolyl})_3\}_2]$	54	Green	—	ca. 3.25	6.2-9.8	—	
$[\text{NiX}_2\{\text{AsMe}_2(p\text{-Me}_2\text{NC}_6\text{H}_4)_2\}]$	66	Red	—	—	—	—	
$[\text{NiX}_2\{\text{PMe}_2(p\text{-Me}_2\text{NC}_6\text{H}_4)_2\}]$	66	Red	—	—	—	—	
$[\text{NiBr}_2\{\text{P}(\text{CH}_2\text{Cl})_3\}_2]$	158	Red	158-159	Diamag.	1.5	—	
$[\text{NiI}_2\{\text{P}(\text{CH}_2\text{Cl})_3\}_2]$	158	Brown-black	125-126	Diamag.	—	—	
$[\text{NiX}_2(\text{PMe}_2\text{CF}_3)_2]$	40	—	—	Diamag.	—	—	
$[\text{NiX}_2(\text{PAllPh}_2)_2]$	55	—	—	—	—	—	
$[\text{NiX}_2(\text{PBz}_2\text{Ph})_2]$	55	—	—	Diamag.	1.7-3.2	—	
$[\text{NiX}_2(\text{PBzPh}_2)_2]$	55	—	—	ca. 3	1.2-7.7	—	

increased donor strength; this is further neatly demonstrated by a comparison of AsMe_2Ph and $\text{AsMe}_2(p\text{-Me}_2\text{NC}_6\text{H}_4)$, where only the latter, with its increased availability of electrons on the arsenic atom, gave a stable complex (66).

Primary and secondary phosphines, as with halides of other metals, behave differently than tertiary phosphines. Phenyl-phosphine forms $[\text{NiBr}_2(\text{PH}_2\text{Ph})_4]$ (287), and diethyl-phosphine similarly gives six-coordinate complexes, $[\text{NiX}_2(\text{PHEt}_2)_4]$ (278). However, dicyclohexyl-phosphine behaves "normally" to give $[\text{NiBr}_2(\text{PHCy}_2)_2]$ (285), and diphenyl-phosphine yields yet another type of product by reacting with nickel bromide to form the diphosphide $[\text{Ni}(\text{PPh}_2)_2(\text{PHPh}_2)_2]$ (286).

b. *Halide Complexes with Polydentate Ligands.* Nickel halides form complexes of the type $[\text{NiX}_2(\text{diphosphine})]$, where diphosphine = $\text{Et}_2\text{PC}_2\text{H}_4\text{PEt}_2$ (453), $\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$, $\text{Me}_2\text{PC}_2\text{H}_4\text{PMe}_2$ (50), or $\text{Cy}_2\text{P}(\text{CH}_2)_3\text{PCy}_2$ (280), which are considered to have a *cis*-square-planar configuration. The structures of similarly formulated complexes derived from the diphosphines Cy_2PFCy_2 (283) or $\text{Cy}_2\text{P}(\text{CH}_2)_6\text{PCy}_2$ (280) are less certain. The diphosphines may also form 2:1, as well as 1:1, complexes, but dias differs in forming only 2:1 complexes with nickel halides (372). There is no doubt that this ligand is chelated in the complexes $[\text{NiX}_2(\text{dias})_2]$, although in other complexes of the type $[\text{NiX}_2\text{L}_2]$, where L is for example dimethyl-*o*-methylthiophenyl-arsine (306), Ph_2PPH_2 (282), or $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (50), the ligand is probably behaving in a monodentate way. The complexes $[\text{NiX}_2(\text{dias})]$ may, however, be prepared from $[\text{Ni}(\text{CO})_2\text{dias}]$ (379). This oxidation of Ni(0) complexes to Ni(II) complexes is a general one applied also to complexes of triphenyl-phosphine (454) and of *o*-phenylenebisdiethyl-phosphine (86). The complexes $[\text{NiX}_2(\text{dias})_2]$ (210) and the related $[\text{NiX}_2(\text{diphosphine})_2]$, although conducting in nitrobenzene solution, are probably fully covalent in the solid state.

The complex $[\text{NiBr}_2(\text{triarsine})]$ (21, 22) is of special interest as a five-coordinate derivative of nickel(II). An X-ray examination of this compound shows that the probable configuration is that of a distorted square pyramid (314). $[\text{NiI}_2(\text{tetraarsine})]$ (20) is a simple octahedral complex, assuming complete coordination.

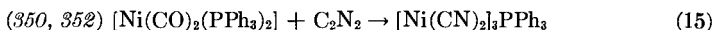
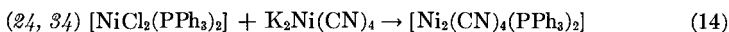
c. *Hydride and Organic Complexes.* A very unstable hydride, possibly $[\text{NiHCl}(\text{PPr}_3)_2]$, has been shown to be present (NMR spectrum) in the system $[\text{NiCl}_2(\text{PPr}_3)_2] + \text{NaBH}_4$ (202). Similar alkyl derivatives, e.g., $[\text{NiClMe}(\text{PPr}_3)_2]$, and most aryl derivatives are also too unstable to be isolated in a pure condition. Nevertheless, stable aryl derivatives of the types $[\text{NiXR}(\text{PR}'_3)_2]$ and $[\text{NiR}_2(\text{PR}'_3)_2]$ ($\text{R} = o$ -substituted aryl) have been prepared (106, 109). The complex $[\text{NiI}_2\text{F}_5(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)]$, prepared

by reacting $[\text{Ni}(\text{CO})_2(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)]$ with perfluoroethyl iodide, provides a good example of the stabilization of metal-carbon σ -bonds through the influence of fluorine (342). The related acetylides $[\text{Ni}(\text{C}:\text{CR})_2(\text{PR}'_3)_2]$ are also stable, with $[\text{Ni}(\text{C}:\text{CPh})_2(\text{PEt}_2\text{Ph})_3]$ providing an isolated example of a five-coordinate complex (109).

The π -allyl derivative of nickel, $[\text{NiCl}(\pi\text{-C}_3\text{H}_5)(\text{PPh}_3)]$, has recently been prepared by treatment of $[\text{Ni}(\text{CO})_3\text{PPh}_3]$ with allyl chloride (226). Complexes of the type $[\text{Ni}(\text{olefin})(\text{PPh}_3)_2]$ have been briefly described (445) and will doubtless be further investigated. A comparison with the analogous platinum complexes would be of considerable interest.

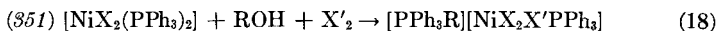
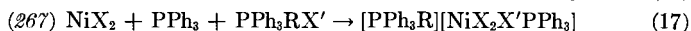
d. Cyanide Complexes. Complexes of nickel cyanide, since the CN^- anion is isoelectronic and isostructural with carbon monoxide, should resemble complexes of nickel carbonyl. They are thus of potential interest as catalysts, but, due mainly to difficulties of preparation, have been but little investigated (see Section VIII,A,7).

An unstable complex, thought to be $[\text{Ni}(\text{CN})_2(\text{PPh}_3)_2]$ (50), was formed by reacting $\text{Ni}(\text{CN})_2$ with molten triphenyl-phosphine; other complexes have been obtained by indirect methods:



e. Complex Salts Containing Quaternary Phosphonium Ions. The early work of Reppe and Schweckendiek (403) with nickel halide-triphenyl-phosphine complexes as catalysts (see Section VIII,A,7) showed that the complexes $[\text{NiX}_2(\text{PPh}_3)_2]$ reacted with alkyl and aryl halides (RX') to form complexes of formulas $\text{NiX}_2(\text{PPh}_3)_2 \cdot \text{RX}'$ and $\text{NiX}_2(\text{PPh}_3)_2 \cdot 2\text{RX}'$.

It is only recently that the obviously correct formulations as $[\text{PPh}_3\text{R}][\text{NiX}_2\text{X}'\text{PPh}_3]$ and $[\text{PPh}_3\text{R}]_2[\text{NiX}_2\text{X}'_2]$ have been made (152, 154). Many complexes of these types (and with HX' in place of RX') have since been prepared, mainly for trial as catalysts, by the reactions:



The four-coordinate anions contain tetrahedrally coordinated nickel, substantiated by magnetic moments ($\mu_{\text{eff}} = 3.4\text{--}3.9$) in a few cases. Table VI lists the known complexes, most of them necessarily reformulated.

In spite of showing that $\text{NiBr}_2(\text{PPh}_3)_2 \cdot \text{BuBr}$ and $\text{NiBr}_2(\text{PPh}_3)_2 \cdot 2\text{PhBr}$

TABLE VI
 QUATERNARY PHOSPHONIUM SALTS OF NICKEL(II)

Complex	Reference	Color	M.p. (°C)	μ_{eff} (B.M.)
$[\text{PPh}_3\text{Bu}][\text{NiCl}_3(\text{PPh}_3)]$	454	Blue	176	—
$[\text{PPh}_3\text{CH}_2\text{Ph}][\text{NiCl}_3(\text{PPh}_3)]$	28	Green-blue	196	—
$[\text{PPh}_3\text{Bu}][\text{NiCl}_2\text{Br}(\text{PPh}_3)]$	351, 403	Blue-green	150	—
			171	—
$[\text{PPh}_3\text{Bu}][\text{NiClBr}_2(\text{PPh}_3)]$	454	Blue	167–168	—
$[\text{PPh}_4][\text{NiClBr}_2(\text{PPh}_3)]$	454	Green	203–205	—
$[\text{PHPh}_3][\text{NiBr}_3(\text{PPh}_3)]$	267	Green	178–180	—
$[\text{PPh}_3\text{Et}][\text{NiBr}_3(\text{PPh}_3)]$	454	Green	162	—
$[\text{PPh}_3\text{Bu}][\text{NiBr}_3(\text{PPh}_3)]$	267, 403	Green	177–178	—
$[\text{PPh}_3\text{Bu}^{\text{iso}}][\text{NiBr}_3(\text{PPh}_3)]$	454	Blue-green	167	—
$[\text{PPh}_3\text{Bu}^{\text{tert}}][\text{NiBr}_3(\text{PPh}_3)]$	152	Green	221	3.4 (338)
$[\text{PPh}_4][\text{NiBr}_3(\text{PPh}_3)]$	454	Green	210	—
$[\text{PPh}_3\text{Et}][\text{NiBr}_2\text{I}(\text{PPh}_3)]$	454	Violet-brown	160	—
$[\text{PPh}_3\text{Bu}][\text{NiBr}_2\text{I}(\text{PPh}_3)]$	454	Violet-brown	125	—
$[\text{PPh}_3\text{Bu}][\text{NiBrI}_2(\text{PPh}_3)]$	353	Green	217	—
$[\text{PPh}_3\text{Bu}][\text{NiI}_3(\text{PPh}_3)]$	35, 267	Blue	176	—
$[\text{PEt}_2\text{Ph}(1-\text{C}_{10}\text{H}_7)][\text{NiBr}_3(\text{PEt}_2\text{Ph})]$	109	Blue	186–188	3.4
$[\text{PPh}_3\text{Me}]_2[\text{NiCl}_4]$	194	Blue	198	—
$[\text{PPh}_4]_2[\text{NiCl}_4]$	454	Blue	260	—
$[\text{PPh}_4]_2[\text{NiCl}_2\text{Br}_2]$	454	Blue	253–255	—
$[\text{PHBu}_2]_2[\text{NiBr}_4]$	403	—	117–118	—
$[\text{PPh}_4]_2[\text{NiBr}_4]$	152, 403	Blue	273	3.8 (338)
$[\text{AsPh}_3\text{Me}]_2[\text{NiCl}_4]$	193	Blue	—	3.89
$[\text{AsPh}_3\text{Me}]_2[\text{NiI}_4]$	193	Red	—	3.49
$[\text{NEt}_4][\text{NiBr}_3\text{PPh}_3]$	152, 154	Green	266	3.68
$[\text{NBu}_4][\text{NiI}_3\text{PPh}_3]$	152, 154	Red	132–135	3.46

had considerable molar conductivities in acetone and that the former gave PPh_3BuBr , and no PPh_3 , on decomposition, Yamamoto and Oku (458) suggested fully covalent structures containing phosphorus(V).

2. Ni(III) Complexes

The red Ni(II) complex $[\text{NiBr}_2(\text{PEt}_3)_2]$ is readily oxidized with bromine to the black Ni(III) complex $[\text{NiBr}_3(\text{PEt}_3)_2]$ ($\mu_{\text{eff}} = 1.7\text{--}1.9$ B.M.) (290, 292). The structure of this five-coordinate complex is probably that of a tetragonal pyramid rather than a trigonal bipyramid, but the decisive X-ray analysis is difficult (410), due in part to the relative instability of the compound. The corresponding complexes with chelating ligands, $[\text{NiBr}_3(\text{dias})]$ (379) and $[\text{NiBr}_3(\text{diphosphine})]$ (50, 453), may well be octahedral polymers.

Much more stable complexes of Ni(III) are obtained by oxidation (air + HX) of $[\text{NiX}_2(\text{chelate})_2]$, chelate = dias (373) or $\text{Me}_2\text{PC}_2\text{H}_4\text{PMe}_2$ (50). The products, $[\text{NiX}_2(\text{chelate})_2]\text{X}$, have magnetic moments corresponding to one unpaired electron for the metal.

3. Ni(IV) Complexes

Only one compound containing nickel(IV) has been isolated; the complex $[\text{NiCl}_2(\text{dias})_2]\text{Cl}$ is oxidized by nitric acid in the presence of perchloric acid to give $[\text{NiCl}_2(\text{dias})_2](\text{ClO}_4)_2$ (376).

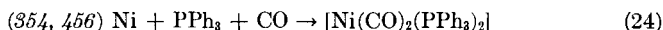
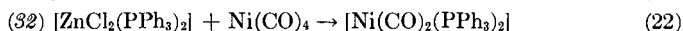
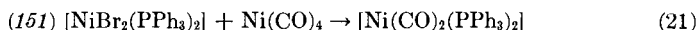
4. Nitrosyl Complexes

Blue nitrosyls of the type $[\text{Ni}(\text{OH})(\text{NO})(\text{MeOH})_2]$ have long been known. The first related complex containing phosphine ligands was $[\text{NiBr}(\text{NO})(\text{PPh}_3)_2]$, prepared by Feltham (178) by treatment of $[\text{NiBr}_2(\text{PPh}_3)_2]$ with NaNO_2 , possibly in an attempt to prepare the unknown $[\text{Ni}(\text{NO}_2)_2(\text{PPh}_3)_2]$. A series of analogous complexes, $[\text{NiX}(\text{NO})(\text{PR}_3)_2]$, has recently been prepared via reduction of $[\text{Ni}(\text{NO}_3)_2(\text{PR}_3)_2]$ to $[\text{Ni}(\text{NO}_3)(\text{NO})(\text{PR}_3)_2]$ with carbon monoxide (49). The complexes $[\text{NiI}(\text{NO})(\text{AsPh}_3)_2]$ and $[\text{NiI}(\text{NO})(\text{SbPh}_3)_2]$ are obtained from $[\text{NiI}(\text{NO})]_4$ (228), and $[\text{NiCl}(\text{NO})(\text{PPh}_3)_2]$ from $[\text{NiCl}_2(\text{NO})]$ (8). These four-coordinate nitrosyl complexes are deeply colored and possibly have a tetrahedral structure with the nickel atom, formally Ni(I), having the same electronic configuration as it has in Ni(0) complexes. Triphenyl-phosphine behaves differently than triphenyl-arsine and -stibine with $[\text{NiI}(\text{NO})]_4$, since the product is the dimeric $[\text{NiI}(\text{NO})\text{PPh}_3]_2$ (228).

The product obtained on treatment of $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$ with nitric oxide is claimed by Griffith *et al.* (203) to be $[\text{Ni}(\text{NO})_2(\text{PPh}_3)_2]$. However, only one NO stretching frequency was observed and it is suggested here that an alternative product might be $[\text{Ni}(\text{NO}_2)(\text{NO})(\text{PPh}_3)_2]$, i.e., a member of the series $[\text{NiX}(\text{NO})(\text{PR}_3)_2]$. This is, in fact, only one of the products which Feltham (as cited in 417) claims to have isolated from this reaction.

5. Carbonyl Complexes

The carbon monoxide of nickel tetracarbonyl may be replaced in a stepwise manner by suitable ligands. Phosphines, arsines, and stibines normally replace one or two molecules of carbon monoxide to form $[\text{Ni}(\text{CO})_3\text{L}]$ and $[\text{Ni}(\text{CO})_2\text{L}_2]$ (see Table VII). Only $[\text{Ni}(\text{CO})(\text{PMe}_3)_3]$ (45) and possibly $[\text{Ni}(\text{CO})(\text{PF}_3)_3]$ (131) of the trisubstituted type have been described. The mono- and disubstituted types can be prepared by other methods, e.g.,



Tri(β -cyanoethyl)-phosphine gives the disubstituted product $[\text{Ni}(\text{CO})_2\{\text{P}(\text{C}_2\text{H}_4\text{CN})_3\}_2]$ (346), but also behaves anomalously in forming $[\text{Ni}(\text{CO})\text{P}(\text{C}_2\text{H}_4\text{CN})_3]_n$ (345) containing bridging carbonyl groups.

Chelate ligands form the complexes $[\text{Ni}(\text{CO})_2(\text{chelate})]$, chelate = dias (379), other diarsines, and various diphosphines (85, 199), more stable than the dicarbonyl complexes with monodentate ligands.

TABLE VII
COMPLEXES OF THE TYPES $[\text{Ni}(\text{CO})_3\text{L}]$ AND $[\text{Ni}(\text{CO})_2\text{L}_2]$

Complex	Reference	Color	M.p. ($^{\circ}\text{C}$)
$[\text{Ni}(\text{CO})_2(\text{PEt}_3)_2]$	46	—	—
$[\text{Ni}(\text{CO})_2(\text{PBu}_3)_2]$	346, 403	Orange	liq.
$[\text{Ni}(\text{CO})_3\text{PPh}_3]$	403, 454	Colorless	123
$[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$	403, 454	Colorless	206–209
$[\text{Ni}(\text{CO})_3\text{P}(p\text{-tolyl})_3]$	354, 403	—	158
$[\text{Ni}(\text{CO})_3\text{AsEt}_3]$	51	Colorless	liq.
$[\text{Ni}(\text{CO})_2(\text{AsEt}_3)_2]$	51	Yellow	liq.
$[\text{Ni}(\text{CO})_3\text{AsPh}_3]$	403	—	105
$[\text{Ni}(\text{CO})_3\text{SbPh}_3]$	30, 403	—	105–109
$[\text{Ni}(\text{CO})_2(\text{SbPh}_3)_2]$	29	—	—
$[\text{Ni}(\text{CO})_2\text{PPh}_3\text{SbPh}_3]$	29	—	—
$[\text{Ni}(\text{CO})_2\{\text{P}(\text{CF}_3)_3\}_2]$	56, 176	—	–31
$[\text{Ni}(\text{CO})_2\{\text{P}(\text{C}_2\text{H}_4\text{CN})_3\}_2]$	346	White	140 d
$[\text{Ni}(\text{CO})_3\text{PCl}_3]$	346	—	—
$[\text{Ni}(\text{CO})_3\text{SbCl}_3]$	449	Buff	—

All these substitution products are assumed to have a tetrahedral configuration, like nickel carbonyl itself. Much has been written on the nature of the Ni—P or Ni—As bonds contained in the complexes. Infrared studies on $[\text{Ni}(\text{CO})_2\text{dias}]$ and calculation of the stretching force constants showed the C—O bonds to be similar to those in $\text{Ni}(\text{CO})_4$, and it was concluded that the structure involving Ni—C and Ni—As double bonds dominates (384). Comparison of the infrared spectra and dipole moments of a series of dicarbonyl derivatives showed that the P—Ni and As—Ni bonds in $\text{Ni}(0)$ complexes have essentially the same bond order, estimated to lie between 1.4 and 1.7 (86). It is difficult to define the extent of double bonding from kinetic data, but Meriwether and Fiene (346) suggest that the bonds are primarily σ in character, with strong contributions from

π -bonding occurring only in complexes of phosphorus halides and phosphites. Finally, an attempt has been made to study the P—Ni bond by measuring the nuclear magnetic resonance spectra of P^{31} -phosphine complexes (347).

6. Complexes of Ni(0) Other Than Carbonyl Derivatives

By treatment of $Ni(CO)_4$ with PCl_3 , Irvine and Wilkinson (271) prepared $[Ni(PCl_3)_4]$, the first example of a complex of Ni(0) containing four phosphorus donor atoms. Chatt (131) had suggested earlier the analogy between PF_3 and CO, but was unsuccessful in attempts to prepare $[Ni(PF_3)_4]$ from $Ni(CO)_4$. This phosphorus trifluoride complex and $[Ni(PBr_3)_4]$ (416, 448) may, however, be prepared from $[Ni(PCl_3)_4]$. Phenyl-dichloro-phosphine (321) and phosphorus triisocyanate and triisothiocyanate (450) replace all the carbon monoxide from $Ni(CO)_4$ in a similar way to PCl_3 .

A further development in this field was the production of $[Ni(PCl_2Me)_4]$ from metallic nickel and the phosphine at reflux temperature (400). Methyl-dichloro-phosphine and methyl-dibromo-phosphine and -arsine (312) are thus the only monodentate ligands, apart from CO, known to form a Ni(0) complex directly from the metal. The aromatic diphosphines *o*- $C_6H_4(PEt_2)_2$ and $Ph_2PC_2H_4PPh_2$ behave similarly to PCl_2Me and form $[Ni(diphosphine)_2]$ (86). This last type of complex may also be prepared from nickel carbonyl or by reduction of $[NiX_2(diphosphine)_2]$ with, for example, sodium borohydride (91).

Monodentate organophosphines have not given fully substituted derivatives by these methods, but $[Ni(PEt_3)_4]$ has been prepared from bis- π -allylnickel (444); a method possibly capable of wider application.

All these Ni(0) complexes are considered to have tetrahedral structures; the Raman spectrum of $[Ni(PF_3)_4]$ is in accord with this (452). The points made about the nature of the P—Ni bond in the earlier discussion of substituted carbonyl complexes are relevant also to these Ni(0) complexes. It is clear that only ligands with increased double-bonding capacity (either by substitution with strongly electronegative atoms or groups or by the proximity of a suitable aromatic residue) are capable of directly forming "fully substituted" nickel derivatives. Other factors may also be important, for example, why PCl_3 and PCl_2Ph do not react with metallic nickel in the same way as PCl_2Me .

Bisacrylonitrile nickel, $[Ni(CH_2=CHCN)_2]$, prepared by Schrauzer (411) by interaction of nickel carbonyl and acrylonitrile, is a novel type of complex of Ni(0). It is coordinatively unsaturated and thus very unstable; further coordination with triphenyl-phosphine provides the derivatives $[Ni(CH_2=CHCN)_2PPh_3]$ and $[Ni(CH_2=CHCN)_2(PPh_3)_2]$ (412, 413). The

latter is considerably more stable, possibly due to its ability to assume a tetrahedral configuration.

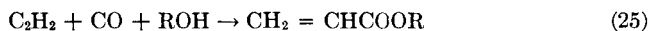
7. Complexes of Nickel as Catalysts

The catalytic properties of transition metal complexes containing phosphine, arsine, or stibine ligands are most marked when the metal is nickel. Reppe (151, 403) studied the complexes, particularly those containing triphenyl-phosphine, of a large number of transition metals and invariably obtained the best results with nickel complexes. Later workers in the field of catalysis have, in consequence, usually restricted themselves to an examination of nickel complexes only.

a. Polymerization of Olefins. Ethylene, methylacrylate, vinyl acetate, and styrene are polymerized by using $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$ as catalyst (25). With the same catalyst, butadiene is dimerized to cyclooctadiene (30–40%) and vinylcyclohex-1-ene (10%) (402); trimer (cyclododecatriene) may also be obtained when using alternative Ni(0) compounds (446).

b. Polymerization of Acetylenes. Acetylene itself is polymerized under suitable conditions (e.g., 100–120°/10 atm) to give mixtures of benzene and styrene when using the catalyst $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$ (348, 403, 456), $[\text{NiBr}_3\text{PPh}_3][\text{PPh}_3\text{Bu}]$ (29), or $[\text{Ni}(\text{CN})_2]_3\text{PPh}_3$ (352). When using more active catalyst systems, such as the unstable complexes $[\text{NiHX}(\text{PR}_3)_2]$ (201, 309) or $[\text{NiMe}_2(\text{PR}_3)_2]$ (50), acetylene forms a brown-black linear polymer even at room temperature and pressure. Substituted acetylenes such as propargyl alcohol (403), phenylacetylene (404), and $(:\text{CCH}_2\text{OR})_2$ (190) are trimerized when using the catalyst $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$ or $[\text{Ni}(\text{CO})_3\text{PPh}_3]$. Other catalysts used for the cyclic polymerization of acetylenes include $[\text{Ni}(\text{PCl}_3)_4]$ (300), $[\text{Ni}(\text{CO})_2(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)]$ (270), and $[\text{Ni}(\text{CH}_2=\text{CHCN})_2(\text{PPh}_3)_1 \text{ or } 2]$ (414).

c. Preparation of α,β -Unsaturated Carboxylic Acids. In the work concerned with the production of acrylic acid or its esters by the reaction,



Repe (cited in 151) showed that phosphine complexes were more active catalysts than the nickel halides alone and, further, that the activity of complexes such as $[\text{NiBr}_2(\text{PPh}_3)_2]$ was enhanced by the presence of an alkyl halide. This led to a thorough study of complexes of the types $[\text{NiBr}_2(\text{PPh}_3)_2]$ (268, 349), $[\text{NiBr}_3(\text{PPh}_3)][\text{PPh}_3\text{Bu}]$ (27, 457) (see Section VIII,A,1,e), and $[\text{Ni}(\text{CN})_2]_3\text{PPh}_3$ (350) as catalysts in the synthesis of unsaturated carboxylic acids and their derivatives.

d. Miscellaneous. Alcohols are carbonylated to give aliphatic carboxylic acids or their esters, using catalytic systems containing $[\text{NiX}_2(\text{PPh}_3)_2]$

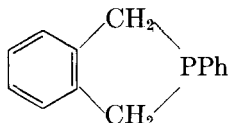
(355). Other catalytic applications of a number of complexes have been reported without specific exemplification.

B. PALLADIUM

1. Halide Complexes

a. Complexes with Monodentate Ligands. Tertiary phosphines, arsines, and stibines complex with palladium(II) salts to form the square-planar derivatives $[\text{PdX}_2\text{L}_2]$ (see Table VIII). These derivatives are stable (the stibine complexes being least stable), readily crystallized, and of well-defined melting point. They have, in consequence, been used in many instances to characterize compounds of Group VB elements, particularly in the work of Mann and his co-workers (37, 149, 150, 159, 221, 323, 324-326). A *trans* arrangement of ligands with a consequent low dipole moment (measured value ca. 1 D) is invariably the case with the phosphine and arsine complexes, but solutions of the stibine complexes have been shown to contain up to 40% of the *cis* isomer in equilibrium and this less soluble isomer may separate from the solution (129). The ultraviolet spectra of certain simple complexes have been measured and shown to be affected by changes in constitution in the same way as related nickel complexes (422). Mixed complexes of the type $[\text{PdX}_2(\text{PR}_3)(\text{amine})]$ will be discussed below as products obtained from bridged complexes.

The vacant $5p$ orbital of the four-coordinate complexes is only rarely filled by further coordination. Complexes of the type $[\text{PdX}_2\text{L}_3]$, where $\text{L} = \text{AsMePh}_2$ (369), PMePh_2 (219), PEt_2Ph (50), or



(334), may be $d^8\text{-dsp}^3$ complexes in the solid state. They readily dissociate to lose one molecule of ligand, L , but in the presence of excess ligand may ionize in solution to $[\text{PdXL}_3]^+\text{X}^-$.

b. Complexes with Polydentate Ligands. Chatt and Mann (100) prepared 1:1 and 2:1 complexes of the types $[\text{PdCl}_2(\text{diarsine})]$ and $[\text{PdCl}_2(\text{diarsine})_2]$, from several ditertiary arsines. On mixing a palladium(II) salt and diarsine, the salt $[\text{Pd}(\text{diarsine})_2][\text{PdCl}_4]$ is first formed, which breaks down on heating to the 1:1 complex, this latter coordinating with further diarsine to form the 2:1 complex. Analogous 1:1 complexes may also be obtained from $[\text{PdX}_2\text{en}]$ by a ligand displacement reaction (437).

Further work on complexes of *o*-phenylenebisdimethyl-arsine(dias) (208, 210, 211) has shown that, although the complexes $[\text{PdX}_2(\text{dias})_2]$ are

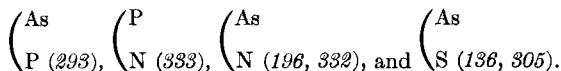
TABLE VIII
SIMPLE TERTIARY PHOSPHINE, ARSINE, AND STIBINE COMPLEXES OF Pd(II) HALIDES

Complex	Reference	Color	M.p. (°C)
[PdCl ₂ (PMe ₃) ₂]	335	Yellow	282 d
[PdCl ₂ (PEt ₃) ₂]	61, 327	Yellow	139
[PdBr ₂ (PEt ₃) ₂]	262	Orange	132
[PdI ₂ (PEt ₃) ₂]	50	Orange	138
[Pd(NO ₃) ₂ (PEt ₃) ₂]	50	Yellow	182 d
[PdCl ₂ (PPr ₃ ⁿ) ₂]	327	Yellow	96
[PdBr ₂ (PPr ₃ ⁿ) ₂]	12	Orange-yellow	88
[PdX ₂ (PPr ₃ ⁱ) ₂]	422	—	—
[PdCl ₂ (PBu ₃ ⁿ) ₂]	327	Yellow	66
[PdBr ₂ (PBu ₃ ⁿ) ₂]	327	Yellow	73
[PdI ₂ (PBu ₃ ⁿ) ₂]	327	Orange	65
[Pd(NO ₂) ₂ (PBu ₃ ⁿ) ₂]	70	—	141–142
[PdCl ₂ (PAm ₃ ⁿ) ₂]	327	Yellow	47
[PdCl ₂ (PEt ₂ Ph) ₂]	50	Yellow	138
[PdBr ₂ (PEt ₂ Ph) ₂]	262	Orange	133
[Pd(NO ₃) ₂ (PEt ₂ Ph) ₂]	50	Yellow	174–176
[PdCl ₂ (PBu ₂ Ph) ₂]	100	Orange	47
[PdCl ₂ (PPh ₃) ₂]	100	Yellow	270 d
[PdCl ₂ (AsMe ₃) ₂]	327	Pale yellow	235
[PdBr ₂ (AsMe ₃) ₂]	335	Orange	229
[Pd(NO ₂) ₂ (AsMe ₃) ₂]	335	Lemon	234 d
[Pd(SCN) ₂ (AsMe ₃) ₂]	335	Yellow	124
[PdCl ₂ (AsEt ₃) ₂]	62, 327	Orange	116
[Pd(NO ₂) ₂ (AsEt ₃) ₂]	327	—	—
[PdCl ₂ (AsPr ₃ ⁿ) ₂]	327	Orange	55
[PdBr ₂ (AsPr ₃ ⁿ) ₂]	327	—	49
[PdCl ₂ (AsBu ₃ ⁿ) ₂]	327	Orange	54
[Pd(NO ₂) ₂ (AsBu ₃ ⁿ) ₂]	70	—	96
[PdCl ₂ (AsAm ₃) ₂]	327	Orange	10–11
[PdCl ₂ (AsMe ₂ Ph) ₂]	310	Orange	170–173
[PdBr ₂ (AsMePh ₂) ₂]	369	Orange	178
[PdI ₂ (AsMePh ₂) ₂]	307	Brown-orange	—
[PdCl ₂ (SbMe ₃) ₂]	129, 356	—	150–165 d
[PdCl ₂ (SbEt ₃) ₂]	288	Yellow	90 d
[PdCl ₂ (SbPr ₃ ⁿ) ₂]	129	Yellow	66 d
[PdCl ₂ (SbBu ₃ ⁿ) ₂]	129	Yellow	65 d
[PdCl ₂ (SbPh ₃) ₂]	129	Yellow	140 d

conducting in nitrobenzene solution, they are six-coordinate in the solid state. The crystal structure of [PdI₂(dias)₂] has been determined; the central metal atom is surrounded by four arsenic atoms in a square plane, and the two iodine atoms complete a distorted octahedral arrangement with elongated metal-iodine bonds.

Complexes related to these diarsine complexes have been derived from

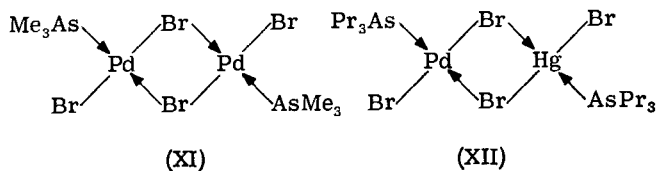
many other chelating ligands, e.g., various ditertiary phosphines (91, 213, 261, 282, 283, 453) and ligands containing two dissimilar donor atoms, which may be represented:



Complexes derived from tritertiary arsines and a tetratertiary arsine have been compared in order to study the factors influencing the coordination numbers in Pd(II) complexes (409).

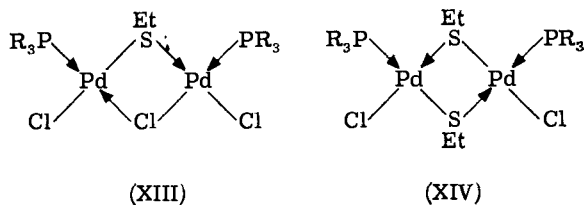
2. Bridged Di-Palladium Derivatives

Treatment of a solution of the complex $[\text{PdCl}_2\text{L}_2]$ with ammonium chloro palladite results in the formation of a more deeply colored binuclear complex $[\text{Pd}_2\text{Cl}_4\text{L}_2]$ (328, 335). Wells (441) has shown that $[\text{Pd}_2\text{Br}_4(\text{AsMe}_3)_2]$ has the *trans*-planar symmetrical structure (XI). The stibine complexes in this class are again the least stable (119). Chelate ligands do not form bridged complexes of this type (100). Bridged complexes containing a bridging nitro group (70) or oxalate radical (101), or with two different metal atoms, e.g., structure (XII) (329), may also be prepared.



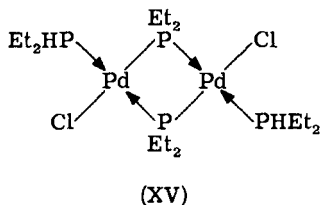
When L is phosphine or arsine, the halogeno-bridged complexes react with monoamines (am) to form the stable derivatives *trans*- $[\text{PdX}_2\text{Lam}]$ (120, 328). Studies of the infrared spectra of a series of these derivatives enabled the effect of L on the NH stretching frequency to be determined (77, 78).

Treatment of $[\text{Pd}_2\text{Cl}_4(\text{PR}_3)_2]$ with ethane thiol results in replacement of the bridging chlorine atoms to yield (XIII) and (XIV) (84, 99), this



cis configuration being established by the high dipole moments of the compounds.

The initial work on complexes of palladium with primary and secondary phosphine suggests interesting developments in the field of bridged complexes. Issleib and co-workers have shown that both diphenyl-phosphine (286) and phenyl-phosphine (287) react with palladous chloride with elimination of HCl. The product $[\text{PdCl}(\text{PPh}_2)(\text{PHPh}_2)]_2$ and several related complexes have been shown by Hayter (218, 219) to contain a phosphorus bridge rather than a chlorine bridge. The structure (XV), for the product



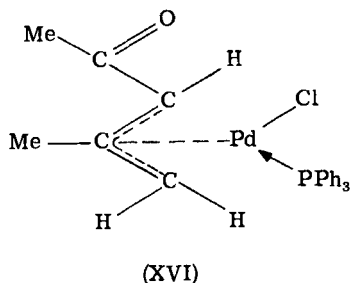
from diethyl-phosphine, is supported by a preliminary X-ray examination. The bridge is split on treatment with tertiary phosphines to form a phosphide of the type $[\text{PdCl}(\text{PR}_2)(\text{PEt}_3)_2]$.

3. Hydride and Organic Complexes

Palladium hydrides of the type $[\text{PdHX}(\text{PR}_3)_2]$ are more stable than the corresponding nickel compounds, although not sufficiently stable to be readily isolated in a pure state (73).

Alkyl and aryl derivatives of the types $[\text{PdXR}(\text{PEt}_3)_2]$ and $[\text{PdR}_2(\text{PEt}_3)_2]$ are also intermediate in stability between their unstable nickel and stable platinum analogues, being readily prepared by alkylation or arylation of $[\text{PdX}_2(\text{PEt}_3)_2]$ (63, 140). The complexes *trans*- $[\text{PdXR}(\text{PEt}_3)_2]$ absorb carbon monoxide at room temperature and pressure to form the acyl derivatives *trans*- $[\text{PdX}(\text{COR})(\text{PEt}_3)_2]$ (48).

Mesityl oxide forms a π -allylic complex with palladium(II) chloride from which may be derived a stable phosphine complex $[\text{PdCl}(\text{C}_6\text{H}_9\text{O})\text{PPh}_3]$ of probable structure (XVI) (394).



4. $Pd(0)$ Complexes

Malatesta and Angolette (316) have prepared complexes of the type $[PdL_4]$ ($L = PPh_3$ and $AsPh_3$) and $[Pd\{P(p-ClC_6H_4)_3\}_3]$, which by their method of preparation should not contain metal hydride as do some of the analogous derivatives of platinum. The complex $[Pd(PPh_3)_4]$ has also been prepared by the action of PPh_3 on $[Pd(\pi-C_5H_5)(\pi-C_6H_9)]$ (183). Compounds of this last type could be useful intermediates for the preparation of other $Pd(0)$ complexes.

Complexes of $Pd(0)$ containing monodentate ligands, apart from their ready oxidation, are prone to dissociation. Complexes of the type $[Pd(\text{diphosphine})_2]$ are much more stable. These have been prepared by reduction of, for example, $[PdX_2(\text{diphosphine})_2]$ (91), or by direct reaction of metal and *o*-phenylenebis(diethyl-phosphine) (90).

C. PLATINUM

1. $Pt(II)$ Complexes

a. Halide Complexes with Monodentate Ligands. Square-planar complexes of the type $[PtX_2L_2]$ are readily formed by $Pt(II)$ halides and related compounds (see Table IX). As described previously, $Ni(II)$ and $Pd(II)$ halides also form stable four-coordinate complexes, and in a *trans*- $[MX_2L_2]$ series the stability decreases $M = Pt > Pd > Ni$. However, platinum differs from nickel and palladium in also forming stable *cis* compounds; in fact only the *cis* isomers have been isolated in a pure condition with certain ligands, e.g., PPh_3 . This applies in most examples of tertiary stibine complexes, although the very soluble *trans* isomers exist as the major component in equilibrium with the less soluble *cis* isomers in solution.

In many cases, particularly with trialkyl-phosphines and -arsines, mixtures of *cis* and *trans* isomers result from the preparation, and their separation and isomerization have been studied by Chatt and Wilkins (126–128, 130). The fact that the isomerization is photochemically effected (206) may not always have been taken into account. The isomers differ in the following ways: (1) *trans* isomers are more strongly colored; (2) *cis* isomers are much less soluble in organic solvents and usually have higher melting points; (3) *cis* isomers have large dipole moments.

The dipole moments of the *cis* isomers are generally in the range 9–13 D and may be contrasted with a value of 4.4 D for *cis*- $[PtCl_2(PF_3)_2]$ (131), which demonstrates the effect of the increased drift of *d*-electrons from the Pt atom into the *d* orbitals of the phosphorus under the influence of the very electronegative fluorine atoms.

Nuclear-spin coupling constants (J_{Pt-P}) are larger for *cis*- $[PtCl_2(PBu_3)_2]$

TABLE IX
 SIMPLE TERTIARY PHOSPHINE, ARSINE, AND STIBINE COMPLEXES OF Pt(II) HALIDES

Complex	Reference	Color	M.p. (°C)	Dipole moment (D)
<i>cis</i> -[PtCl ₂ (PMe ₃) ₂]	39, 62	White	324-326	13.1
<i>cis</i> -[PtCl ₂ (PMe ₃ CF ₃) ₂]	39	White	188-190 d	9.2
<i>trans</i> -[PtCl ₂ {PMe(CF ₃) ₂ } ₂]	39	Yellow	85-87	0
<i>cis</i> -[PtCl ₂ (PEt ₃) ₂]	61, 288	White	191-192	10.7
<i>trans</i> -[PtCl ₂ (PEt ₃) ₂]	61, 288	Yellow	142-143	~0
<i>cis</i> -[PtBr ₂ (PEt ₃) ₂]	288	White	201-202	11.2
<i>trans</i> -[PtBr ₂ (PEt ₃) ₂]	288	Yellow	134-135	~0
<i>cis</i> -[PtI ₂ (PEt ₃) ₂]	288	Pale yellow	→ <i>trans</i>	8.2
<i>trans</i> -[PtI ₂ (PEt ₃) ₂]	288	Dark yellow	136-137	~0
<i>cis</i> -[Pt(NO ₂) ₂ (PEt ₃) ₂]	288	White	192-193 d	—
<i>trans</i> -[Pt(NO ₂) ₂ (PEt ₃) ₂]	288	White	201-202	~0
<i>cis</i> -[Pt(NO ₃) ₂ (PEt ₃) ₂]	288	White	182-183	—
<i>trans</i> -[Pt(NO ₃) ₂ (PEt ₃) ₂]	288	Yellow	125-126	2.75
<i>cis</i> -[PtCl ₂ (PPr ⁿ) ₂]	288	White	149-150	11.5
<i>trans</i> -[PtCl ₂ (PPr ⁿ) ₂]	126, 288	Yellow	85-86	~0
<i>cis</i> -[PtBr ₂ (PPr ⁿ) ₂]	68	White	160-161	—
<i>trans</i> -[PtBr ₂ (PPr ⁿ) ₂]	68	Yellow	96-97	—
<i>trans</i> -[PtI ₂ (PPr ⁿ) ₂]	130	Yellow	118-119	—
<i>cis</i> -[PtCl ₂ (PBu ⁿ) ₂]	288	White	144	11.5
<i>trans</i> -[PtCl ₂ (PBu ⁿ) ₂]	288	Yellow	65-66	~0
<i>trans</i> -[Pt(NO ₂) ₂ (PBu ⁿ) ₂]	70	White	148	—
<i>cis</i> -[PtCl ₂ (PEe ⁿ) ₂]	130	White	124-125	—
<i>cis</i> -[PtCl ₂ (PPh ₃) ₂]	288	White	310 d	—
<i>cis</i> -[PtBr ₂ (PPh ₃) ₂]	319	Orange	300 d	—
<i>cis</i> -[PtI ₂ (PPh ₃) ₂]	319	Orange-yellow	285	—
<i>cis</i> -[PtCl ₂ (PMePh ₂) ₂]	274	Yellow-white	—	—
<i>trans</i> -[PtCl ₂ (PPh ₂ CF ₃) ₂]	41	Pale yellow	63-65	0
<i>trans</i> -[PtCl ₂ {PPh(CF ₃) ₂ } ₂]	41	—	134-136	0
<i>cis</i> -[PtCl ₂ (PEt ₂ Ph) ₂]	288	White	202-203	—
<i>trans</i> -[PtCl ₂ (PEt ₂ Ph) ₂]	288	Yellow	123	~0
<i>trans</i> -[PtI ₂ (PEt ₂ Ph) ₂]	288	Yellow	137-138	—
[PtCl ₂ (PCl ₃) ₂]	415	—	—	—
<i>cis</i> -[PtCl ₂ (AsMe ₂ Et) ₂]	130	Pale yellow	177-178	—
<i>trans</i> -[PtCl ₂ (AsMe ₂ Et) ₂]	130	Yellow	173-174	—
<i>cis</i> -[PtCl ₂ (AsEt ₃) ₂]	288	Off-white	142	10.5
<i>trans</i> -[PtCl ₂ (AsEt ₃) ₂]	288	Yellow	120-121	~0
<i>cis</i> -[PtBr ₂ (AsEt ₃) ₂]	401	Colorless	113-114	—
<i>trans</i> -[PtBr ₂ (AsEt ₃) ₂]	288, 401	Yellow	120	—
<i>cis</i> -[PtI ₂ (AsEt ₃) ₂]	401	Yellow	87-88	—
<i>trans</i> -[PtI ₂ (AsEt ₃) ₂]	288	Orange-yellow	93-94	—
<i>cis</i> -[Pt(NO ₂) ₂ (AsEt ₃) ₂]	288	White	169-170	—
<i>trans</i> -[Pt(NO ₂) ₂ (AsEt ₃) ₂]	288	White	199-200	—
<i>cis</i> -[PtCl ₂ (AsPr ⁿ) ₂]	126	—	131-132	—

TABLE IX (Continued)

Complex	Reference	Color	M.p. (°C)	Dipole moment (D)
<i>trans</i> -[PtCl ₂ (AsPr ₃ ⁿ) ₂]	288	Yellow	52	—
<i>trans</i> -[PtCl ₂ (AsBu ₃ ⁿ) ₂]	288	Yellow	54	~0
<i>trans</i> -[Pt(NO ₂) ₂ (AsBu ₃ ⁿ) ₂]	70	White	102–103	—
<i>cis</i> -[PtCl ₂ (AsPh ₃) ₂]	288	Off-white	ca. 300 d	—
<i>trans</i> -[PtCl ₂ (AsPh ₃) ₂]	288	Yellow	ca. 300 d	—
[PtI ₂ (AsPh ₃) ₂]	319	Apricot	276	—
<i>cis</i> -[PtCl ₂ (AsBu ₂ Ph) ₂]	130	White	120–121	—
<i>trans</i> -[PtCl ₂ (AsBu ₂ Ph) ₂]	130	Yellow	40–41	—
<i>cis</i> -[PtCl ₂ (AsMePh ₂) ₂]	58	Pale yellow	211–215	—
[PtBr ₂ (AsMePh ₂) ₂]	307	Yellow	—	—
<i>trans</i> -[PtI ₂ (AsMePh ₂) ₂]	368	Orange	229	—
[PtCl ₂ (AsMe ₂ Ph) ₂]	58	Yellow	167	—
[PtBr ₂ (AsMe ₂ Ph) ₂]	369	Yellow	201	—
<i>cis</i> -[PtCl ₂ {As(CH=CH ₂) ₃ } ₂]	313	—	90	—
[PtCl ₂ (SbMe ₃) ₂]	356	Pale yellow	—	—
<i>cis</i> -[PtCl ₂ (SbEt ₃) ₂]	288	Green-yellow	104	9.2
<i>cis</i> -[PtBr ₂ (SbEt ₃) ₂]	288	Green-yellow	132	—
<i>trans</i> -[PtI ₂ (SbEt ₃) ₂]	288	Yellow	68–69	~0
<i>trans</i> -[Pt(NO ₂) ₂ (SbEt ₃) ₂]	288	Green-yellow	200–205 d	~0
<i>cis</i> -[PtCl ₂ (SbPr ₃ ⁿ) ₂]	288	Green-yellow	80–81	—
<i>cis</i> -[PtBr ₂ (SbPr ₃ ⁿ) ₂]	6	Yellow	93–95	—
<i>cis</i> -[PtCl ₂ (SbBu ₃) ₂]	288	Green-yellow	62–63	10.9
<i>cis</i> -[PtCl ₂ (SbPh ₃) ₂]	288	Yellow	ca. 140 d	9.3

than for the *trans* isomer, suggesting that π -bonding is significantly stronger in the former (396). The far-infrared spectra of similar types of complexes have been measured in order to study the influence of the neutral ligand upon $\nu_{\text{Pt-X}}$ (6).

The Pt(II) complexes react in solution with further phosphine or other neutral ligand. For example, [PtCl₂(PEt₃)₂] forms [Pt(PEt₃)₄]Cl₂ (61, 289), [Pt(PEt₃)₂(NH₃)₂]Cl₂ (296), and [Pt(PEt₃)₂(thiourea)₂]X₂ (204). An application of this type of reaction was to show that [PtCl₂(PPh₃)₂] (too insoluble for dipole moment measurement) formed the [Pt(PPh₃)₂en]⁺⁺ cation with ethylenediamine (en), thus demonstrating the *cis* configuration of the starting complex (205).

Complexes with dissimilar neutral ligands, e.g., [PtX₂(PR₃)amine], are readily obtained from halogeno-bridged complexes as will be seen later. The spectra of a wide variety of these complexes have been studied (75, 76, 78, 80, 164).

Five-coordinate complexes of the type [PtX₂L₃] are uncommon: [PtBr₂-(AsMePh₂)₃] dissociates very readily in solution and it is difficult to differen-

tiate between a five-coordinate structure and the salt $[\text{PtBr}(\text{AsMePh}_2)_3]\text{Br}$ (369).

b. Halide Complexes with Polydentate Ligands. With bidentate ligands, Pt(II) complexes of the two types $[\text{PtX}_2(\text{chel})]$ and $[\text{PtX}_2(\text{chel})_2]$ are formed in an analogous way to the Pd(II) derivatives. Complexes with dias have been the most thoroughly investigated (207, 210, 211). $[\text{PtI}_2(\text{dias})_2]$ has been shown to be isomorphous with $[\text{PdI}_2(\text{dias})_2]$ and has thus a distorted octahedral structure in the solid state. Other bidentate ligands used include ditertiary phosphines (50, 102), dimethyl-*o*-(methylthio)phenyl-arsine (134), α -picolyldimethyl-arsine (196), and dimethyl-pent-4-enylarsine $[\text{Me}_2\text{As} \cdot (\text{CH}_2)_3 \cdot \text{CH}=\text{CH}_2]$ (297). This last example is of particular interest since it involves a tertiary arsenic atom and a C=C double bond as the donor centers of a chelate group.

Tri- and tetratertiary arsines have been similarly employed as ligands (22, 53). Preliminary X-ray examination of $[\text{PtBr}_2(\text{trias})]$ shows it to be mainly ionic. On this evidence it may be concluded that the tendency to form five-coordinate complexes is $\text{Pt(II)} < \text{Pd(II)} < \text{Ni(II)}$, although this may be a function of the particular ligands involved. The crystal structure of $[\text{PtI}(\text{QAS})][\text{BPh}_4]$ (QAS = tris(*o*-diphenylarsinophenyl)-arsine) has been examined and the cation shown to have a trigonal bipyramidal arrangement of ligands at the Pt atom (315).

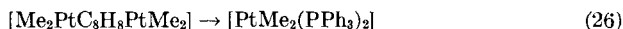
c. Hydride Complexes. Reduction of the complexes *cis*- $[\text{PtX}_2(\text{MR}_3)_2]$ ($\text{M} = \text{P}$ or As) produces the complexes *trans*- $[\text{PtHX}(\text{MR}_3)_2]$ (72, 113), which are much more stable than the corresponding palladium complexes. The usual reducing agent employed is hydrazine hydrate, but there are many other alternatives including ethanol and KOH (110).

The *trans*-square-planar structure has been confirmed by examination of the crystal structure of $[\text{PtHBr}(\text{PEt}_3)_2]$ (391). The hydrogen atom has a very high *trans*-effect and labilizes the anionic ligand in *trans* position to itself. Conversely, the anionic ligand influences the metal-hydrogen bond, as is shown by study of the infrared spectra of a series of hydrides $[\text{PtHX}(\text{PR}_3)_2]$ (74); for example, when $\text{X} = \text{NO}_2$, $\nu_{\text{Pt-H}} = 2242 \text{ cm}^{-1}$, and when $\text{X} = \text{CN}$, $\nu_{\text{Pt-H}} = 2041 \text{ cm}^{-1}$.

A series of complexes $[\text{PtH}_2(\text{PPh}_3)_n]$ ($n = 2, 3$, or 4) has recently been reported (137), being products previously formulated $[\text{Pt}(\text{PPh}_3)_n]$ (319). However, only $[\text{PtH}_2(\text{PPh}_3)_2]$ is substantiated by infrared spectra, a value of $\gamma_{\text{Pt-H}} = 1670 \text{ cm}^{-1}$ probably being indicative of a *trans*-dihydride.

d. Organic Complexes. Alkyl and aryl derivatives of the types $[\text{PtXR}(\text{PR}'_3)_2]$ and $[\text{PtR}_2(\text{PR}'_3)_2]$ are readily obtained (107, 108), and the former react with carbon monoxide under pressure to form $[\text{PtX}(\text{COR})(\text{PR}'_3)_2]$ (48). All these complexes are similar to, but considerably more stable than, their palladium analogues. It is usual to derive the alkyl and aryl complexes

from the halides $[\text{PtX}_2(\text{PR}_3)_2]$, but the stabilizing phosphine ligand has been introduced by the unusual reaction (163):

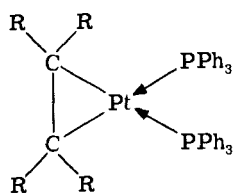


It is interesting to speculate whether the complex obtained by reaction of platonic chloride with tri(β -chlorovinyl)-arsine, formulated $[\text{Pt}(\text{CH}=\text{CHCl})_2\{\text{As}(\text{CH}=\text{CHCl})_3\}_2]$, was really the first monomeric σ -bonded organo-platinum derivative (326).

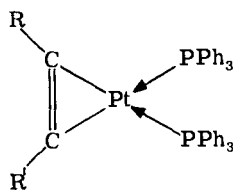
Studies of the infrared spectra of the alkyl and acyl complexes have shown the influence of various ligands on the metal-alkyl (4, 7) and on the metal-acyl (5) groupings.

Kinetic studies on several series of compounds, typified by *trans*- $[\text{MCl}(o\text{-tolyl})(\text{PET}_3)_2]$ ($\text{M} = \text{Ni}, \text{Pd}, \text{or Pt}$), show the rapid decrease in reactivity of the chloride ligand in passing from nickel to platinum [5,000,000(Ni):100,000(Pd):1(Pt)], and the relative *trans*-effect of a range of ligands substituted for (*o*-tolyl) in the above formula (36).

Olefins and acetylenes form the complexes $[\text{Pt}(\text{olefin})(\text{PPh}_3)_2]$ (114) and $[\text{Pt}(\text{acetylene})(\text{PPh}_3)_2]$ (105) by treatment of the reduction product of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ with the unsaturated hydrocarbon. These products are *cis*-planar Pt(II) complexes of probable related structures (XVII) and (XVIII).



(XVII)

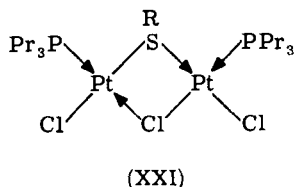
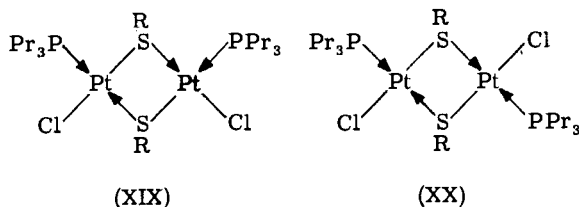


(XVIII)

e. Bridged Di-Platinum Derivatives. The binuclear halogen-bridged platinum complexes $[\text{Pt}_2\text{X}_4(\text{MR}_3)_2]$ ($\text{M} = \text{P}, \text{As}, \text{or Sb}$) have a *trans*-planar symmetrical structure like their palladium analogues. They are most conveniently prepared by heating together the complex $[\text{PtX}_2(\text{MR}_3)_2]$ and platinous chloride (68, 117). Monoamines (am) react with these bridged compounds to form the complexes *trans*- $[\text{PtX}_2\text{Lam}]$ (118). These unsymmetrical complexes have proved particularly amenable to physical measurements directed at assessment of the part played by the filled *d* orbitals of Pt(II) in its complexes.

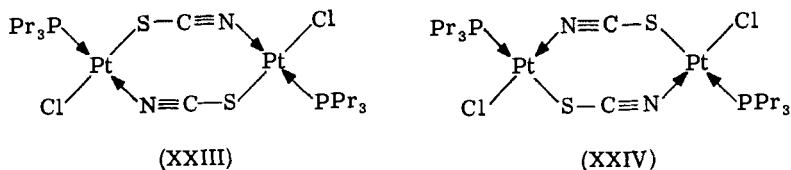
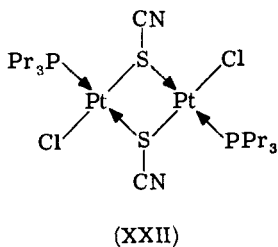
In contrast to the halogeno-bridged complexes, both thio-bridged and thiocyanato-bridged complexes exhibit isomerism (83). Separation of isomers by chromatography is only partially successful (295). With two

sulfur atoms in the bridging positions, *cis* and *trans* isomers, typified by structures (XIX) and (XX), are obtained, but with one bridging sulfur



and one bridging chlorine atom only the *cis* isomer, e.g., (XXI), is obtained (87).

The thiocyanato-bridged complexes were first assumed to be related to the thio-bridged complexes as in structure (XXII) (69), but it has since



been shown that the two isomeric forms are represented by (XXIII) and (XXIV) (71, 88, 392).

2. Pt(IV) Complexes

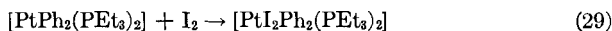
The Pt(IV) state is in general considerably more stable than the Pd(IV) state, and it may be assumed that complexes of the latter are too unstable to be readily isolated.

Platinic salts are reduced by tertiary phosphines to give complexes of Pt(II). Complexes of Pt(IV) are, however, readily obtained by the oxidation of a phosphine (67) or arsine (368) complex of Pt(II) with halogens:



Cis and *trans* isomers of the product may be obtained. Complexes of Pt(II) with polydentate ligands may be similarly oxidized (22, 210).

Alkyl and aryl derivatives of Pt(IV) can be obtained by the reactions (107, 108):



3. Carbonyl Complexes

The halogeno-bridged carbonyl complexes $[\text{Pt}_2\text{X}_4(\text{CO})_2]$ react with methyldiphenyl-arsine or phosphorus trichloride to give the unstable impure products $[\text{PtX}_2(\text{CO})(\text{AsMePh}_2)]$ (273) and $[\text{PtX}_2(\text{CO})(\text{PCl}_3)]$ (274). This type of complex can also be obtained by splitting the halogen bridge of $[\text{Pt}_2\text{X}_4(\text{PR}_3)_2]$ with carbon monoxide.

Malatesta and Cariello (319) treated $[\text{Pt}(\text{PPh}_3)_n]$ with carbon monoxide under pressure to obtain unstable mixtures of $[\text{Pt}(\text{CO})_x(\text{PPh}_3)_y]$. Products of more definite composition, $[\text{Pt}_3(\text{CO})_4(\text{PR}_3)_4]$, have been obtained by alternative methods but their structure is uncertain (50).

4. Pt(0) Complexes

The only established compounds of Pt(0) are of the type $[\text{Pt}(\text{diphosphine})_2]$, prepared by reduction of $[\text{PtCl}_2(\text{diphosphine})_2]$ (102). Although it has been suggested that the complexes $[\text{Pt}(\text{PPh}_3)_n]$ are really hydrides, several reactions (e.g., with methyl iodide, olefins, and acetylenes) have been described which give products not containing a metal hydride. The exact nature of all these complexes is thus still uncertain, and complexes of the type $[\text{Pt}(\text{PR}_3)_3 \text{ or } 4]$, free from hydride, almost certainly exist (11, 322).

By analogy with Pd(0), a possible preparative method for Pt(0) complexes would utilize a π -dienyl- π -enyl-Pt(II) complex.

IX. Group IB

A. COPPER

1. Halide Complexes

a. Complexes with Monodentate Ligands. Salts of Cu(II) are readily reduced by tertiary phosphine and arsine ligands and complexes of Cu(II) have not been established. Some complexes previously formulated to con-

tain Cu(II), e.g., $[\text{CuCl}_2(\text{PPh}_3)_2]$ (31), are diamagnetic and thus contain only Cu(I). However, the complex $[\text{CuCl}_2(\text{PCy}_3)_2]$ (276) is green, which may be indicative of the presence of Cu(II); magnetic measurements are necessary to confirm this.

With Cu(II) compounds particular care is necessary in the interpretation of results. In one instance, the product from cupric chloride and methyldiphenyl-arsine was found to be paramagnetic and formulated as $[\text{Cu}_2\text{Cl}_3(\text{AsMePh}_2)_3]$ (343, 344), a complex of Cu(I) and Cu(II). The product, when pure, was later shown to be $[\text{Cu}(\text{OAsMePh}_2)_4][\text{CuCl}_2]_2$ (375).

Complexes of Cu(I) are known with ligand to metal ratios of 4:1, 3:1, 2:1, and 1:1. Methyldiphenyl-arsine is notable in forming complexes of all four types. Nyholm (378) has formulated the products as $[\text{Cu}(\text{AsMePh}_2)_4]\text{X}$, $[\text{CuX}(\text{AsMePh}_2)_3]$, $[\text{Cu}(\text{AsMePh}_2)_4][\text{CuX}_2]$, and $[\text{CuCl}(\text{AsMePh}_2)]_4$, respectively. Other ligands give complexes of one or more of these types, although not necessarily with formulations analogous to those previous. The 1:1 complexes are probably best known, and cuprous iodide readily forms this type with trialkyl-phosphines and -arsines. All the products are tetrameric and thus formulated $[\text{CuI}(\text{MR}_3)]_4$ (331). X-ray analysis of $[\text{CuIAsEt}_3]_4$ shows it to have a structure with the four copper atoms, each four-coordinate, at the apices of a regular tetrahedron (440).

Other examples of 2:1 complexes may not all be dimeric salts. A product formulated as $[\text{CuI}(\text{PEt}_3)_2]$ (348) melts as low as 38° ; $[\text{CuI}(\text{PMe}_2\text{Ph})_2]$ is a nonelectrolyte, as are certain other related complexes (66). Three-coordination has not been firmly established, however, and the products are not necessarily monomeric. In any further investigation in this particular field, the related "mixed" complexes of the type $[\text{CuBrP}(\text{OPh})_3\text{AsPh}_3]$ (19) may be worth further consideration.

The few 3:1 complexes described all readily dissociate, making their constitution difficult to determine.

Isolation of the 4:1 complexes may be aided by the use of anions having poor coordinating properties, as for example with $[\text{Cu}(\text{PPh}_3)_4]\text{ClO}_4$ (155).

Cuprous halides form complexes $[\text{CuX}(\text{PH}_3)_2]$ which lose phosphine, the iodide least readily, to give $[\text{CuX}(\text{PH}_3)]$ (264). The structure of these products has not been determined; they apparently decompose at low temperature. Primary and secondary phosphine complexes are represented by $[\text{CuCl}(\text{PH}_2\text{Ph})]_4$ (287) and $[\text{CuCl}(\text{PHPh}_2)]_4$ (286).

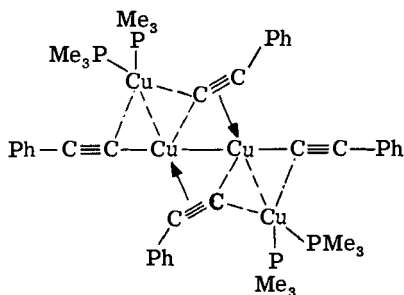
b. Complexes with Polydentate Ligands. From the above section it may be concluded that Cu(I) shows a strong tendency towards four-coordination even though it forms a variety of complexes with monodentate ligands. Complexes with polydentate ligands also show this tendency. With bidentate ligands two types of complex are formed: $[\text{Cu}(\text{chel})_2]\text{X}$ and $[\text{Cu}(\text{chel})_2][\text{CuX}_2]$ where *chel* = dias (294), *o*-diethylphosphino phenyl-

diethyl-arsine (145), or dimethyl-*o*-methylthiophenyl-arsine (132). As might be anticipated, a tridentate ligand forms the complex $[\text{CuI}(\text{triarsine})]$ (21). The tri- α -pyrryl-phosphine (PPyr_3) in the monomeric complexes $[\text{CuX}(\text{PPyr}_3)]$ is probably behaving as a tridentate ligand (277).

2. Organic Complexes

The product obtained from the action of cyclopentadiene and tripropylphosphine on cuprous oxide, formulated $[\text{Cu}(\text{C}_5\text{H}_5)(\text{PPr}_3)_2]$ (418), has some historical interest as the first reported cyclopentadienyl compound of a transition metal. The analogous reaction with triethylphosphine has, however, since been shown to produce $[\text{Cu}(\text{C}_5\text{H}_5)\text{PEt}_3]$ (451).

Acetylene complexes of copper have recently been investigated by Coates and co-workers (47, 141, 142). Treatment of a cuprous alkyl or aryl acetylide with a tertiary phosphine first gives $[\text{RC}\equiv\text{C}\cdot\text{Cu}\cdot\text{PR}'_3]_n$. The complex in which $\text{R} = \text{Ph}$ and $\text{R}' = \text{Me}$ has been shown by Corfield and Shearer to be tetrameric ($n = 4$) in the solid state, with the rather unexpected structure (XXV). This polymerization may be re-



(XXV)

duced by further coordination with phosphine, resulting, for example, in $[\text{PhC}\equiv\text{C}\cdot\text{Cu}(\text{PMe}_3)_2]$ and $[\text{PhC}\equiv\text{C}\cdot\text{Cu}(\text{PMe}_3)_3]$, this last complex being particularly unstable.

B. SILVER

Unlike the A subgroups, the IB subgroup shows greater similarity between its first two members than between its second and third.

1. Halide Complexes

a. Complexes with Monodentate Ligands. The 1:1 complexes $[\text{AgI}(\text{MR}_3)]_4$ ($\text{R} = \text{alkyl}$) (336) are all assumed to contain tetrahedrally coordinated $\text{Ag}(\text{I})$, since $[\text{AgI}(\text{AsEt}_3)]_4$ is isomorphous with $[\text{CuI}(\text{AsEt}_3)]_4$. Complexes of $\text{Ag}(\text{I})$ and $\text{Cu}(\text{I})$ of this type dissociate on heating and are much less

stable than the corresponding complexes of Au(I). Tertiary alkyl phosphines are conveniently stored as their silver complexes, from which they can be regenerated when required. Where R = aryl, as for example in [AgBr(PPh₃)] (31), it is not known whether the complexes exist in a similar tetrameric form. It is interesting that [Ag(SCN)(PPr₃)_n]_n is polymeric in a different way. Ag—SCN—Ag—SCN chains are bound in pairs by Ag—S cross-linking and a distorted tetrahedral configuration results about the silver atom (423). The complex Ph₃BiAgClO₄ (366) requires further investigation to determine whether, as is unlikely, the bismuth is coordinated.

With the 2:1 complexes, for example [AgX(AsMe₂Ph)₂], [AgX(AsMePh₂)₂] (57), and related complexes (65, 66), the three-coordination, of interest due to its comparative rarity, appears to be more firmly established than with the Cu(I) analogues.

No 3:1 complexes have been described, but 4:1 complexes are exemplified by [Ag(PPh₃)₄](ClO₄) (155).

b. Complexes with Bidentate Ligands. As was the case with copper, two types of complex are formed with chelating ligands. One obtains both types, viz., [Ag(chel)₂]X and [Ag(chel)₂][AgX₂], from a particular ligand (132, 145, 196, 302, 453) less often than with the corresponding copper complexes.

2. Organic Complexes

Complexes typified by [Ag(C≡CPh)PEt₃]_n are obtained in a similar manner to their copper analogues, but are considerably less stable (47, 142). They are undoubtedly associated in solution but decomposition hinders more precise structural determination.

C. GOLD

1. Halide Complexes

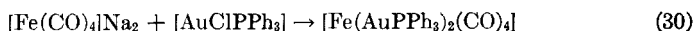
a. Au(I). Cahours and Gal (61, 62) showed that auric chloride treated with triethyl-phosphine or -arsine gives the aurous complex [AuCl(EEt₃)]. The analogous complex [AuClPPh₃] was later shown to be monomolecular (301). Mann and his co-workers (336) further investigated the trialkyl-phosphine and -arsine complexes. The former are much more stable and can be distilled without decomposition. Aurous halides with dimethyl-phenyl- and methyldiphenyl-arsine give the 1:1 complexes, but aurous cyanide behaves anomalously, possibly due to polymerization (173), although [AuCNPEt₃] has been described (418).

Even though, in contrast to Cu(I) and Ag(I), the preferred coordination number for Au(I) is two, it is perhaps surprising that the 1:1 complexes only rarely coordinate further. The only 2:1 complex described is

$[\text{AuI}(p\text{-Me}_2\text{NC}_6\text{H}_4\text{PMe}_2)_2]$, but this is largely ionized in solution (65). Another higher coordinate product is typified by $[\text{AuClPET}_3(\text{NH}_3)_2]$ (301).

Four-coordinate Au(I) is, however, well established in the complexes $[\text{Au}(\text{chel})_2]\text{X}$, where $\text{chel} = \text{dias}$ (209, 212, 377) and other tertiary diarsines and diphosphines (145, 213). The complex $[\text{Au}(\text{dias})_2]\text{I}$ has an X-ray diffraction pattern identical to that of $[\text{Cu}(\text{dias})_2]\text{I}$, both being presumed to have a tetrahedral configuration about the metal (212). Certain ligands, which are capable of chelating with a metal, do not form chelate complexes with aurous halides. Formation of products of the type $\text{XAu}(\text{diphosphine})\text{AuX}$, where diphosphine = triethylene-diphosphine (261) or 1,2-bis(diethylphosphine)ethane (453), demonstrates that high chelating power is necessary to overcome the preference for Au(I) to be two-coordinate.

An interesting application of $[\text{AuClPPh}_3]$ has been recently reported by Nyholm (381) in the preparation of complexes containing metal-metal heterobonds, e.g.,



Similarly, the carbonyl manganates (-1) and -cobaltates (-1) react to form $[\text{Mn}(\text{AuPPh}_3)(\text{CO})_5]$ and $[\text{Co}(\text{AuPPh}_3)(\text{CO})_4]$. This could be the start of a new field of work on metal-metal bonds.

b. *Au(III)*. Gold differs from copper and silver in readily forming complexes other than with the metal in the univalent state. Mann and Purdie (330) found that the complexes $[\text{AuXPR}_3]$ are oxidized by halogens to the Au(III) complex $[\text{AuX}_3\text{PR}_3]$, which in turn may be reduced back to the Au(I) complex with sulfur dioxide. An X-ray analysis of $[\text{AuBr}_3\text{PMe}_3]$ has shown it to have a square-planar structure (395). No *cis-trans* isomerism has been observed in complexes of the type $[\text{AuXX}'_2\text{PR}_3]$, presumably due to ease of isomerization to the more stable form.

Four-coordinate complexes of Au(III) with bidentate ligands are exemplified by $[\text{Au}(\text{dias})_2]\text{X}_3$ (209, 212, 377), formed by oxidation of $[\text{Au}(\text{dias})_2]\text{X}$. The complexes $[\text{AuI}(\text{dias})_2](\text{ClO}_4)_2$ and $[\text{AuI}_2(\text{dias})_2](\text{ClO}_4)$ have also been described. The former is more likely to be six-coordinate, although the hybridization involved in the formation of any six-coordinate Au(III) complex is difficult to explain.

2. Organic Complexes

The complexes $[\text{AuXPR}_3]$ on treatment with the appropriate organo-metallic reagent (e.g., Grignard) form the stable derivatives $[\text{AuR}'\text{PR}_3]$ (64). Alkynyl derivatives may be prepared similarly or by treatment of the aurous acetylide with a phosphine (143). The chemical and thermal stabilities of these products are intermediate between those of analogous organopalladium(II) and platinum(II) complexes.

Trimethyl gold forms complexes of the type $[\text{AuMe}_3\text{PPh}_3]$, which liberate ethane on heating (144).

X. Discussion

The nature of the ligand-metal bond and the significance of the vacant $3d$ orbitals of the phosphorus have been considered in several types of phosphine complex. Of possibly greater importance is the stabilization effect of phosphine and arsine ligands in assisting the study of the bonding of hydrogen and other anionic ligands in suitable stable complexes. The range of hydride and organic complexes stabilized by phosphine and arsine ligands is shown in Table X, which gives one example of each of the main types.

The other principal use of phosphine, arsine, and, to a lesser extent, stibine ligands lies in the stabilization of unusual oxidation states. Table XI gives one typical example for each oxidation state of the transition metals.

There are many spaces in both Tables X and XI which are likely to be subsequently filled. Oxidation states which ought to be exemplified include $\text{Ru}(0)$, $\text{Os}(0)$, $\text{Os}(I)$, $\text{Tc}(0)$, $\text{W}(II \text{ and } IV)$, Nb and Ta (various), and $\text{Ti}(0)$.

Further speculation can readily be made by consideration of an alternative classification of complexes, according to electronic configuration and coordination number, as shown in Table XII. Types of complex which it ought to be possible to prepare would thus include: $[\text{Ni}^I\text{XL}_3]$ (*a*) (other than $[\text{NiX}(\text{NO})(\text{PR}_3)_2]$), $[\text{Ru}^0(\text{diphosphine})_2]$ (*b*), $[\text{Cr}^I\text{X}(\text{CO})(\text{diphosphine})_2]$ (*c*), $[\text{W}^{II}\text{X}_2\text{L}_4]$ (*d*), and $[\text{V}^I\text{X}(\text{CO})_4\text{L}]$ (*e*).

It may be seen from Tables X and XI that chelating ligands play an important part under the heading of stabilization. Of the many chelating ligands studied, *o*-phenylenebisdimethyl-arsine, first prepared by Chatt and Mann, is outstanding in its versatility. Nyholm and his co-workers have shown that it forms complexes with a large number of transition elements. The metal in these complexes often has an unusually high oxidation state and may exhibit also an unusual coordination number. More recent studies involving the use of tertiary diphosphines suggest that, as a class, they are equally versatile with particular emphasis on their ability to stabilize low oxidation states. Other polydentate ligands are being used increasingly to achieve unusual coordination numbers. The stereochemical arrangements involved, which are necessitated by the nature of the polydentate ligand, are of considerable interest. Structural determination by X-ray analysis, particularly of complexes of unusual coordination number (i.e., other than 2, 4, or 6) or otherwise novel types, should be the ultimate aim wherever practicable in order to increase our fundamental knowledge of the constitution of complexes. Information so far obtained from X-ray

TABLE X
HYDRIDE AND ORGANIC COMPLEXES STABILIZED BY TERTIARY ORGANOPHOSPHINES AND ARSINES

Group VII	Group VIIIA	Group VIIIB	Group VIIIC	Group IB
[MnH(CO) ₄ PPh ₃]	[FeHCl(Me ₂ PC ₂ H ₄ PMe ₂) ₂]	[CoH(CO) ₃ PPh ₃]	—	—
[MnMe(CO) ₄ PPh ₃]	[Fe(C ₆ Cl ₅) ₂ (PEt ₂ Ph) ₂]	[CoPh(CO) ₃ PPh ₃]	[NiBr(<i>o</i> -tolyl)(PEt ₃) ₂]	—
[Mn(COMe)(CO) ₄ PPh ₃]	—	[Co(COMe)(CO) ₃ PPh ₃]	—	—
—	—	—	[Ni(olefin)(PPh ₃) ₂]	—
—	[RuH ₂ (Et ₂ PC ₂ H ₄ PEt ₂) ₂]	[RhHX ₂ (AsMePh ₂) ₃]	[PdHBr(PEt ₃) ₂]	—
—	[RuClMe(Ph ₂ PC ₂ H ₄ PPh ₂) ₂]	[RhBr(1-naphthyl) ₂ (PPr ₃) ₂]	[PdClMe(PEt ₃) ₂]	—
—	—	—	[PdCl(COMe)(PEt ₃) ₂]	—
—	—	[RhCl(diene)(PPh ₃)]	—	—
[ReH ₃ (PPh ₃) ₄]	[OsHCl(Et ₂ PC ₂ H ₄ PEt ₂) ₂]	[IrH ₃ (PPh ₃) ₃]	[PtHCl(AsEt ₃) ₂]	—
—	—	—	[PtClPh(PEt ₃) ₂]	[AuMePEt ₃]
—	—	—	[PtCl(COPh)(PEt ₃) ₂]	—
—	[OsCl ₂ (diene)(PEtPh ₂) ₂]	—	[Pt(olefin)(PPh ₃) ₂]	—
[ReCl(acetylene) ₂ PPh ₃]	—	—	[Pt(acetylene)(PPh ₃) ₂]	—

TABLE XI
EXAMPLES OF OXIDATION STATES OF TRANSITION METALS IN COMPLEXES WITH P, AS, AND Sb LIGANDS

Oxidation state	Group IV	Group V	Group VI	Group VII
-1	—	$[\text{V}(\text{CO})_5\text{PPh}_3]^-$	—	$[\text{Mn}(\text{CO})_4\text{PPh}_3]^-$
0	—	$[\text{V}(\text{CO})_4(\text{PPh}_3)_2]$	$[\text{Cr}(\text{Me}_2\text{PC}_2\text{H}_4\text{PMe}_2)_3]$	$[\text{Mn}(\text{CO})_4\text{PPh}_3]$
1	—	—	—	$[\text{MnCl}(\text{CO})_3(\text{PPh}_3)_2]$
2	—	—	$[\text{CrCl}_2(\text{PEt}_3)]_n$	$[\text{MnI}_2(\text{PPh}_3)_2]$
3	$[\text{TiCl}_3(\text{Et}_2\text{PC}_2\text{H}_4\text{PEt}_2)]$	$[\text{VCl}_3(\text{PEt}_3)_2]$	$[\text{CrCl}_3(\text{PEt}_3)_2]_2$	$[\text{MnCl}_2(\text{dias})\text{H}_2\text{O}]\text{ClO}_4$
4	$[\text{TiCl}_4(\text{dias})]$	$[\text{VCl}_4(\text{dias})_2]$	—	—
0	—	—	$[\text{Mo}(\text{CO})_5\text{PPh}_3]$	—
2	—	—	$[\text{MoBr}_2(\text{CO})_3\text{dias}]$	$[\text{TeCl}_2(\text{dias})_2]$
3	—	—	—	$[\text{TeCl}_2(\text{dias})_2]\text{Cl}$
4	$[\text{ZrCl}_4(\text{dias})_2]$	—	$[\text{MoBr}_4(\text{dias})]$	—
5	—	—	—	$[\text{TeCl}_4(\text{dias})]\text{Cl}$
0	—	—	$[\text{W}(\text{CO})_4(\text{PPh}_3)_2]$	$[\text{Re}(\text{CO})_4\text{PPh}_3]_2$
1	—	—	—	$[\text{ReCl}(\text{CO})_3(\text{PPh}_3)_2]$
2	—	—	—	$[\text{ReCl}_2(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2]$
3	—	—	—	$[\text{ReCl}_3\text{PPh}_3]$
4	$[\text{HfCl}_4(\text{dias})_2]$	—	—	$[\text{ReI}_4(\text{PPh}_3)_2]$
5	—	—	—	$[\text{ReCl}_4(\text{dias})_2]\text{ClO}_4$

Oxidation state	Group VIIIA	Group VIIIB	Group VIIC	Group IB
-1	—	[Co(CO) ₃ PPh ₃] ⁻	—	—
0	[Fe(CO) ₃ (PPh ₃) ₂]	[Co(CO) ₃ PEt ₃] ₂	[Ni(CO) ₂ (PPh ₃) ₂]	—
1	[FeI(CO) ₂ dias]	[CoBr(NO) ₂ PPh ₃]	[NiBr(NO)(PPh ₃) ₂]	[CuIAsEt ₃] ₄
2	[FeCl ₂ (PPh ₃) ₂]	[CoCl ₂ (PEt ₃) ₂]	[NiBr ₂ (PEt ₃) ₂]	[CuCl ₂ (PCy ₃) ₂]
3	[FeCl ₃ (AsPh ₃) ₂] ₂	[CoCl ₂ (Et ₂ PC ₂ H ₄ PEt ₂) ₂]Cl	[NiBr ₃ (PEt ₃) ₂]	—
4	[FeCl ₂ (dias) ₂][FeCl ₄] ₂	—	[NiCl ₂ (dias) ₂](ClO ₄) ₂	—
0	—	—	[Pd(Ph ₂ PC ₂ H ₄ PPh ₂) ₂]	—
1	—	[RhCl(CO)(PPh ₃) ₂]	—	[AgIAsEt ₃] ₄
2	[RuCl ₂ (AsMePh ₂) ₄]	[RhCl ₂ (AsMe ₂ Ph) ₄]	[PdCl ₂ (PEt ₃) ₂]	—
3	[RuCl ₃ (AsMePh ₂) ₃]	[RhCl ₃ (PEt ₃) ₃]	—	—
0	—	—	[Pt(Ph ₂ PC ₂ H ₄ PPh ₂) ₂]	—
1	—	[IrCl(CO)(PPh ₃) ₂]	—	[AuClPEt ₃]
2	[OsBr ₂ (SbPh ₃) ₄]	[IrBr ₂ (AsMe ₂ Ph) ₄]	[PtCl ₂ (PEt ₃) ₂]	—
3	[OsBr ₃ (AsPh ₃) ₃]	[IrCl ₃ (PEt ₃) ₃]	—	[AuBr ₃ PMe ₃]
4	[OsBr ₄ (AsPh ₃) ₂]	[IrCl ₄ (PPh ₃) ₂]	[PtCl ₄ (PPr ₃) ₂]	—

TABLE XII
SOME RELATIONSHIPS BETWEEN OXIDATION NUMBER, ELECTRON CONFIGURATION, AND COORDINATION NUMBER^a

Configu- ration	Coordina- tion number	Group V	Group VI	Group VII	Group VIIIA	Group VIIIB	Group VIIIC	Group IB
<i>d¹⁰</i>	4	—	—	—	—	[Co ^{-I} (CO) ₃ PPh ₃] ⁻	[Ni ⁰ (CO) ₂ (PPh ₃) ₂] [Pd ⁰ (PPh ₃) ₄] [Pt ⁰ (Ph ₂ PC ₂ H ₄ PPh ₂) ₂]	[Cu ^I Cl(AsMePh ₂) ₂] [Ag ^I IPe ₃] ₄ [Au ^I (dias) ₂]I
<i>d⁹</i>	4	—	—	—	—	[Co ⁰ (Me ₂ PC ₂ H ₄ PMe ₂) ₂]	(a)	[Cu ^I Cl ₂ (PCy ₃) ₂] ^b
<i>d⁸</i>	6	—	—	—	—	—	[Ni ^{II} (dias) ₃] ⁺⁺	[Au ^{III} I ₂ (dias) ₂] ⁺
	5	—	—	[Mn ^{-I} (CO) ₄ PPh ₃] ⁻	[Fe ⁰ (CO) ₄ PPh ₃]	[Co ^I (CO) ₃ (PPh ₃) ₂] ⁺	[Ni ^{II} Br ₂ trias]	[Au ^{III} I(dias) ₂] ^{++b}
	4	—	—	—	(b)	[Rh ^I Cl(CO)(PPh ₃) ₂]	[Pd ^{II} Cl ₂ (PEt ₃) ₂]	[Au ^{III} Br ₂ PMes]
<i>d⁷</i>	5	—	—	[Mn ⁰ (CO) ₄ PPh ₃]	[Fe ^I (CO) ₂ dias]	[Co ^{II} Cl ₂ (CO)(PEt ₃) ₂]	[Ni ^{III} Br ₃ (PEt ₃) ₂]	—
<i>d⁶</i>	6	[V ^{-I} (CO) ₄ PPh ₃] ⁻	[Cr ⁰ (CO) ₄ (PPh ₃) ₂]	[Mn ^{II} (CO) ₄ PPh ₃]	[Fe ^{II} Cl ₂ (CO) ₂ (PEt ₃) ₂]	[Co ^{III} I ₃ trias]	[Ni ^{IV} Cl ₂ (dias) ₂] ⁺⁺	—
<i>d⁵</i>	6	[V ⁰ (CO) ₄ (PPh ₃) ₂]	(c)	[Mn ^{II} Br ₂ (CO) ₂ dias]	[Fe ^{II} Br ₂ (dias) ₂] ⁺	—	—	—
<i>d⁴</i>	6	(e)	(d)	[Re ^{III} Cl ₃ (PEt ₃ Ph) ₃]	[Os ^{IV} Cl ₂ (dias) ₂] ⁺⁺	—	—	—

^a See text for explanation of italic letters in parentheses.

^b Constitution not fully established.

TABLE XIII
 CRYSTAL STRUCTURE DETERMINATIONS (X-RAY)

Coordination number	Complex	Reference	Structure
2	[AuCl(PCI ₃)]	16	Linear
4	[Co(C ₉ H ₁₁) ₂ (PEt ₂ Ph) ₂]	393	<i>trans</i> -Planar
	[NiBr ₂ (PEt ₃) ₂]	191, 410	<i>trans</i> -Planar
	[NiCl ₂ (PPh ₃) ₂]	435	Tetrahedral
	[Ni(NO ₃) ₂ (PEt ₃) ₂]	191, 410 ^a	Favors tetrahedral
	[Pd ₂ Br ₄ (AsMe ₃) ₂]	441	<i>trans</i> -Planar
			Symmetrical
	[Pd ₂ Cl ₂ (PEt ₂) ₂ (PHEt ₂) ₂]	218 ^a	Phosphorus-bridged Planar
	[PtBr ₂ (PEt ₃) ₂]	182 ^a	<i>trans</i> -Planar
	[PtHBr(PEt ₃) ₂]	391	<i>trans</i> -Planar
	[PtBrtrias]Br	22 ^a	Ionic
	[Pt ₂ Cl ₂ (SCN) ₂ (PPr ₃) ₂]	392	Thiocyanato-bridge (two isomers)
	[CuIASEt ₃) ₄	440	Tetrahedral
	[PhC:CCuPMe ₃) ₄	141	(see structure XXV)
	[Ag(SCN)PPr ₃) _n	423	Tetrahedral (distorted)
	[AuBr ₃ PMe ₃]	395	Planar
5	[NiBr ₃ (PEt ₃) ₂]	410 ^a	—
	[NiBr ₂ trias]	314	Square pyramid (distorted)
	[PtI(tetraarsine)] ⁺	315	Trigonal bipyramid
6	[W(CO) ₄ (PEt ₃) ₂]	265 ^a	Octahedral
	[ReOCl ₃ (PEt ₂ Ph) ₂]	174	<i>trans</i> -Octahedral
	[OsHBr(CO)(PPh ₃) ₃]	389 ^a	Octahedral
	[PdI ₂ (dias) ₂]	211 ^a	Distorted octahedral (Pt analogue isomorphous)
8	[TiCl ₄ (dias) ₂]	138 ^a	Dodecahedral

^a Preliminary results.

analysis is summarized in Table XIII. X-ray determination is usually concerned primarily with the stereochemistry of the central metal atom, but it may be mentioned that the arrangement of the three organic groups and the metal about the phosphorus or arsenic atom is, as expected, tetrahedral or nearly so.

Phosphine itself does not readily form well-characterized complexes, but primary and secondary phosphines form derivatives often notable for their dissimilarity to the complexes derived from the corresponding tertiary

phosphine. Issleib and co-workers have demonstrated this in many instances, and it is clear that the further study of complexes from primary and secondary phosphines will be of value. A particular instance of the potential importance here is provided by the preparation of binuclear phosphorus-bridged compounds, recently prepared by other methods also.

The recent discovery of the reactions of alcohols with phosphine complexes, or with a phosphine plus a metal halide, provides an added incentive to the study of phosphine, arsine, and stibine complexes. So far the reactions, involving reduction or reductive carbonylation, have been applied to derivatives of Ru, Os, Rh, Ir, and Pt. The possible application to catalytic work involving alcohols (or other compounds capable of hydrogen ion transfer) is obvious, and it would be particularly valuable to extend the number of "active" metals to include some first-row transition elements.

It is clear that recent events in the field of phosphine and arsine complexes have provided a fresh impetus in a variety of directions. Further developments of considerable importance are inevitable.

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ANHYDROUS METAL NITRATES

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I. Introduction

Until recent years, the field of metal nitrate chemistry was largely concerned with compounds containing the nitrate ion. There are two obvious reasons for this. Firstly, most of the known anhydrous metal nitrates were ionic compounds; secondly, solution properties were normally studied in aqueous media. Covalent bonds between metal atoms and nitrate groups cannot normally withstand the combined effects of high dielectric constant and solvation by water molecules, so that the effects observed in aqueous solution are properties of the free ions. Survey of the literature (Section VIII) reveals that nitrates of many metals are known in hydrated form, but that until recently very few anhydrous nitrates had been prepared. This applies particularly to the transition metals, where attempts to remove the molecules of water from the hydrate usually lead to hydrolytic decomposition through hydroxide nitrates to the hydroxide or the oxide, with evolution of nitric acid.

The presence of water, therefore, imposes severe limitations on the chemical behavior of the nitrate group; in this environment it cannot display its full versatility, and the present literature on this subject gives an entirely false impression of the range of behavior of which the nitrate group is capable. Anhydrous metal nitrates which are strongly covalent in character can be prepared in nonaqueous media (Section II). Some of these compounds are found to be volatile and monomeric in nonaqueous solution, and are strong oxidizing agents. Again, covalent bonding can involve one or two (or perhaps even three) of the oxygen atoms in the nitrate group, and the chemical reactivity of the covalent nitrate group seems to vary markedly with the number of oxygen atoms involved in bonding.

This versatility in nitrate chemistry forms the main theme of this article. It is not yet possible to present a completely systematic picture, since the anhydrous nitrates of some metals have still to be prepared and many aspects of the bonding and reactivity of metal nitrates have not yet been explored. Attention will therefore be focused on individual compounds which are representative of particular structures or properties. The article includes a brief summary of properties characteristic of free nitrate ions and ionic nitrates, so that comparison can be made with the covalent nitrates and their derivatives. Section VIII gives a systematic review of the metal nitrates now known, surveyed on the basis of the Periodic Table. Coordination complexes containing nitrate groups as ligands are not included unless they have some direct bearing on the properties of the simple nitrate. Again, we have regarded a general treatment of the molecular addition compounds of metal nitrates as being beyond the scope of this article, but some discussion of them is inevitable. For example, metal nitrates often

crystallize from liquid dinitrogen tetroxide as addition compounds with the tetroxide, and some simple nitrates (e.g., iron) are at present known only in this form.

II. Preparative Methods

Methods are subdivided below according to the reagent or reaction medium employed. Examples illustrating each method are given here, and further examples will be found in Section VIII.

A. CRYSTALLIZATION FROM AQUEOUS SOLUTION

This simple method is available for the nitrates of sodium, potassium, rubidium, caesium, thallium(I), barium, lead, and silver, each of which will crystallize from aqueous solution at room temperature. Solutions of the nitrates, free from other anions, are obtained by the usual methods e.g., reaction of nitric acid with the metal or its carbonate or oxide. These nitrates may also be prepared, of course, by the more complicated techniques described below, but the use of such techniques is unnecessary in these cases.

In crystallizing in anhydrous form from water, the nitrates of the alkali metals (sodium to caesium) resemble the chlorates, but differ from the salts of many di- and tribasic oxy-acids, e.g., sulfates, phosphates, and carbonates, which are usually heavily hydrated. The same difference can be observed in the oxy-acid salts of some complex ions; tetramminecopper(II) sulfate crystallizes as the monohydrate $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$, whereas the nitrate $[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$ crystallizes in anhydrous form.

B. DEHYDRATION OF HYDRATES

A limited number of anhydrous nitrates may be obtained in this way. Lithium nitrate crystallizes from aqueous solution as the hydrate $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$, from which anhydrous LiNO_3 is obtained on heating. The nitrates of the alkaline earth metals show an interesting gradation. Barium, strontium, and calcium nitrates crystallize from aqueous solution at 20° as $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, respectively, and anhydrous strontium and calcium nitrates are readily obtained on heating the hydrates. However, when the hydrates $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Be}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ are heated, hydrolysis occurs and nitric acid is evolved.

Efforts to obtain the anhydrous compound from the nitrate hydrate are more successful if the temperature at which dehydration is carried out is reduced. The anhydrous nitrates of lanthanum, praseodymium, and neodymium are obtained by heating the hexahydrates, whereas cerium(III) nitrate was not obtained in this way (1). However, Walden and Birr (2) claimed to have prepared anhydrous $\text{Ce}(\text{NO}_3)_3$ by dehydration of its

hydrate over phosphoric oxide in a desiccator at 140° . Anhydrous manganese(II) nitrate has also been obtained by dehydration of the solid hydrate over phosphoric oxide in a vacuum desiccator at room temperature (3), but similar treatment of zinc nitrate hydrate gave an insoluble basic salt.

A number of claims are made in early work which cannot be accepted without some reserve, since it was not always established by analysis that the product was in fact the anhydrous nitrate, and physical techniques for confirming the presence of the nitrate group (and the absence of water) in the product were often not available. Hydrated scandium nitrate, $\text{Sc}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, is said to give anhydrous $\text{Sc}(\text{NO}_3)_3$ under vacuum at 100° (4), and the pentahydrate $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ loses its water of crystallization in a dry atmosphere (5). These observations are not consistent with the results of thermogravimetric analysis of these compounds (6), but the temperature ranges involved in the two cases are quite different. Cadmium nitrate can be prepared by heating its hydrate (7); this is feasible in view of the ionic character of the anhydrous salt. When gallium metal is dissolved in concentrated nitric acid, and the product freed from water and excess nitric acid by powdering in a vacuum or in a stream of dry air, the product is said to be anhydrous $\text{Ga}(\text{NO}_3)_3$ (8). The process of dehydration over phosphoric oxide in a vacuum desiccator can be a lengthy operation. A product believed to be anhydrous bismuth nitrate was prepared by desiccation of the hydrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ for a period of one year (9); the monohydrate may also be heated gently in an atmosphere of dry carbon dioxide (10).

C. METATHESIS OR DISPLACEMENT IN NONAQUEOUS SOLVENTS

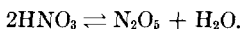
There are two main reasons why this method has been little used. Firstly, it usually involves reaction of the metal halide with silver nitrate, and the limited solubility of these compounds in organic solvents raises immediate problems. Secondly, anhydrous metal nitrates formed in this way tend to crystallize from solution as addition compounds with organic solvents, and the final removal of combined solvent is often as difficult as is the removal of water. The formation of a bismuth nitrate in acetone solution by reaction of bismuth trichloride with silver nitrate has been described (11), and analogous reactions leading to the formation of the corresponding nitrates in acetone were carried out with solutions of SbCl_3 , FeCl_3 , CoCl_2 , ZnCl_2 , CdBr_2 , HgCl_2 , and SnCl_2 . In none of these reactions, however, was the solid anhydrous nitrate isolated. Guntz and Martin (12) attempted the preparation of anhydrous nitrates by using displacement reactions between metals and silver nitrate solutions. Manganese and copper metals were added to solutions of silver nitrate in acetone and in

phenyl cyanide, and the metals manganese, copper, nickel, and cobalt were added to solutions of silver nitrate in liquid ammonia. In all cases displacement occurred, and solvated nitrates were obtained as products. Displacement of silver from a solution of silver nitrate in methyl cyanide by copper gives the cuprous salt, and evaporation of the resulting solution yields the addition compound $\text{CuNO}_3 \cdot 4\text{CH}_3\text{CN}$. Efforts to remove the solvent resulted in decomposition of the nitrate (13, 14). The same complex has been prepared by reaction of copper powder with a solution of cupric nitrate in methyl cyanide (14).

An attempt has been made to prepare uranium tetranitrate by addition of the stoichiometric amount of silver nitrate in methyl cyanide to a solution of uranium tetrachloride in acetone. After removal of silver chloride, the green solution of uranium tetranitrate was evaporated under vacuum at room temperature, but as the product separated it decomposed spontaneously to uranyl nitrate (15). In this instance the difficulty encountered in the preparation lies not so much in the technique employed as in the inherent instability of uranium(IV) nitrate.

D. REACTIONS IN ANHYDROUS NITRIC ACID

Surprisingly, this method has met with little success. It might have been supposed that reaction of anhydrous metal halides with pure nitric acid would yield the anhydrous nitrate with evolution of hydrogen chloride, but this is not the case. The reaction of anhydrous nitric acid with CrCl_2 , CrCl_3 , MnCl_2 , FeCl_2 , FeCl_3 , CoCl_2 , NiCl_2 , and CuCl_2 has been studied; in all cases hydrated nitrates were produced (16). It is concluded that nitric acid reacts with anhydrous metal chlorides as though it were an equilibrium mixture of the free acid, acid anhydride, and water:



The transition metal ions have a strong affinity for water, which is removed by precipitation of the hydrated salt. Solvolysis to give nitrates is no doubt the first step in the reaction of the chlorides SiCl_4 , TiCl_4 , SnCl_4 , and SbCl_5 with pure nitric acid, but the products obtained were the metal oxides combined with some water or nitric acid (17).

The behavior of picrates and acetates has also been studied. Potassium and thallium(I) picrates reacted with nitric acid and on evaporation at 40° , under reduced pressure, crystalline mixtures of the nitrates with picric acid were obtained. Zinc, copper, and nickel picrates did not give pure nitrates, but on reaction of lead picrate with nitric acid, pure lead nitrate precipitated at room temperature (17). The replacement of the acetate by the nitrate group has some unusual features. It has been observed in the authors' laboratory that the stability of a metal acetate-nitrate often

exceeds that of the simple acetate or nitrate; this is no doubt connected with the close similarity in shape and dimensions of the two groups. In consequence, we have found that in reactions of anhydrous metal acetates with nitrate ions, partial replacement frequently occurs. Jander and Wendt (17) studied the reaction between zinc acetate and nitric acid; the product contained nitrate and acetate groups in equivalent amounts. Cadmium acetate, however, reacted to give pure cadmium nitrate and acetic acid.

E. USE OF DINITROGEN PENTOXIDE IN NITRIC ACID

The main disadvantage in the use of nitric acid alone arises from the water which may be produced either by dissociation or in the course of reaction. One method of obviating this is to use solutions of dinitrogen pentoxide in nitric acid, so that any water produced in the system is immediately converted into nitric acid. Furthermore, the pentoxide undergoes ionic dissociation, $\text{N}_2\text{O}_5 \rightleftharpoons \text{NO}_2^+ + \text{NO}_3^-$, in solution in nitric acid (18), so that this medium has obvious promise for the production of nitrates. The fact that it has been little used is no reflection on its potentialities; many metal nitrates have not yet been prepared, and more recent experiments using dinitrogen pentoxide have tended to concentrate on the application of the pentoxide alone or dissolved in aprotic solvents.

Anhydrous nitrates of copper(II), manganese(II), nickel(II), and cobalt(II) were prepared by condensation of dinitrogen pentoxide onto solutions of the nitrate hydrates in nitric acid (19). Kolb (20) and Misciatelli (21) reported the preparation of anhydrous thorium tetranitrate by this method, and the reaction has been studied in more detail by Ferraro and associates (22). The hydrate $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ was treated with a solution of dinitrogen pentoxide in 100% nitric acid at 25°. Under these conditions, the first product isolated was the addition compound $\text{Th}(\text{NO}_3)_4 \cdot 2\text{N}_2\text{O}_5$; the combined pentoxide was removed by heating at 150–160° for 4 hours under vacuum, to leave the anhydrous nitrate. Späth (23) used a modification of this technique to prepare what was probably the first authentic sample of anhydrous uranyl nitrate. The dihydrate was dissolved in fuming nitric acid, and the solution treated with dinitrogen pentoxide and dinitrogen tetroxide. A light yellow product precipitated which contained combined oxides of nitrogen; the latter were removed by vacuum treatment at 163°. There is some doubt about the purity of products thought by Marketos (24) and Ditte (25) to be anhydrous uranyl nitrate.

F. USE OF DINITROGEN PENTOXIDE ALONE

This oxide has not been used in the past to the same extent for the preparation of anhydrous nitrates as has dinitrogen tetroxide, but recent work (26) indicates that its reaction with hydrated nitrates may be a fairly

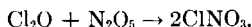
general method for the preparation of anhydrous nitrates. In many cases the same products are obtained as with dinitrogen tetroxide, but there are some instances in which it offers definite advantages. It is more reactive, and is of particular value in the preparation of nitrates of the early transition metals where oxide-nitrates are usually formed. In practice, its manipulation is more difficult since at any temperature above 0° it begins to decompose into the tetroxide and oxygen, and the range of solvents in which it can be dissolved without reaction is not so extensive as for dinitrogen tetroxide. It is known to dissolve in carbon tetrachloride, chloroform, and sulfuryl chloride (27), but there is little other information on its solubility in, or reactions with, organic solvents. In consequence, it has often been used undiluted in reactions with solids [e.g., CrO_3 , KCrO_3Cl (27), UO_3 (28)] or liquids [e.g., CrO_2Cl_2 (27)]. Pure dinitrogen pentoxide melts at 41° , but as usually prepared from nitric acid and phosphoric oxide it contains some nitric acid and dinitrogen tetroxide, and the impure material can be handled in the form of a liquid at 30° (29). In the liquid state it is virtually a non-conductor, and is presumed to have the structure $\text{O}_2\text{N}\cdot\text{O}\cdot\text{NO}_2$ found for the vapor; any self-ionization in the liquid will no doubt give the NO_2^+ and NO_3^- ions characteristic of the solid state. In reaction with halides, metal nitrates are produced and nitryl chloride is evolved. Dinitrogen pentoxide has also been found to react directly with some metals [e.g., Na, K, Mg, Fe, Cu, Zn, Cd, Hg (30, 31)].

Whether or not the presence of dinitrogen tetroxide in the pentoxide is a disadvantage appears to depend on the type of metal compound used in the reaction. In the preparation of zirconium and hafnium tetranitrates from the tetrachlorides (32), and titanium tetranitrate from the hydrate (26), Field and Hardy employed the impure pentoxide. However, Gibson *et al.* found that the reaction of uranium trioxide with dinitrogen pentoxide was erratic so long as dinitrogen tetroxide was present, but proceeded smoothly with the pure pentoxide (28). The reaction follows the same pattern when the pentoxide is used in solution in carbon tetrachloride. The adduct $\text{UO}_2(\text{NO}_3)_2\cdot\text{N}_2\text{O}_5$ is obtained as the initial product, and its thermal stability is lower than that of the corresponding adduct $\text{UO}_2(\text{NO}_3)_2\cdot\text{N}_2\text{O}_4$ obtained in reactions with dinitrogen tetroxide. The addition compound $\text{UO}_2(\text{NO}_3)_2\cdot\text{N}_2\text{O}_5$ was also obtained in an interesting solid-solid reaction involving UO_3 and the pure pentoxide. Uranium trioxide (325-mesh) was stirred with pure dinitrogen pentoxide in powder form at 0 – 10° , when a light orange mixture was originally formed. Within 10 minutes the powder conglomerated into beads; at this stage, the mixture suddenly turned bright yellow in color without any evident heat of reaction, giving a finely divided powder of the compound $\text{UO}_2(\text{NO}_3)_2\cdot\text{N}_2\text{O}_5$ (28). It seems likely that reaction of UO_3 actually occurs with N_2O_5 vapor, but the use of mixed

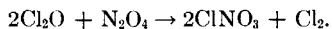
powders is a convenient method of maintaining a high concentration of pentoxide vapor at the surface of the metal oxide.

G. REACTIONS INVOLVING HALOGEN NITRATES

Since dinitrogen pentoxide is solid at room temperature, it is difficult to find a generally applicable technique by which the pure compound can be used at low temperatures. Some metal nitrates are only stable at low temperatures, and there are obvious disadvantages in the use of the pentoxide alone in these cases. The difficulty can be overcome by the use of the halogen nitrates, which are low melting. Chlorine nitrate is prepared by condensing together chlorine monoxide and dinitrogen pentoxide in a liquid-air bath. The mixture is then held for some hours at -80° , when the following reaction occurs:

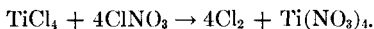


The liquid may then be allowed to warm to room temperature (33). The compound may also be prepared by reaction of chlorine monoxide with dinitrogen tetroxide at -30° (34):



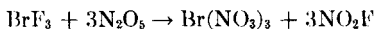
Chlorine nitrate melts at -107° , to a yellow liquid. The heat of vaporization is 7.3 kcal/mole, and the Trouton constant 25.1; by extrapolation, the boiling point is 18° (35). The infrared spectrum indicates that the structure is $\text{Cl}\cdot\text{O}\cdot\text{NO}_2$ (36). The chlorine atom is believed to carry a partial positive charge, $\text{Cl}^{\delta+}\text{-ONO}_2^{\delta-}$, so that in reaction the compound is a ready source of nitrate ions (37).

Because of its low melting point, reactions with liquid chlorine nitrate can be carried out conveniently at the temperature of solid carbon dioxide (-80°). For example (37),

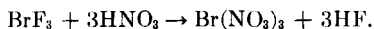


Chlorine, and excess of unreacted chlorine nitrate, can be readily removed in vacuum at -80° . Similarly, the nitrates $\text{B}(\text{NO}_3)_3$ (-78°), $\text{Al}(\text{NO}_3)_3$ (-7°), and $\text{Sn}(\text{NO}_3)_4$ (-60°) are said to be prepared by this method at the temperatures shown. Reactions of chromyl and vanadyl chlorides with chlorine nitrate yield the oxide-nitrates $\text{CrO}_2(\text{NO}_3)_2$ and $\text{VO}(\text{NO}_3)_3$.

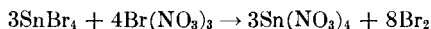
Some relevant reactions have also been carried out with bromine trinitrate, prepared by the reactions:



or



However, the compound melts with decomposition at 48° , so that it does not have the physical advantages of chlorine nitrate. It reacts with tin tetrabromide at -40° according to the equation:



and the colorless tin tetranitrate formed sublimes in vacuum at 40° (37).

This preparative technique has considerable potential value, and it is unfortunate that these interesting reactions have been published without analytical or physical evidence to support the identity of the products.

H. REACTIONS WITH ACETYL NITRATE

Dinitrogen pentoxide may also be used indirectly in the liquid state at 0° by dissolving it in acetic anhydride, when it is converted to acetyl nitrate. Crude acetyl nitrate prepared in this way has been purified by distillation under a pressure of 70 mm, the fraction boiling at $20-25^{\circ}$ being used for the preparation of metal nitrates (38). To date, the only reactions studied appear to be those with copper, lead, and magnesium oxides which are converted to the corresponding anhydrous nitrates in 3 hours at 0° . Acetyl nitrate decomposes above 60° , and explodes on rapid heating. It is probably desirable to dilute the compound with such liquids as carbon tetrachloride, and the method obviously merits further study. Benzoyl and benzyl nitrates did not give satisfactory results (39).

I. REACTIONS IN DINITROGEN TETROXIDE

This compound provides an excellent medium for the preparation of many anhydrous nitrates. It is liquid at room temperature (m.p. -11.2° , b.p. 21.15°) and is commercially available in some countries. A product of high purity may be prepared conveniently in the laboratory by heating dried lead nitrate (40, 41). The N_2O_4 molecule is represented by a single structure, $\text{O}_2\text{N}\cdot\text{NO}_2$, in the solid (42) and gaseous states (43). In the liquid state this structure predominates, but other structures are present also; the polarization properties of the liquid have been interpreted on the basis of a small content of $\text{NO}^+\cdot\text{NO}_3^-$ ion pairs (44). Chemical evidence is entirely consistent with the formation of NO^+ and NO_3^- ions, so that the equilibrium

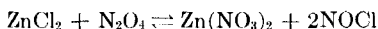


represents the typical self-dissociation of the liquid. This has been confirmed by several elegant methods (45, 46). The ionization will be extremely small in the pure liquid, but is enhanced when the tetroxide (dielectric constant 2.42) is diluted with liquids of high dielectric constant; Raman

spectra of solutions of the tetroxide in pure nitric acid indicate complete dissociation into NO^+ and NO_3^- ions (47).

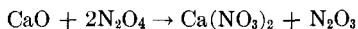
1. Solvolysis

It follows from the above that solvolysis of metal salts in this medium will result in the formation of anhydrous metal nitrates. Some metal chlorides undergo solvolysis, but the exact influence which the particular metal, its valency, and the ionic or covalent character of the chloride have on the extent to which solvolysis occurs is not yet fully understood. The anhydrous chlorides AgCl , NaCl , KCl , BeCl_2 (48), FeCl_3 (49), SnCl_4 (50), and CrCl_3 (51) do not react with liquid dinitrogen tetroxide. Traces of moisture, however, can promote reaction, and the reaction between moist potassium chloride and dinitrogen tetroxide is a standard method for the preparation of nitrosyl chloride (52). With some chlorides an equilibrium occurs; for example, when pure zinc chloride is treated with dinitrogen tetroxide at 20° , the liquid is immediately colored red:

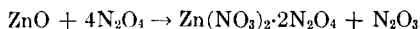


but six successive treatments with the liquid tetroxide were necessary for complete conversion of chloride to nitrate (53). In contrast, the reverse reaction is completed in a single stage. Some chlorides, e.g., TiCl_4 (54), UCl_4 , and UCl_5 (55), undergo ready solvolysis. The solvolysis of bromides and iodides has not been studied to any extent. On very little evidence, it would appear that solvolysis occurs with increasing readiness in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$.

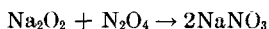
The reaction of liquid dinitrogen tetroxide with oxides to yield anhydrous nitrates was probably first noted by Oswald (56), who obtained sodium nitrate in this fashion. Subsequent studies have shown this method to be a general one. However, at room temperature and pressure the reactions are frequently slow. For example, after 40-hour contact at 20° , conversion of calcium oxide to nitrate:



is only 50% complete (57). Zinc oxide reacts more rapidly:



and the tetroxide addition compound has no cohesive character, so that the reaction is 95% complete after 20 hours at 20° (57). Sodium peroxide reacts slowly:



and the extent of reaction is only 20% after 48 hours at 20° (57). The reactions often proceed more readily in closed containers at elevated temperatures and the resultant high pressures (58, 59); this is a useful modification of the method in the case of anhydrous nitrates with high thermal stability. The oxides which have been studied are listed in Table I. Where an N₂O₄ adduct is first formed, the tetroxide can be removed by heating under vacuum.

TABLE I
REACTION OF METAL OXIDES WITH LIQUID DINITROGEN TETROXIDE

Oxide	Product	Reference
Na ₂ O ₂	NaNO ₃	57
MgO	Mg(NO ₃) ₂ ·N ₂ O ₄	58, 60
CaO	Ca(NO ₃) ₂	56-58, 61-63
SrO	Sr(NO ₃) ₂	58
BaO, BaO ₂	Ba(NO ₃) ₂	58, 64
L ₂ O ₃	L(NO ₃) ₃	65, 66
(L = Y, La, Pr, Nd, Sm, Gd)		
UO ₃ , U ₃ O ₈ , UO _{2.2}	UO ₂ (NO ₃) ₂ ·N ₂ O ₄	59
CuO, Cu ₂ O	Cu(NO ₃) ₂ ·N ₂ O ₄	58
Ag ₂ O, AgO	AgNO ₃	58, 63, 67
ZnO	Zn(NO ₃) ₂ ·2N ₂ O ₄	57, 58, 68, 69
Hg ₂ O, HgO	Hg(NO ₃) ₂ ·N ₂ O ₄	58, 70
PbO, Pb ₃ O ₄ , PbO ₂	Pb(NO ₃) ₂	58

Solvolysis has also been studied to a limited extent using metal hydroxides and metal carbonates. Sodium hydroxide, when carefully dried, reacts vigorously with liquid dinitrogen tetroxide, and the product shows 94% conversion to nitrate (71). Magnesium hydroxide also reacts, but conversion to nitrate is not complete (60). Dry lithium carbonate (60) and sodium carbonate (71) also react:

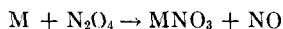


and the same reaction has been reported for magnesium carbonate (60), calcium carbonate (62), and zinc carbonate (72). As these are again solid-liquid reactions, they also require very long contact for complete reaction; reaction rates are increased in the presence of traces of water but nitrite is then introduced into the product. These reactions would not normally be used as preparative methods for the metal nitrates referred to, but they may be of use in other instances.

Some salts, which are not attacked by liquid dinitrogen tetroxide alone, do undergo rapid solvolysis when the tetroxide is diluted by electron-donor solvents. This aspect is discussed below.

2. Reaction with Metals

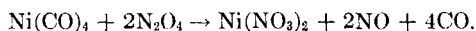
Dinitrogen tetroxide resembles water in that it attacks only a limited number of metals at room temperature. The reaction, represented by the equation



has been observed for the alkali metals (73, 74), zinc (68), and mercury (70), but most other metals [including barium, strontium, and calcium (48)] do not react in the massive state. Reactivity does sometimes vary with physical state; metallic silver deposited as a mirror from ammoniacal silver nitrate solution is readily attacked by the liquid tetroxide. Where reaction with metals does occur, some of the nitric oxide formed remains in the liquid as dinitrogen trioxide; this enhances the dielectric constant of the medium in the neighborhood of the metal surface, and increases reaction rate. The trioxide appears to take no part in the reaction, since products from reaction mixtures containing up to 70% of dinitrogen trioxide consist entirely of the metal nitrate (68).

3. Reaction with Metal Carbonyls

This method has been found to be an excellent one for the preparation of anhydrous nitrates of some transition metals. The carbonyl groups are not oxidized in the course of the reaction, e.g.,



No interfering anions are therefore involved, since carbon monoxide escapes from the system. The reactions can be conducted using the metal carbonyl and dinitrogen tetroxide alone, but are more readily controlled in the presence of an organic solvent. The rate of reaction depends greatly on the physical state of the metal carbonyl. Liquid carbonyls (nickel tetracarbonyl and iron pentacarbonyl) react violently; solid carbonyls react much more slowly, and reaction rate is a function of surface area. All reactions are strongly dependent on temperature; dimanganese decacarbonyl and dicobalt octacarbonyl react quite readily with dinitrogen tetroxide at room temperature, but reaction stops almost completely at 0°. The reactions with nickel tetracarbonyl and iron pentacarbonyl, which proceed with explosive violence at 0°, can be moderated somewhat at lower temperatures. By this method the anhydrous nitrates of manganese (75), cobalt (76), and nickel (77, 78) have been prepared. They are first isolated as the adducts $Mn(NO_3)_2 \cdot N_2O_4$, $Co(NO_3)_2 \cdot 2N_2O_4$, and $Ni(NO_3)_2 \cdot N_2O_4$, from which the dinitrogen tetroxide can be removed by heating under vacuum. With iron

and chromium carbonyls the products are the adducts $\text{Fe}(\text{NO}_3)_3 \cdot \text{N}_2\text{O}_4$ (49) and $\text{Cr}(\text{NO}_3)_3 \cdot 2\text{N}_2\text{O}_4$ (51), which cannot be so decomposed.

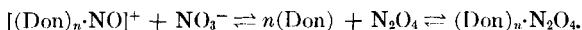
The two main conditions for the formation of simple anhydrous nitrates are that the dinitrogen tetroxide should be in the liquid state, and in large excess. Reaction between metal carbonyl and nitrogen dioxide vapors gives rise to nitrites as initial products [e.g., $\text{Ni}(\text{NO}_2)_2$ (78)]. In the liquid state, the isolation of intermediate products (the metal carbonyl nitrates) is seldom possible, but the compound $\text{Mn}(\text{CO})_5\text{NO}_3$ has been obtained from the reaction of dimanganese decacarbonyl with controlled amounts of dinitrogen tetroxide (79).

4. Use of Dinitrogen Tetroxide-Solvent Mixtures

Dinitrogen tetroxide is almost unique among nonaqueous solvents in that its reactivity can be modified, often to a remarkable extent, by dilution with organic solvents. Those solvents which behave in this way are of two types, the inert solvents and the electron-donor solvents. The inert solvents stimulate tetroxide reactivity by increasing the dielectric constant of the medium, and hence the self-ionization of dinitrogen tetroxide to NO^+ and NO_3^- ions. The presence of organic solvents also enables reaction products such as nitrates to dissolve in the medium; because of the small dielectric constant (2.42) of liquid dinitrogen tetroxide, no simple inorganic salts dissolve in the pure liquid. Nitromethane is a typical inert diluent; it is miscible in all proportions with dinitrogen tetroxide (80) and has a dielectric constant of 37. Although copper metal does not react with nitromethane or dinitrogen tetroxide alone, reaction is vigorous with a solution containing 75–90 mole % of nitromethane, and the electrical conductivity of the mixture is also at its maximum at this composition. The solution becomes green, and the compound $\text{Cu}(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$ separates on evaporation. The product of reaction of the mixture with zinc metal, $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$, is the same compound as is produced in dinitrogen tetroxide alone. Indium metal dissolves in a nitromethane-dinitrogen tetroxide mixture (though not in the tetroxide alone) and the nitrate $\text{In}(\text{NO}_3)_3$ separates as a tetroxide adduct (81). Uranium metal dissolves more slowly, and the maximum rate of reaction occurs at 30 mole % nitromethane (82). The liquid turns green, due partly to the presence of a U(IV) species in solution; when all the metal is dissolved the green color disappears, since the U(IV) oxidized by the tetroxide to U(VI) in solution is no longer replaced by more U(IV) from the metal. The compound $\text{UO}_2(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$ separates from the solution in a form which depends upon the composition of the medium. It can be thrown out of solution in an equimolar N_2O_4 - CH_3NO_2 mixture as a light yellow powder by addition of excess dinitrogen tetroxide; alternatively, it can be obtained in the form of beautiful large yellow crystals (up to 1 cm

in length) by allowing dinitrogen tetroxide vapor to dissolve slowly in a concentrated solution of the yellow powder in nitromethane (83). It is probable that the nitrates of many other metals can be prepared in this way, but nitromethane solutions have not been much used because the same products are often prepared more rapidly by using mixtures of the tetroxide with electron-donor solvents.

The dinitrogen tetroxide molecule is electron-deficient, and this leads to the formation of addition compounds with many organic solvents which possess an atom capable of donating electrons to the tetroxide. The composition and some properties of these compounds in the solid state have been studied in the case of carboxylic acids (84), esters (84, 85), anhydrides (85), ketones (84, 85), ethers (86-92), nitriles (84, 85), nitrosamines (84, 93), sulfoxides (94), and amines (95, 96). The liquid state is rather more complicated; the NO^+ ion as well as the N_2O_4 molecule is electron-deficient, and each species is associated with solvent molecules. The liquid mixtures are best represented by the equilibrium



The ultraviolet spectra of these mixtures indicate that discrete molecules of addition complex are not formed, but that partial electron transfer to the N_2O_4 and NO^+ species occurs (97). By the use of such physical properties as the vapor pressure (98), viscosity (99), volume of mixing (100), and heat of mixing (81), it is possible to arrange donor solvents in order of the degree to which they associate with dinitrogen tetroxide; this is also the order in which they stimulate the self-ionization, and thus the chemical reactivity, of dinitrogen tetroxide.

One of the major advantages in the use of these mixtures in preparative work arises from the fact that metal halides, which do not undergo solvolysis in the tetroxide alone, will often react vigorously with donor solvent mixtures. Ethyl acetate and methyl cyanide have found widest use in this connection. The anhydrous chlorides BeCl_2 (48) and FeCl_3 (49) are unreactive in the pure liquid tetroxide, but nitrosyl chloride is evolved copiously on addition of ethyl acetate. Reactivity of the tetroxide with metals is also stimulated by addition of donor solvents; manganese, cobalt, copper, cadmium, indium, and uranium are examples of metals which react with ethyl acetate-dinitrogen tetroxide mixtures, but not with the tetroxide alone. Dimethyl sulfoxide has been recently shown to be an excellent diluent for reactions with metals. It has the high dielectric constant of 46 (101), excellent donor properties towards dinitrogen tetroxide (94), and is a good solvent for metal salts. Its mixtures with dinitrogen tetroxide react with vanadium, molybdenum, antimony, silver, bismuth, and lead (102), but

aluminium, titanium, iron, chromium, nickel, and tin show little or no tendency to react even in this medium.

A variety of products may be obtained on crystallization from these solutions. The product varies with the metal concerned, and also with the solvent and its concentration; they may be classified as follows:

- (a) pure metal nitrate;
- (b) metal nitrate- N_2O_4 addition compound;
- (c) metal nitrate-solvent addition compound;
- (d) metal nitrate- N_2O_4 -solvent addition compound.

Examples of each type of product are given in Table II; where addition compounds are obtained, the anhydrous nitrate may sometimes be isolated

TABLE II
PRODUCTS OF REACTION OF METALS WITH DINITROGEN
TETROXIDE-ELECTRON DONOR SOLVENT MIXTURES

Metal	Reaction medium: N_2O_4 mixed with	Product	Reference
Cadmium	Ethyl acetate	$\text{Cd}(\text{NO}_3)_2$	67
Manganese	Ethyl acetate	$\text{Mn}(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$	75
Cobalt	Ethyl acetate	$\text{Co}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$	103
Uranium	Ethyl acetate	$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{CH}_3\text{COOC}_2\text{H}_5$	70
Indium	<20% Methyl cyanide	$\text{In}(\text{NO}_3)_3 \cdot 2\text{N}_2\text{O}_4$	81
	>20% Methyl cyanide	$\text{In}(\text{NO}_3)_3 \cdot 2\text{CH}_3\text{CN}$	81
Copper	5-30% Phenyl cyanide	$\text{Cu}(\text{NO}_3)_2 \cdot 2\text{C}_6\text{H}_5\text{CN} \cdot 4\text{N}_2\text{O}_4$	104
Bismuth	Dimethyl sulfoxide	$\text{Bi}(\text{NO}_3)_3 \cdot 3(\text{CH}_3)_2\text{SO}$	102

by heating the adduct under vacuum. However, this is not invariably the case, and each adduct is an individual problem in this respect.

J. USE OF MOLTEN SALTS

In all methods so far discussed in this section, both the reagents and the reaction medium have been readily volatile, and where the product is soluble they may be removed from this product by vaporization. The main problem in the use of molten salts as reaction media lies in the difficulty of isolating a soluble product, and the method has been little used for the preparation of anhydrous nitrates. Anhydrous mercury(II) nitrate has been prepared by dissolving the dihydrate in molten mercuric bromide (105); water of crystallization evaporated at the temperatures corresponding to the liquid range of mercury(II) bromide (238-320°). Anhydrous lanthanum nitrate has been prepared by reaction of lanthanum oxide, La_2O_3 , with molten ammonium nitrate at 170°. When the solution became

clear, the temperature was raised slowly and excess ammonium nitrate removed by volatilization (106). Clearly this method is of use only in the case of nitrates having high thermal stability.

III. The Nitrate Ion

A. DIMENSIONS

The nitrate ion has a symmetrical planar structure, and is geometrically similar to the ions BO_3^{3-} and CO_3^{2-} , with which it is isoelectronic. The N—O bond distance is near 1.22 Å (107, 108). A value of 2.19 Å for the ionic radius of the nitrate ion was calculated from the lattice parameters of cubic modifications of rubidium and thallium nitrates (109); this is to be compared with the "thermochemical" radius (1.89 Å) based on the lattice energies of the alkali nitrates (110). In a study of the physical properties of melts of the alkali metal nitrates, Janz and James (111) have proposed a disk-like model for the nitrate ion, formed by rotating the planar ion about its C_3 axis. When the N—O distance is corrected to allow for the Van der Waals radius of the oxygen atoms, a disk is obtained having diameter 4.62 Å and thickness 2.2 Å. The corresponding volume of the nitrate ion, 24.8 Å³, is then the same as that of the spherical chloride ion.

B. ELECTRONIC STRUCTURE

The nitrogen atom may be considered to form three planar sp^2 hybrid orbitals, leaving one p orbital perpendicular to this plane. The sp^2 hybrid orbitals overlap with oxygen orbitals, but it is not yet certain whether the oxygen bonding orbitals are sp hybrids or pure p orbitals. The molecular orbitals for a molecule of type AB_3 have been drawn up by Walsh (112), using pure p orbitals on atom B, and applied to the nitrate ion. Friend and Lyons (113) prefer to consider sp hybridization for each oxygen atom. If three bonds are thus formed between the sp hybrid orbitals of the three oxygen atoms, and the three sp^2 hybrids of the nitrogen atom, the p orbitals perpendicular to the plane of the NO_3 group will form π molecular orbitals. For each oxygen atom there remains an sp orbital (n_{sp}) and a pure p orbital (n_p), each of which is nonbonding. The increasing orbital energy sequence (113) is then

$$3\sigma, 3n_{sp}, \pi_1, 2n_p, \pi_2, \pi_3, n_p, \pi_4^*, 3\sigma^*.$$

The π_1 orbital is bonding, the π_2 and π_3 orbitals are nonbonding and degenerate, and the π_4^* orbital is antibonding. As there are 24 electrons to be arranged in the molecular orbitals, it follows that the π_4^* orbital and the three antibonding σ^* orbitals will be left vacant. Using more detailed calculations, McEwen (114) has refined this energy sequence.

In each approach, three π orbitals are filled (only one of which is a bonding orbital) and this accounts satisfactorily for the observation that the N—O bond length (1.22 Å) approaches the classical N=O double bond length of 1.19 Å.

C. ELECTRONIC ABSORPTION SPECTRUM

The absorption spectrum of the nitrate ion has been the subject of several investigations. There are two absorption bands. A high intensity band occurs near 200 $m\mu$, and a value of 10,000 has been reported for the extinction coefficient (115, 116). The low intensity band occurs at 302.5 $m\mu$, with an extinction coefficient of 7.06 per ion (117). These values were determined for aqueous solutions of metal nitrates. The spectrum for an aqueous solution of sodium nitrate is given in Fig. 1 (116). The precise values for λ_{\max} and ϵ are influenced by the presence of other electrolytes in the solution.

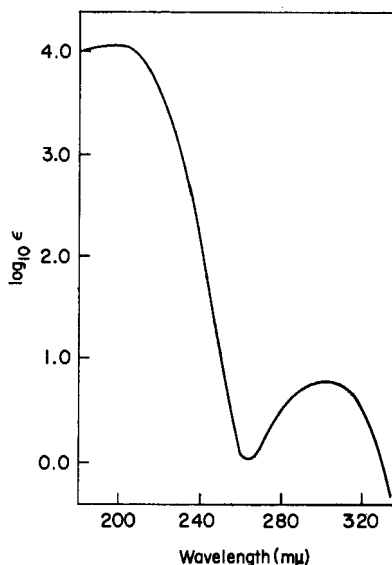


FIG. 1. Ultraviolet absorption spectrum of an aqueous solution of sodium nitrate.

There has been much discussion as to the origin of these two absorption bands. One school of thought (118, 119) attributes the high intensity band to a charge-transfer process from the nitrate ion to surrounding solvent. Another view (113, 114, 116) is that the absorption is due to excitation of an electron from either of the filled π_2 or π_3 orbitals to the vacant antibonding π orbital, π_4^* (a $\pi \rightarrow \pi^*$ type of transition which is symmetry-allowed). There is more general agreement on the low intensity band. This can be

attributed to a symmetry-forbidden internal transition in the nitrate ion, and the intensity and polarization data (113) are consistent with this being an $n \rightarrow \pi^*$ transition. There is an additional possibility, however, that it may be a weakly allowed $n \rightarrow \sigma^*$ transition (114).

The ultraviolet spectra of ionic metal nitrates in the solid state are essentially the same as in aqueous solution, though change of cation introduces some variation in both absorption and λ_{\max} (120). For solid sodium nitrate, Friend and Lyons (113) showed that the low intensity band moves from the value of 302.5 m μ found for aqueous solutions to about 284 m μ ; more recently, Cleaver and associates (121) have compared the ultraviolet spectra of crystalline nitrates of sodium, potassium, rubidium, and caesium. On heating the solids, abrupt shifts in absorption maxima occur at solid phase transition points and at the melting points. The electronic spectra for molten ionic nitrates are again similar to those observed for the solids and aqueous solutions; the electronic transitions are influenced by interactions between the nitrate ion and surrounding cations in the melt, so that the characteristics of the spectrum vary with the cation used. Detailed measurements have been carried out on the pure alkali metal nitrates (121) and on molten mixtures (121, 122). Systematic changes in the cation composition of a binary melt produce systematic shifts in the energy of the $n \rightarrow \pi^*$ transition. For example, λ_{\max} for molten potassium nitrate at 352°C is 306 m μ ; addition of anhydrous calcium nitrate rapidly increases the intensity of this absorption band, and when the electrical equivalent fraction of Ca^{2+} ions is 0.558, λ_{\max} is reduced to 290 m μ (122).

D. VIBRATIONAL SPECTRUM

In the study of the structure of anhydrous metal nitrates, the infrared spectrum has proved, to date, to be the most important physical property. Thus, when a nitrate ion becomes bonded covalently to a metal atom, the molecular symmetry alters and in consequence the number of vibrational frequencies and their selection rules also vary. The free nitrate ion will be discussed here, and the relation between spectra and type of covalent bonding will be treated in Section V.

The nitrate ion belongs to the symmetry point group D_{3h} . It can be shown (123) that the free ion possesses four fundamental vibration frequencies; two of these are each doubly degenerate, and the other two are nondegenerate. One of the latter (the totally symmetrical N—O stretch) is not infrared active but appears in the Raman spectrum. The modes of vibration for the nitrate ion (123) are given in Fig. 2. The four frequencies are numbered ν_1 , ν_2 , ν_3 , and ν_4 , in the order in which the irreducible representations to which they belong, occur. The symmetry species are also shown

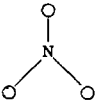

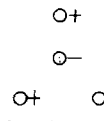
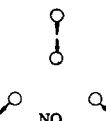
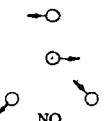
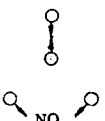
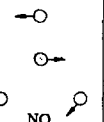
 NITRATE ION	$\nu_1(A_1')$	$\nu_2(A_2'')$	$\nu_3(E')$ Degenerate		$\nu_4(E')$ Degenerate	
	 N-O Stretching	 Out-of-plane rocking	 NO ₂ Symmetric stretching	 NO ₂ Asymmetric stretching	 NO ₂ Symmetric bending	 NO ₂ Asymmetric bending
ACTIVITY R. = RAMAN I.R. = INFRA- RED	R. 1050 cm ⁻¹	I.R. 831 cm ⁻¹	R. and I. R. 1390 cm ⁻¹		R. and I. R. 720 cm ⁻¹	

FIG. 2. Modes of vibration for the nitrate ion.

in Fig. 2. The frequencies calculated for the nitrate ion by Herzberg (123) are:

$$\nu_1 = 1050 \text{ cm}^{-1}; \nu_2 = 831 \text{ cm}^{-1}; \nu_3 = 1390 \text{ cm}^{-1}; \nu_4 = 720 \text{ cm}^{-1}.$$

The alkali metal nitrates, and certain of the alkaline earth metal nitrates, give infrared spectra which resemble closely the predicted spectrum. This is illustrated in Table III where the frequencies are also classified under D_{3h} symmetry.

TABLE III
INFRARED SPECTRA OF SOME ALKALI METAL NITRATES (CM⁻¹)

Compound	ν_1	ν_2	ν_3	ν_4
LiNO ₃	—	840	1374	736
NaNO ₃	—	837	1381	725
KNO ₃	1052 (w)	826	1383	715

The values quoted are those determined by Buijs and Schutte (124); very similar results have been obtained by Ferraro (125), Vratny (126), and Miller and Wilkins (127). It is clear that with metal nitrates of this type, any interaction with the metal ion is insufficient to restrict the normal vibrations of the nitrate ion, and ionic metal nitrates are normally defined as those which give this type of infrared spectrum.

IV. Ionic Metal Nitrates

As explained above, an ionic nitrate is readily recognized by reference to its infrared spectrum. While ionic nitrates are certainly formed by the

most electropositive metals, there is no rigid correlation between the type of metal-to-nitrate bonding and the electropositive character of the metal concerned, particularly so far as the less electropositive metals are concerned. Thus barium nitrate and lead nitrate are both ionic solids; silver nitrate is ionic but cupric nitrate is strongly covalent, and among the anhydrous nitrates of other transition metals no simple pattern has yet emerged from which one might predict the ionic or covalent character. Several factors are no doubt involved, of which the most important is probably the complexing power of the metal towards ligands in which oxygen is the donor atom. Some reference to ionic nitrates has already been made; this section will deal with some of the general properties of simple salts containing the free nitrate ion, using the alkali metal nitrates as typical examples. We shall discuss these nitrates by reference to the vapor, liquid, and solid states.

A. THE VAPOR STATE

The vapors of the alkali metal nitrates do not appear to have been studied, and this aspect of their chemistry has novelty and much potential interest. Until recent years, the concept that anhydrous metal nitrates might be stable as vapors was not generally accepted, and was, indeed, almost a contradiction in terms. The observation (to be discussed in later sections) that some metal nitrates, e.g., copper nitrate, could be stable in the vapor state has perhaps resulted in volatility being related too closely with covalency. The alkali metal nitrates represent the opposite extreme. The ionic solids melt to give stable liquids, which must presumably have finite vapor pressures; if so, it must be possible to distill them. Hardy and Field (255) have recently confirmed this. Nitrates of lithium, sodium, potassium, rubidium, and caesium were each heated at reduced pressure (5×10^{-3} mm Hg) in a silica tube placed in a furnace at 450–500°. A cold finger at 20° was inserted in the tube at such a position that metal nitrate could only reach it via the vapor phase. Distillation began as soon as the nitrate melted, and gram quantities of pure nitrate were collected on the cold finger; the process was most efficient in the case of caesium nitrate. One of the many questions of great interest which arise from these observations is the structure of the vapor species. The fact that the solids are ionic lattices need not necessarily have any bearing on the structure in the vapor, and to regard the vapor as being composed of ion pairs at these relatively low temperatures is to underestimate the potentialities of the nitrate group.

B. THE LIQUID STATE

Many ionic nitrates give stable melts. Some relevant temperatures for the alkali metal nitrates are given in Table IV.

TABLE IV
 STABILITY OF MOLTEN ALKALI METAL NITRATES

Compound	M.P. (°C) (128)	T_1^a	T_2^b (132)
LiNO ₃	255	410 (129)	474
NaNO ₃	308	380 (130)	529
KNO ₃	334	400 (131)	533
RbNO ₃	306	—	549
CsNO ₃	414	600 (129)	584

^a T_1 = temperature (°C) at which decomposition of the melt is first detected.

^b T_2 = temperature (°C) at which the dissociation pressure of oxygen reaches 1 atmosphere.

The initial decomposition of the melt is difficult to detect, so that the temperature T_1 is only an approximate value. Nevertheless, it is clear that melts are stable over a temperature range of at least 70°. Each nitrate decomposes to give nitrite and oxygen in the first instance; since dissociation pressures can be measured with accuracy, the temperature T_2 (Table IV) is a more reliable guide to stability than is T_1 . It is interesting to note that in spite of the wide range of size and polarizing power of the alkali metal ions, the variation in decomposition temperatures is not large, so that the nitrate ions in the melt are behaving essentially as kinetically free species. This is supported by recent measurements of the Raman (111) and infrared (133, 134) spectra of the melts, which show that the nitrate ion does not depart greatly from the D_{3h} symmetry of the free ion. From the Raman spectra, there is a regular variation in stretching force constant with polarizing power of the cation, but this amounts to only 8% on going from caesium nitrate to lithium nitrate.

The most direct evidence for the ionic nature of the melts is furnished by their electrical conductivity (Table V). Specific conductivities (column 2) were determined at the temperatures quoted, which were selected to enable direct comparison to be made for melts near 400°C. The molar conductivities (column 3) were determined at temperatures 10% (°K) above the individual melting points. The high values of conductivity indicate that ionic conduction occurs in the molten salts.

The relatively low melting points of the alkali metal nitrates is a surprising feature; the values given in Table IV are 300–500° lower than those of the corresponding chlorides. From consideration of the lattice energies of the solids (138) it is not immediately obvious why this should be the case. The nonspherical shape of the nitrate ions may be partly responsible; Janz and James (111) have calculated that there is more unoccupied space in the solid nitrates than in the chlorides, which would allow the nitrates

TABLE V
ELECTRICAL CONDUCTIVITY OF THE MOLTEN ALKALI METAL NITRATES

Compound	Specific conductivity ^a (ohm ⁻¹ cm ⁻¹)	Molar conductivity ^a (ohm ⁻¹ cm ²)	Activation energy ^b (kcal/mole)
LiNO ₃	1.61 (402°)	44	3.37
NaNO ₃	1.29 (387°)	55	2.97
KNO ₃	0.83 (405°)	45	3.65
RbNO ₃	0.64 (409°)	33	3.48
CsNO ₃	0.59 (447°)	46	2.97

^a References 135, 136.

^b References 135-137.

to become liquid at lower temperatures than salts such as the chlorides in which spherical ions allow close packing. Many physical properties of the melts are dependent to a lesser degree on anion shape, and there is an extensive analogy between the thermodynamic properties of liquid nitrates or their mixtures, and those of the corresponding halides (109). Surface properties are also similar. Figure 3 compares the surface tensions of the molten nitrates and chlorides of the metals of Groups I and II. The variation in

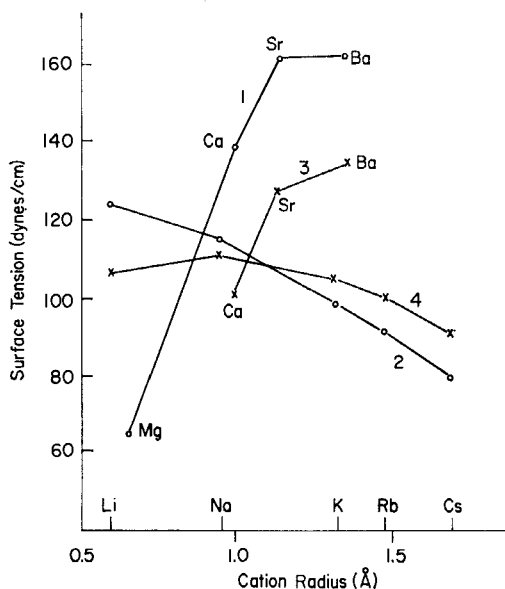


FIG. 3. Surface tensions of molten Group I and Group II metal chlorides and nitrates. 1: Group II chlorides at 1000°. 2: Group I chlorides at 800°. 3: Group II nitrates at 595° (Ba), 615° (Sr), or 560° (Ca). 4: Group I nitrates at 425°.

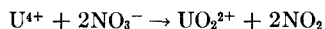
tension with cation size follows the same trend with each anion, and with the alkali metal salts the actual values of surface tension are also similar (128).

The low melting points of the alkali metal nitrates has led to their widespread use as reaction media. The liquids can be handled readily in Pyrex glass apparatus, which is not corroded. The available liquid range can be extended by the use of mixtures, usually of eutectic composition. The low temperatures available by this means are illustrated in Table VI.

TABLE VI
MELTING POINTS OF EUTECTIC MIXTURES OF ALKALI METAL NITRATES (139)

Components	M.P. (°C)
LiNO ₃ —NaNO ₃	206
LiNO ₃ —KNO ₃	125
LiNO ₃ —CsNO ₃	174
LiNO ₃ —NaNO ₃ —KNO ₃	120
NaNO ₃ —KNO ₃	223
NaNO ₃ —RbNO ₃	178
KNO ₃ —RbNO ₃	291
KNO ₃ —CsNO ₃	~200

Although there are many analogies in the physical properties of the molten alkali metal nitrates and chlorides, there are marked contrasts in the type of reaction which can be carried out in the two media. A full discussion on the use of molten nitrates as nonaqueous solvents is outside the scope of this review, but brief reference should be made to the influence which the oxidizing and complexing powers of the nitrate group exert on the type of reaction which is possible. Thus, Gruen (140) has shown that uranium tetrafluoride dissolves in LiCl—KCl eutectic to give stable green solutions. However, if a uranium tetrahalide is added to LiNO₃—KNO₃ at 175°, the reaction



occurs rapidly. Experiments of this type have led to the general conclusions that the U(III), U(IV), and U(VI) states are each stable in solution in molten halides, but that only the U(VI) valency state is stable in molten nitrates. Reduction by metals is possible in molten halides, but not in molten nitrates. Dissolution of neptunium tetrachloride in molten LiNO₃—KNO₃ gives a green solution whose ultraviolet absorption spectrum is almost identical with that of Np(V) in aqueous solution, so that lower oxidation states of neptunium are oxidized to Np(V) in nitrate melts, in contrast to the U(VI) state for uranium. Americium trichloride in LiNO₃—KNO₃ gives a pink solution which is characteristic of Am(III); the fact that oxidation in the nitrate melt does not occur is consistent with

the increasing stability of the lower oxidation states of the transuranium elements as the series is ascended (141). The competition between nitrate and chloride ions as ligands to metal ions can also be observed in molten nitrate media. Cobalt chloride undergoes the simple ionization, $\text{CoCl}_2 \rightarrow \text{Co}^{2+} + 2\text{Cl}^-$, in molten $\text{LiNO}_3\text{--KNO}_3$; the Co^{2+} ion is associated with six NO_3^- ions, perhaps as the complex $[\text{Co}(\text{NO}_3)_6]^{4-}$. On addition of potassium chloride to the melt, the absorption spectrum indicates a change to the complex $[\text{CoCl}_4]^{2-}$ (142). Similar reactions have been studied for solutions of nickel chloride (143), and chromatographic separations of many cations, using molten $\text{LiNO}_3\text{--KNO}_3$ as the liquid medium, can be interpreted satisfactorily on the basis of the relative stability of the complex ions formed (141).

For oxidation-reduction reactions in molten nitrates, a sequence of redox potentials will apply which may differ appreciably from that which is accepted for aqueous solutions. Thus, dichromates dissolve in molten $\text{NaNO}_3\text{--KNO}_3$ eutectic mixtures, but the reaction



proceeds at a measurable rate at 250° (144). When no other ions are present, the reaction



follows, but if other ions, e.g., bromide, are present oxidation can occur (145):



Further work of this kind will define new scales of reactivity which may prove to be important in synthetic inorganic chemistry.

C. THE SOLID STATE

Calculated values for lattice energies are given in Table VII.

TABLE VII
LATTICE ENERGIES (KCAL/MOLE) OF THE ALKALI METAL NITRATES

Reference	LiNO_3	NaNO_3	KNO_3	RbNO_3	CsNO_3
Yatsimirskii (110)	187	176	160	153	148
Waddington (138)	195	176	159	155	145

The values calculated by Yatsimirskii, using the Kapustinskii formula, are seen to be in good agreement with those obtained by Waddington from the values of the hydration heats of the ion pairs.

Crystals of the alkali metal nitrates have interesting optical properties.

In sodium nitrate, for example, the nitrate ions lie in parallel planes perpendicular to the threefold axis of the rhombohedral crystals. In this respect the NO_3^- ions resemble the CO_3^{2-} ions in calcite, and their polarizability is greater when the electric vector of the incident light wave lies in the plane of the groups than it is when the vector is perpendicular to the groups. This leads to birefringence in sodium nitrate which is even more pronounced than the well-known effect in calcite (146).

The chemical properties of ionic metal nitrates are best referred to in comparison with covalent nitrates, and will be treated in this way. For example, solid alkali metal nitrates behave as oxidizing agents when heated, hence the use of potassium nitrate as a constituent of gunpowder. However, oxidizing power increases with the covalency of the metal-nitrate bond, and some covalent nitrates can act as oxidizing agents at room temperature.

V. Covalent Bonding of the Nitrate Group

A. TYPES OF BONDING

One of the most useful comparisons which can be made in this connection is that between the ion NO_3^- and the oxide NO_3 . The two units differ by one electron only, yet the loss of this electron converts a stable ion into a highly unstable oxide. The high stability of the free nitrate ion indicates that the electron distribution in the ion (Section III) is also a stable one. In contrast, the oxide NO_3 has not even been properly characterized; there is some spectroscopic evidence for its formation in the reaction of ozone with dinitrogen pentoxide, or fluorine with nitric acid, and it may be produced as a transient intermediate in some gas phase reactions of nitrogen dioxide. In view of this, it might be argued that any influence, such as covalent bonding, which tends to restrict the distribution of electrons among appropriate molecular orbitals in the nitrate ion must inevitably lead to instability. This point of view is supported by the chemistry of nonmetal nitrates, such as methyl and fluorine nitrates which have the following structures



The C—O or F—O bond modifies the electron distribution in the NO_3 group, so that alkyl nitrates are explosive and fluorine nitrate is highly reactive. Until recent years it was therefore reasonable to deduce that covalent bonding between metal atoms and nitrate groups would lead to instability, and this was also in accord with the chemistry of metal nitrates as indicated by published literature. Thus, the known simple metal nitrates

were almost all ionic salts; anhydrous nitrates were unknown for most of the transition metals, where covalency might have been expected; nitrates were known for some transition metals in the form of hydrates, but here the water molecules coordinate to the metal atom and the nitrate is ionic. Again, the nitrate group was found to occur only rarely in coordination complexes, and even then the substitution of more than one nitrate group into a complex was unusual. In the spectrochemical series, which places ligands in order of their crystal field effects, the nitrate group is often not mentioned (147). This is understandable since the spectra involved are usually measured in aqueous solution, but when ligands are arranged in order of nucleophilic power, as determined by rates of substitution in cobalt complexes in solution in methyl alcohol, the nitrate group again occupies a humble position at the bottom of the list (148).

Recent research work has changed this general picture completely and has shown that nitrate chemistry, as we know it in aqueous medium, is only a small part of the behavior of which the nitrate group is capable. When zinc metal reacts with solutions of ethylammonium nitrate in liquid dinitrogen tetroxide, a crystalline product is obtained of composition $(\text{EtNH}_3)_2[\text{Zn}(\text{NO}_3)_4]$. Conductivity, transport, and other physical measurements show that the $[\text{Zn}(\text{NO}_3)_4]^{2-}$ ion is a stable unit in solution in nitromethane and other nonaqueous solvents, and is therefore a coordination complex in which all ligands are nitrate groups (149). Such complexes will not be discussed in detail in this review, but it is relevant that similar tetranitrato-metal complexes are now known also for manganese (150), iron (151), cobalt (150, 152), nickel (150), and copper (150). The heavy metals give stable hexanitrato complex ions, e.g., $[\text{Ce}(\text{NO}_3)_6]^{2-}$, $[\text{Th}(\text{NO}_3)_6]^{2-}$, and $[\text{U}(\text{NO}_3)_6]^{2-}$ (15, 153). Simple anhydrous nitrates of many metals have now been prepared by reactions carried out in nonaqueous solvents. Some of their properties (e.g., volatility) are quite unexpected, and leave no doubt that in the appropriate environment the nitrate group can be a strong ligand to a metal atom. Recognizing this, Straub *et al.* (150) have calculated the parameter Dq for solutions containing the $[\text{Ni}(\text{NO}_3)_4]^{2-}$ ion in nitromethane, and compared the value with those for some other corresponding Ni(II) complexes (Table VIII). It is of

TABLE VIII
SPECTROCHEMICAL SERIES FOR Ni(II) COMPLEXES

Ligand:	H ₂ O	NO ₃ ⁻	(CH ₃) ₂ SO	Cl ⁻
Dq (cm ⁻¹):	860	801	773	720

considerable interest that NO₃⁻ is found to occupy a position slightly lower than water, but greater than dimethyl sulfoxide or the chloride ion.

It is therefore quite clear that covalent metal nitrates and their derivatives are much more stable than the nonmetal nitrates; and it is possible that some form of back-donation of electrons from a metal atom to the empty orbitals of the nitrate group may make a contribution to this stability. The number, and the nature, of the bonds involved provide the main theme underlying most of the current investigations, and we may now consider the various ways in which such bonding can occur. These are illustrated in Fig. 4.

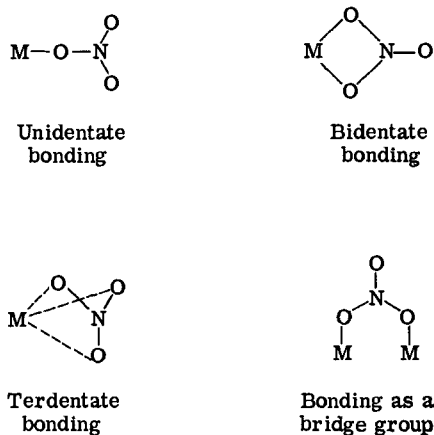


FIG. 4. Types of covalent bonding of the nitrate group.

All four types of bonding are theoretically possible, and we shall now consider each one individually.

B. UNIDENTATE BONDING

Covalent bonding of the nitrate group is readily recognized from its infrared spectrum. In compounds where the nitrate group is bonded through one oxygen atom, the symmetry of the group is lowered from the point group D_{3h} for the free ion to C_{2v} . This results in a loss of degeneracy in the vibrations designated ν_3 and ν_4 for the nitrate ion. There are therefore six vibrations for the covalent nitrate group, and all the vibrations are both Raman and infrared active. They are designated ν_1 , ν_2 , ν_3 , ν_4 , ν_5 , and ν_6 according to the irreducible representations of the point group, C_{2v} . The form of these vibrations (123) is given in Fig. 5, which also shows the symmetry species involved. The original assignment of the vibrational spectrum was assisted by the fact that the highly polarized lines in the Raman spectrum are caused by vibrations of the type A_1 , and further differentiation can sometimes be made by the use of isotopes. By these means the

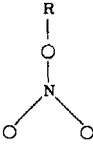
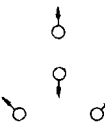
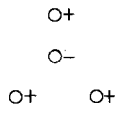
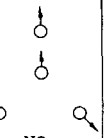
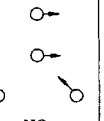
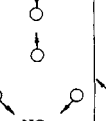
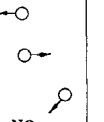
	$\nu_2(A_1)$	$\nu_6(B_2)$	$\nu_1(A_1)$	$\nu_6(B_1)$	$\nu_3(A_1)$	$\nu_5(B_1)$
 NITRATO GROUP	 N-O Stretching	 Out-of-plane rocking	 NO ₂ Symmetric stretching	 NO ₂ Asymmetric stretching	 NO ₂ Symmetric bending	 NO ₂ Asymmetric bending
ACTIVITY R. = RAMAN I. R. = INFRA-RED	R. and I. R.	R. and I. R.	R. and I. R.	R. and I. R.	R. and I. R.	R. and I. R.

Fig. 5. Modes of vibration for the unidentate nitrato group.

bands for nitric acid (154) and methyl nitrate (155) were assigned (Table IX) and the results used as a basis for the assignment of nitrato complexes of the type $M-ONO_2$ (156).

Comparison of Figs. 2 and 5 shows that several important changes have occurred:

- ν_1 for the ion becomes ν_2 in the covalently bonded group. Because of lowering of symmetry, this vibration now becomes active in the infrared, and the appearance of a ν_2 band in the spectrum is therefore a useful indication of the presence of a covalent nitrato group. The different values for ν_2 give some idea of the strength of the covalent bond, and Gatehouse *et al.* (156) have used the variation in this frequency to place a number of nitrato complexes in order of metal-nitrate bond strength.
- ν_2 for the ion becomes ν_6 in the covalent nitrate. Values for ν_6 are almost invariably at lower frequencies than ν_2 for the ion, so that the out-of-plane vibration requires less energy when the nitrate group is bonded to another atom.
- The degenerate vibration ν_3 for the ion is split into ν_1 and ν_4 in the nitrato group. Ferraro (125) has suggested that the extent of this splitting ($\nu_4 - \nu_1$) is a criterion of the strength of the covalent bond, and the values given in Table IX below show that $\nu_4 - \nu_1$ gives the same sequence for covalency as does the variation in ν_2 for the nitrato group. Increase in the strength of the bond to the oxygen atom concerned (Fig. 5) has the effect of fixing this atom in space, and is equivalent to an increase in weight at this position. The influence of such an increase will be more pronounced on the asymmetric than on the symmetric NO_2 stretching frequency, so that

as the metal and the degree of covalency change, ν_4 varies more than does ν_1 . From a detailed study of the infrared spectra of many metal nitrates dissolved in tributyl phosphate, Katzin (253) concludes that a $\nu_4 - \nu_1$ splitting of less than about 100 cm^{-1} can be attributed to electrical asymmetry rather than covalent bonding.

- (d) ν_4 is also a degenerate vibration in the ion, and gives rise to ν_3 and ν_5 in the nitrate group. These vibrations are often very weak and are sometimes not observed in covalent nitrates. Symmetry considerations (Fig. 5) suggest that ν_5 will be affected more than will ν_3 by change in the atom to which the nitrate group is attached.

The actual frequencies for the nitrate group cannot be predicted as for the free nitrate ion, since the absorption frequency will vary according to the strength of the metal-oxygen bond. Since this is generally unknown, the force constants for the nitrogen-oxygen bonds are also unknown. In some nitrates, the nitrate groups may be bonded as bidentate groups; again, in the solid state there are pronounced lattice forces which often give rise to additional spurious absorption bands, so that the infrared spectrum of a simple nitrate in the solid state is not an ideal basis on which to define the typical frequencies for a truly unidentate nitrate group. It is therefore preferable to select a compound in which the nitrate groups are shielded from interaction with one another or with other metal atoms, and where the coordination number of the metal makes it almost certain that the nitrate group is indeed unidentate. Nitratopentacarbonylmanganese is excellent in this respect, and its infrared spectrum is given in Table IX;

TABLE IX
INFRARED SPECTRUM OF THE UNIDENTATE NITRATE GROUP (CM^{-1})

Compound	ν_2	ν_6	ν_1	ν_4	ν_3	ν_5	Ref.
$(\text{CO})_5\text{MnNO}_3$	1010	805	1284	1486	—	—	79
Me_3SnNO_3	1031	780	1268	1488	727	—	158
$(\text{dipy})\text{Pd}(\text{NO}_3)_2$	979	801	1274	1517	—	—	156
CH_3NO_3 (vapor)	854	759	1287	1672	657	578	155
HNO_3 (vapor)	886	765	1320	1710	—	583	154
DNO_3 (vapor)	888	764	1313	1685	—	543	154

ν_3 and ν_5 were not observed in this spectrum, but the more important bands ν_1 , ν_2 , ν_4 , and ν_6 are regarded as quite characteristic of a unidentate nitrate group bonded to a manganese atom. With most of the heavy metals, the variation in these bands is relatively small from one metal to another. Nitratotrimethyltin is also a suitable compound from this point of view, and the infrared bands given by the nitrate group agree closely with those

for the manganese compound (Table IX). The palladium compound listed is perhaps less ideal since two nitrate groups are present, but again agreement is generally good.

In order to determine which infrared bands are most sensitive to change in the degree of covalency, we may compare the spectra for the nitrate-metal complexes with those given by methyl nitrate, nitric acid, and deuterium nitrate (Table IX), in which the nitrate group is bonded to light atoms and the degree of covalency is near 100%. ν_2 is diminished by about 100 cm^{-1} , but the most spectacular change occurs in ν_4 , where the increase in frequency is as much as 200 cm^{-1} . A similar effect is observed with certain metal nitrates, such as the beryllium compounds discussed below, where covalency is believed to be particularly strong.

C. BIDENTATE BONDING

Although there is no doubt that the nitrate group can bond in this way, there are very few authentic examples in which bidentate bonding occurs. This is all the more surprising since the isoelectronic carbonate group is well known as a bidentate ligand, and complexes such as $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$ have long been used as starting materials in synthetic work. This apparent difference in behavior cannot be attributed wholly to the double charge on the carbonate ion since the acetate ion, which is similar in shape and dimensions and carries a single charge, also behaves readily as a bidentate ligand. The earliest examples were provided by the nitrate-uranyl complexes. A series of compounds $\text{M}[\text{UO}_2(\text{NO}_3)_3]$ (where $\text{M} = \text{NH}_4, \text{K}, \text{Rb}, \text{Cs}$) (159) is known and an X-ray study of the rubidium salt leaves no doubt that the complex anion exists as a separate entity (160). Each uranyl group is surrounded by an equatorial ring of six oxygen atoms (at a distance of 2.72 \AA from the uranium atom), which are provided by three bidentate nitrate groups. The structure is shown in Fig. 6a, the six oxygen atoms concerned being joined by dotted lines for clarity. All the physical properties of solutions of alkylammonium uranyl nitrates in nitromethane can be interpreted satisfactorily in terms of the trinitrate-uranyl ion, so that this ion is stable also in solutions in nonaqueous solvents (161). There is X-ray evidence for a similar structure (Fig. 6b) for the addition compound uranyl nitrate-bis(triethylphosphate) in which each nitrate group is bidentate (162). Gatehouse and Comyns (157) and Allpress and Hambly (251) have interpreted the infrared spectra of uranyl nitrate dihydrate (Fig. 6c) and trihydrate (Fig. 6d) on the same model, and this is supported by X-ray data (252). It should be noted that for the trihydrate both a unidentate and a bidentate nitrate group are involved. These two structures account better for the splitting of the planar modes which occur in the infrared spectrum than do other obvious isomeric forms.

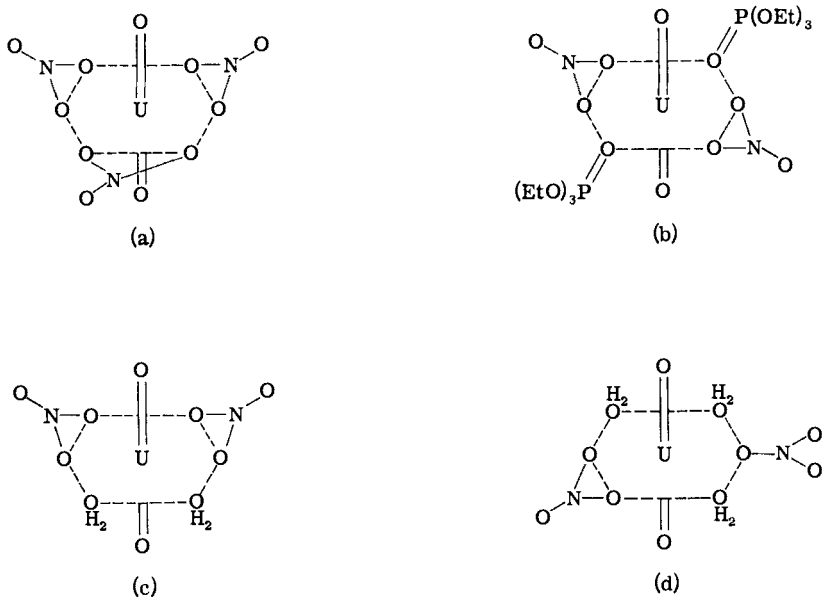


FIG. 6. Bidentate bonding of nitrate groups in uranyl complexes.

The impression given by existing literature, that bidentate bonding by the nitrate group is rare, may well prove to be quite erroneous. We believe that many nitrate complexes and even simple nitrates, in which the nitrate group is at present classed as unidentate, may prove on closer examination to involve bidentate groups. This position arises because no clear distinction can be made at present on the basis of infrared spectra alone (see below) and few studies involving other techniques have been made on these compounds. Three examples will illustrate this point of view. The cupric nitrate molecule in the vapor state, for which both unidentate and terdentate bonding had been proposed, is now found to contain bidentate nitrate groups. Half of the nitrate groups in solid copper nitrate also display some bidentate character. Since this compound has held a key position in this field of study, its structure is discussed individually below. Cobalt nitrate forms a complex $[\text{Co}(\text{Me}_3\text{PO})_2(\text{NO}_3)_2]$ with trimethylphosphine oxide, which might well have been regarded as a 4-coordinate complex. However, on full X-ray analysis of its structure, Cotton and Soderberg (163) found that the cobalt atom is surrounded by six oxygen atoms in irregular 6-coordination, so that the nitrate groups are actually bidentate. Again, the reflectance spectra and the electronic absorption spectra of nitromethane solutions of a series of methyltriphenylarsonium salts of the anion $[\text{M}(\text{NO}_3)_4]^{2-}$ (where $\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{or Cu}$) have been studied

(150). These measurements indicate that the manganese and cobalt complexes are 4-coordinate, but that in the case of nickel and copper the metal atom may be 6-coordinate in the complex. Ultimately it may be found to be generally true that bidentate nitrato groups occur wherever a metal atom has an apparently low coordination number (on the basis of unidentate nitrato bonding) in an environment where a higher coordination number would have been expected.

It has been mentioned that a clear distinction cannot be drawn between unidentate and bidentate nitrato groups on the grounds of infrared spectra alone. This applies to a bridging nitrato group also, and the reason for this is illustrated in Fig. 7.

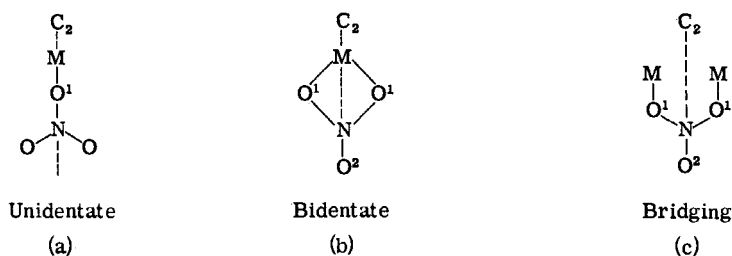


Fig. 7. Symmetry of unidentate, bidentate, and bridging nitrato groups.

Provided that the metal, nitrogen, and oxygen atoms are coplanar, a C_2 axis passing along one N—O bond exists for each structure, and each of the molecules possesses C_{2v} symmetry irrespective of the type of bonding. Each structure would then possess the same elements of symmetry, and give rise to the same six infrared active vibrations. Where the M—O¹ bond order in the unidentate nitrato case approaches unity, the metal will no longer be coplanar with the NO_3 group; the symmetry is reduced to C_s , but six infrared active vibrations will still be observed. When the unidentate group is compared with the bidentate or bridging group, shifts in certain of the frequencies can be predicted, and in this respect infrared studies have proved useful in determining structure. However, the general arguments applied to bidentate and bridging groups are so similar that infrared spectra are unlikely to be of much value in distinguishing between these two modes of bonding. Since these arguments are discussed below in connection with bridge bonding, they need not be referred to at this stage.

D. THE BRIDGING NITRATE GROUP

The first definite evidence that the nitrate group can bond in this way was provided by the crystal structure of anhydrous cupric nitrate (164), shown in Fig. 8. The main feature of the structure is the presence of infinite

chains parallel to the a axis, formed by alternate copper atoms and nitrate groups. Three such chains are shown in Fig. 8, and four more are represented, for clarity, by vertical full lines. The lengths of the bonds joining the copper atoms to oxygen atoms of these bridging nitrate groups are 1.95 and 1.99 Å, which are typical of the shorter Cu—O bonds in previously determined structures in which oxygen is coordinated to copper (165).

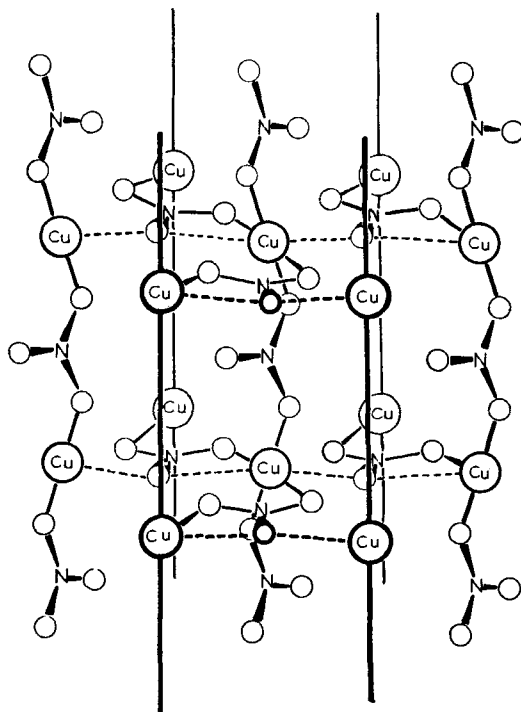


FIG. 8. Structure of solid copper(II) nitrate.

The chains are arranged parallel to each other in a pseudohexagonal manner, and are linked sideways by nitrate groups which lie approximately in planes perpendicular to the chains. In these planes, each nitrate group again bridges two copper atoms, with Cu—O distances of 1.97 and 2.04 Å. The third oxygen atom forms weaker bonds of lengths 2.43 and 2.64 Å to two copper atoms. Since the 2.04-Å and 2.64-Å bonds involve the same copper atom, this nitrate group is displaying some bidentate behavior. Viewing the structure as a whole, the bonding of the nitrate groups is such as to surround each copper atom with a distorted octahedron of oxygen atoms. When copper nitrate reacts with nitrosyl perchlorate, one of the nitrate groups is replaced to give a product $\text{Cu}(\text{NO}_3)(\text{ClO}_4)$ (166); since

two types of nitrate bonding are involved in the structure of copper nitrate, the replacement of half of the nitrate groups in this structure by perchlorate groups may account for the formation of this product.

Although the solid copper nitrate structure indicated the ability of the nitrate group to bridge two metal atoms, the group is nevertheless part of an infinite lattice, and it was obviously desirable to continue to search for a compound in which the nitrate group would act as a bridge group within a single molecule. An excellent example has now been found in basic beryllium nitrate, in which the nitrate group displays bridge bonding to a remarkable extent (167). Beryllium chloride undergoes solvolysis in mixtures of liquid dinitrogen tetroxide and ethyl acetate to give pale straw-colored crystals of the addition compound $\text{Be}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$. When heated in a vacuum, this decomposes in two stages. Dinitrogen tetroxide is evolved rapidly at 50° , leaving anhydrous beryllium nitrate, $\text{Be}(\text{NO}_3)_2$, as a white powder which has no detectable volatility. This is stable to about 125° , when sudden decomposition occurs to give brown fumes of nitrogen dioxide and a volatile beryllium compound which separates from the gas phase as colorless crystals. This has the formula $\text{Be}_4\text{O}(\text{NO}_3)_6$ and is believed (168) to possess the structure shown in Fig. 9. All six nitrate groups bridge

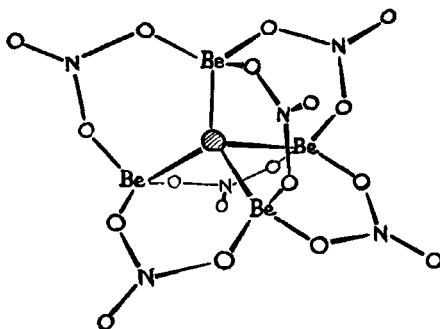


FIG. 9. Basic beryllium nitrate.

beryllium atoms, and it is clear that in the future this property must be regarded as characteristic of nitrate chemistry. There is an obvious analogy with basic beryllium acetate. The outer sphere of oxygen atoms will carry a larger charge than will the methyl groups which occupy these positions in the basic acetate, and in consequence the basic acetate is soluble, but the basic nitrate is insoluble, in nonpolar solvents such as chloroform, benzene, and carbon tetrachloride.

The infrared spectrum of basic beryllium nitrate consists of the following bands (cm^{-1}): 1630 (*vs.b*) 1550 (*sh.on* 1630 band) 1280 (*vs.b*) 1226 (*s.sp*) 1147 (*w*) 1065 (*s.b*) 863 (*s*) 805 (*s*) 767 (*s*) 715 (*w*). These bands have not

all been assigned, especially in the lower frequency range, since Be—O stretching frequencies and ring deformation frequencies occur here also. However, the band which has probably the greatest significance in the present context is the high frequency nitrate vibration at 1630 cm^{-1} . In the particular case of basic beryllium nitrate we have the advantage of having some information about its structure, but it is of interest to examine the kind of conclusions which might be drawn from this high frequency vibration in a case where structure is not known. If the nitrate group is strongly bonded in unidentate fashion, ν_2 , the NO stretching vibration (represented by the stretching of the bond N—O¹, Fig. 7a) decreases towards the limiting value of about 850 cm^{-1} . The vibration ν_4 increases to $1600\text{--}1700\text{ cm}^{-1}$ (Table IX); this vibration is antisymmetrical and therefore would not be polarized in the Raman spectrum. In the case of a bridging nitrate (Fig. 7c) which is strongly coordinated, the bond order of the M—O¹ bonds approaches unity. The bonds N—O¹ are therefore also near to single bonds, which means that the bond N—O² acquires double bond character. In the bridging nitrate, the vibration ν_2 refers to the stretching of this N—O² bond. The N=O stretching frequency lies in the range $1600\text{--}1700\text{ cm}^{-1}$ (absorption at 1696 cm^{-1} has been assigned (169) to the N=O stretch in the vapor of nitrous acid), so that absorption in this range may also be assigned to ν_2 for a bridging nitrate. However, this vibration is a totally symmetrical one, and would thus be a strongly polarized band in the Raman spectrum. Again, the restriction imposed on the NO₂ asymmetrical stretch ν_4 by bridge bonding will decrease the frequency ν_4 to the region of $1200\text{--}1300\text{ cm}^{-1}$. Nakamoto and co-workers (170) have recently reassigned the infrared spectra of a series of unidentate, bidentate, and bridging carbonato complexes on the basis of the arguments discussed above.

It will be seen therefore that the infrared spectrum, taken in conjunction with the Raman spectrum, can be of definite value in determining the mode in which covalent nitrate groups are bonded. Infrared absorption in the $1600\text{--}1700\text{ cm}^{-1}$ region is characteristic only of strong covalent bonding, but if this band can be assigned to either ν_2 or ν_4 with the aid of the Raman spectrum, then the type of bonding can be deduced with some confidence.

E. TERDENTATE BONDING

No compound has yet been found which displays this type of bonding. There seems to be no theoretical reason why this "face-on" or "sandwich" type of bonding should not occur; it would involve overlap of metal d orbitals with π orbitals of the nitrate group of suitable symmetry. This type of bonding was first postulated (171) for the cupric nitrate molecule in the vapor phase, it being considered that a bond capable of maintaining

a heavy metal nitrate as a stable vapor must involve the maximum possible covalency, in which the whole NO_3 group might be expected to participate. This suggestion has since proved to be incorrect (see below).

Any consideration of the infrared spectrum to be expected from a terdentate nitrate is not profitable until it has been possible to examine a compound in which this type of bonding is known to occur. It will be clear from the above discussion that insufficient is known about covalent metal-nitrate bonding to permit forecasts of the circumstances under which any particular structure will occur. Progress in the immediate future therefore depends to a large extent on the discovery of compounds which can be proved to contain new types of bonding. This in turn places renewed emphasis on the need for continued effort in preparative inorganic chemistry.

F. STRUCTURE OF COPPER(II) NITRATE IN THE VAPOR PHASE

This compound will be discussed individually since it illustrates the problems involved and there were no obvious analogies (in contrast to basic beryllium nitrate) on the basis of which the structure could be deduced. The vapor was shown to be monomeric from its vapor pressure (171) and mass spectrum (172). Assuming that each nitrate ion is bonded to the copper ion in the same manner, there are three possible structures for the molecule involving unidentate, bidentate, and terdentate bonding of the nitrate group. It was first suggested that the thermal properties of cupric nitrate were best explained on the basis of a "sandwich" structure. From the vapor pressure-temperature relation (171), the thermodynamic functions for the vaporization process have been calculated, and are given for three temperatures in Table X.

TABLE X
THERMODYNAMIC FUNCTIONS FOR THE VAPORIZATION OF
ANHYDROUS COPPER(II) NITRATE

T (°K)	ΔH (cal/mole)	ΔG (cal/mole)	ΔS (cal/mole/°)
453	15,600	6200	20.8
473	15,600	5730	20.9
493	15,600	5330	20.8

The heat of vaporization ΔH is surprisingly low; it is of the same order as values for the carbonyls of metals of the chromium group, and some cyclopentadienyl compounds (e.g., ferrocene). However, solid copper nitrate does not possess a molecular structure (Fig. 8), so that vaporization is a more complicated process than it is for the metal carbonyls. A study of the structure in the vapor state by electron diffraction was undertaken by

S. H. Bauer at Cornell University. Measurements were made on the vapor from a sample of copper nitrate at 180° ; in a preliminary examination of the data (173) visually estimated intensities were used for the computation of a radial distribution curve, and this indicated an unsymmetrical structure in which the copper was bonded to one unidentate and one terdentate nitrate group. The electron diffraction data have now been fully analyzed, and this structure shown to be incorrect. Of the many models tested, the model with approximately V_d symmetry containing two bidentate nitrate groups is the one which correlates best with the experimental radial dis-

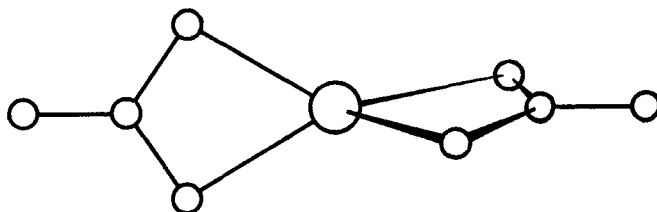


Fig. 10. Structure of copper(II) nitrate in the vapor phase.

tribution curve (174). This structure is shown in Fig. 10. The copper atom has the four nearest oxygen atoms at 2.00 \AA ; the O—Cu—O angle is 70° , and the Cu—N distance is 2.30 \AA . In the nitrate groups the average N—O distance is $1.30 \pm 0.04 \text{ \AA}$, and the ONO angle is 120° .

VI. Influence of Covalency on the Properties of Metal Nitrates

If the study of covalent bonding was of interest from the structural aspect only, it would have limited significance. However, the degree of covalency determines the chemical reactivity as well as the physical properties. In general, the stronger the covalent bond the more reactive does the compound become. The more important properties introduced by covalency will be outlined here, and further examples will be found in the systematic treatment given later.

A. VOLATILITY

Ability to exist in the gas phase is generally indicative of covalency in nitrates. Covalent nitrates are not usually stable in the liquid state, but can often be sublimed; it is this ability to pass directly from the solid state to the stable vapor which can be attributed to covalency. It should be remembered, however, that the alkali metal nitrates can be distilled. The sublimation of cupric nitrate and basic beryllium nitrate has already been referred to. The anhydrous nitrates of zinc (30), mercury (70), zirconium (32), and hafnium (30) also sublime as do some addition compounds, such

as $\text{Fe}(\text{NO}_3)_3 \cdot \text{N}_2\text{O}_4$ (49) and $\text{Al}(\text{NO}_3)_3 \cdot 2\text{CH}_3\text{CN}$ (175). The term "volatile metal nitrate" has been applied by the present authors to those nitrates which sublime readily at pressures of 10^{-1} – 10^{-2} cm Hg and at low temperatures (100–200°). It now seems likely that the covalent nitrates of other metals (e.g., nickel and manganese) classified as nonvolatile may in fact show some slight tendency to sublime on heating under sufficiently high vacuum. On the other hand, heavy metal nitrates [e.g., $\text{Cd}(\text{NO}_3)_2$] which show an infrared spectrum typical of an ionic structure, and which do not give stable melts, are not likely to sublime whatever the experimental conditions.

The only vapor pressure measurements which have been carried out are those on cupric nitrate (Table XI). The stability of the vapor is greater

TABLE XI
VAPOR PRESSURE OF ANHYDROUS COPPER NITRATE

Temperature: (°C)	157.0	172.8	186.4	189.5	202.0	215.2	222.6
Vapor pressure: (mm Hg)	0.32	0.59	0.99	1.15	1.87	2.84	3.59

than that of the solid; in the absence of other gases there is no evidence for the decomposition of the vapor below 226°, whereas decomposition of the solid is measurable even below 190° (171).

B. SOLUBILITY IN ORGANIC SOLVENTS

Covalent bonding enhances solubility in polar organic solvents. This is to be expected, since covalent nitrates usually dissolve as monomers in which there is the minimum of residual electrical field. The actual solubility values also depend upon the readiness with which the metal is solvated. The solubilities of two covalent nitrates [$\text{Cu}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$] are compared with those for the ionic silver nitrate in Table XII (176).

TABLE XII
SOLUBILITY OF ANHYDROUS NITRATES

Solvent	Solubility ^a (gm/100 gm solvent)		
	$\text{Cu}(\text{NO}_3)_2$	$\text{Zn}(\text{NO}_3)_2$	AgNO_3
Water	150 (25°)	128 (25°)	228
Ethyl acetate	151 (25°)	> 136	2.7
Nitromethane	5.1	0.45	(negligible)
Methyl cyanide	33.7	71	112

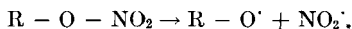
^a At 20° except where otherwise stated.

The high solubility of all three compounds in methyl cyanide is primarily the result of the high complexing power of methyl cyanide towards each of the metal atoms; each compound crystallizes from solution as an addition compound with methyl cyanide. The complexing power of nitromethane is very weak; all three solubilities are considerably reduced, but the influence of covalent bonding can now be seen. The most striking feature is the very high solubility of copper and zinc nitrates in ethyl acetate, compared with the value for silver nitrate. This is not due entirely to differences in nitrate bonding, however, since cadmium nitrate, which is ionic, is very soluble in ethyl acetate. It is relevant that copper and zinc form many stable complexes in which oxygen is the donor atom, whereas silver coordinates more readily with the nitrogen atom. It is also interesting to note that anhydrous copper nitrate is much more soluble in ethyl acetate than in water; 1 mole dissolves in 7.0 moles of water, but in only 1.41 moles of ethyl acetate. The heats of solution of the anhydrous salt in a large excess of water or ethyl acetate are 17.2 ± 0.1 and 15.9 ± 0.3 kcal/mole, respectively (247).

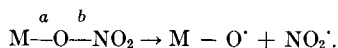
No simple anhydrous nitrate has been found which is soluble without decomposition in nonpolar solvents such as the aromatic or aliphatic hydrocarbons.

C. DECOMPOSITION IN WATER

When anhydrous metal nitrates are added to water, dissociation usually takes place to give the hydrated metal cation and nitrate anions. Beryllium nitrate, in which there is strong covalent bonding, behaves differently (48). When added to water, brown fumes are evolved; when hydrolyzed in sodium hydroxide solution, both nitrate and nitrite ions are produced. The amount of nitrite produced is about 5% of the nitrate added, and is largely independent of the concentration of the sodium hydroxide solution, within the range 0.05–2 *N*. The anhydrous (ionic) nitrates of barium, strontium, calcium, and magnesium dissolve in water to give metal and nitrate ions only, and the unusual behavior of beryllium nitrate is attributed to the strength of the metal-oxygen bond. Thus with the alkyl nitrates the dissociation into radicals is known to be an important step in their pyrolysis (177):

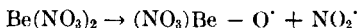


This dissociation may also occur in a nitrate group covalently bonded to a metal:



The dissociation occurs at bond *a* or bond *b*, or at both bonds, depending on their relative strengths. The size and polarizing power of the beryllium

atom is presumably sufficient to raise the bond strength of *a* to the same order as that of *b*. In addition to the usual form of ionization, the dissociation



is therefore considered also to occur to a small extent. The NO_2^\cdot radicals are responsible for the brown fumes on addition to water in an open vessel; when beryllium nitrate is hydrolyzed in a closed vessel in sodium hydroxide solutions, hydrolysis will occur to give equal quantities of nitrate and nitrite, so that about 10% of the original nitrate dissociates in this way.

It is of interest to compare the behavior of basic beryllium nitrate. In this compound each nitrate group is part of a 6-membered ring (Fig. 9). The NO_2^\cdot radical can no longer break away as in the simple nitrate, since two oxygen atoms are now bonded to beryllium atoms. This compound hydrolyzes slowly in alkaline solution to give nitrate ions only.

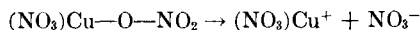
In nonaqueous media, such as ethyl acetate, anhydrous beryllium nitrate dissolves and gives a pale yellow color to the solution; the absorption spectrum shows that the color is due to nitrogen dioxide (48). It is likely that as further nitrates are prepared, other examples of such behavior will be found. Certain ruthenium nitrates are also believed to give nitrite on hydrolysis (178).

D. REACTION WITH ALIPHATIC COMPOUNDS

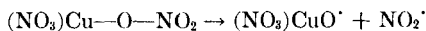
Ionic metal nitrates do not react with organic solvents at room temperature, but the behavior of certain covalent metal nitrates is in sharp contrast to this. The reaction of anhydrous copper nitrate with ethers has been examined in some detail (179, 184). If a small amount of diethyl ether is added to an excess of copper nitrate, reaction is vigorous and nitrogen dioxide and acetaldehyde are evolved. On one occasion, ether was slowly evaporated from a solution of copper nitrate in ether at 50°. When the solution became viscous, brown fumes were suddenly evolved and this was followed by a violent explosion. The reaction occurs only under conditions in which the strong covalent bonds between copper and the nitrate groups are maintained. Whether or not the copper nitrate-ether reaction occurs can therefore be determined by the solvent in which the reaction is carried out. Thus when ether vapor is passed into a solution of copper nitrate in nitrobenzene (in which the copper nitrate is present as a monomer), a reaction occurs, since coordination or solvation of the copper atom by nitrobenzene is insufficient to weaken the $\text{Cu}-\text{NO}_3$ bond. When ethyl acetate or methyl cyanide is used as solvent, no reaction occurs, even though copper nitrate is still a monomer in these solvents. These solvents presumably solvate the copper atom more strongly, and in consequence weaken

the Cu—NO₃ bond to such a degree that reaction with ether is no longer possible.

Since reaction is a function of covalency, it is suggested that it involves the type of dissociation already proposed for beryllium nitrate. The position is summarized as follows:

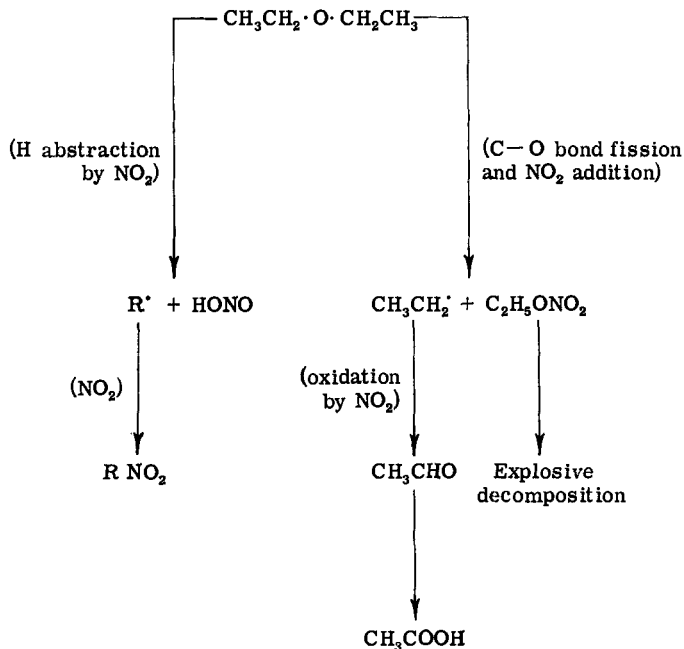


(in basic solvents; no reaction with ether)



(the nitrate alone in contact with ether, or in solution in weakly basic solvents; ether attacked by NO₂[•]).

The anhydrous nitrate is therefore regarded as a low temperature source of NO₂ radicals, which is consistent with the observation that the greater the nitrate:ether ratio, the more vigorous does the reaction become. The reaction between NO₂ and the ether is complex, but will include reactions of the type set out in the following scheme:



A green solid product remains, which has a remarkably consistent analysis corresponding to Cu₂(OH)(CH₃COO)(NO₃)(NO₂), and nuclear magnetic resonance confirms that all carbon present is in the form of the acetate ion. The ions NO₃⁻ and OH⁻ may well result from the NO₃·Cu·O[•] radical

originally produced; nitrite is formed in the course of hydrogen abstraction, and acetate as a result of oxidation.

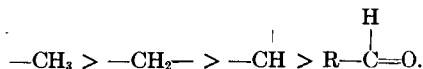
It follows from the above that diethyl ether is attacked at the C—O rather than the C—C bonds. Examination of a series of ethers, and other compounds containing the C—O bond, has shown that copper nitrate is a highly specific reagent. The results are summarized in Table XIII. There

TABLE XIII
BEHAVIOR OF COPPER NITRATE TOWARDS ORGANIC SOLVENTS

Compound	Behavior
Dimethyl ether	Addition compound $\text{Cu}(\text{NO}_3)_2 \cdot 1.5\text{Me}_2\text{O}$; very slow reaction with excess nitrate
Diethyl ether	Reaction under all conditions; explosive with excess nitrate
Di- <i>n</i> -propyl ether	Nitrate dissolves and reacts
Di-isopropyl ether	No solution or reaction
Di- <i>n</i> -butyl ether	Nitrate dissolves and reacts
Ethyl acetate	Solution but no reaction
Tetrahydrofuran	Reaction, with flashes of light, on contact; fairly stable solution
Dioxan	Solution but no reaction

is a sharp contrast in the behavior of dimethyl and diethyl ethers. Dimethyl ether was condensed onto copper nitrate at -70° ; on warming to -20° , ether evaporated to leave a pale blue solid which melted at -12° and was stable up to 50° .

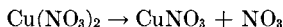
Ether is evolved from the molecular compound $\text{Cu}(\text{NO}_3)_2 \cdot 1.5\text{Me}_2\text{O}$, on addition of water. The difference in reactivity might have been explained if dimethyl ether acted as a strong ligand to copper, thus preventing reaction by weakening the Cu—NO₃ bond, but there is no evidence that its coordinating powers differ so greatly from those of diethyl ether. However, if we interpret the reactions as involving attack by NO₂ on the ether, then there is an analogy with the high temperature nitration of paraffins and ether by nitrogen dioxide. With the paraffins, the lowest members are the least reactive of the series (180, 181), and the higher aliphatic ethers give higher yields of nitro compounds (182). There is also a striking difference in the behavior of copper nitrate with *n*-propyl and isopropyl ether, so that the hydrogen atoms in α position to the oxygen atom play an important role in the reaction. This is also in accord with the known hydrogen abstraction reactions of the NO₂ free radical. The ease with which hydrogen is abstracted from an organic molecule depends on the strength of the C—H bonds; for paraffins and aldehydes this is represented by the series



From this mechanism it is understandable that the groups $\text{RCH}_2\text{—O—}$ and $\text{R}_2\text{CH—O—}$ should differ in reactivity.

The reaction of copper nitrate with nitromethane is perhaps the most surprising chemical property so far observed for a covalent metal nitrate, especially as nitromethane serves as a very satisfactory inert medium for reactions of dinitrogen tetroxide. Solutions of copper nitrate are stable indefinitely at room temperature, but reaction occurs if the solution is kept at the boiling point (101°) for some time (176). There is a delay period which is characteristic of free radical reactions, followed by sudden reaction. On boiling 0.135 *M* solution for 2 minutes, the solution suddenly evolves nitrogen dioxide copiously, and a green complex copper salt is deposited. More dilute solutions behave similarly, but longer delay times are involved. Copper nitrate dissolves readily as a monomer in nitromethane, but since the latter is a very weak ligand it will not decrease the strength of the Cu—NO_3 bond. Conditions are therefore ideal for the dissociation of the nitrate to the nitrogen dioxide radical. Its reaction with nitromethane at 100° is nevertheless surprising, and it is possible that nitromethane reacts in the enol form, $\text{CH}_2=\text{NO}(\text{OH})$.

Although a mechanism based on dissociation to give NO_2 radicals can therefore correlate these unusual properties of covalent nitrates, an alternative mechanism in which the molecule decomposes to give nitrogen trioxide is a possibility in cases where the metal concerned has an available lower valency. For example, with copper nitrate the dissociation



would be involved. It has been shown (183) that nitrogen trioxide is the active species in certain gas phase reactions of nitrogen dioxide, but not enough is yet known of the properties of nitrogen trioxide to determine whether this mechanism is feasible.

Reaction mechanisms involving the release of NO_3 or NO_2 free radicals have been postulated also for the reaction of titanium tetranitrate with *n*-dodecane (26). With these reactants in 1:2 mole ratio, reaction at 20° for 30 minutes gave about 10% of an alkyl nitrate. Reaction for 16 hours in 1:1 mole ratio gave a carboxylic acid together with alkyl nitrate and a nitroalkane; no alkyl nitrite was found. The products resemble those obtained by Titov and Shehitov (185) from the reaction of paraffins with dinitrogen pentoxide, where the NO_3 radical is again considered to be the active species.

The reaction of metal nitrates with aliphatic hydrocarbons is influenced by the structure of the hydrocarbon. In the work of Topchiev (186) and Konovalov (187) (in which hydrated nitrates were used) branched-chain hydrocarbons were usually found to react rather more readily than the

straight-chain hydrocarbons. This contrasts with the behavior of ethers discussed above (Table XIII).

E. AROMATIC NITRATION BY METAL NITRATES

Aromatic hydrocarbons do not undergo nitration by ionic metal nitrates (186), since the free nitrate ion does not readily give rise to NO_2 or NO_3 radicals. Nitration is possible, however, by using covalent metal nitrates. In 1925 Menke (188) observed that iron, copper, nickel, cobalt, aluminium, cerium, and uranyl nitrates could function as strong nitrating agents towards aniline and phenol, whereas the nitrates of the alkali or alkaline earth metals either failed to react or were poor nitrating agents. Bacharach (189) confirmed this, and showed that lithium nitrate was more reactive than the nitrates of the other alkali metals. In these reactions the metal nitrates (hydrated when the anhydrous salt was not known) were dissolved in acetic anhydride, anhydrous acetic acid, or mixtures of the two liquids, and it was assumed that acetyl nitrate, or acetylorthonitric acid $(\text{CH}_3\text{COO})_2\text{N}(\text{OH})_3$, was the species responsible for nitration. The reactions gave rise to *o*-nitration, as does acetyl nitrate. This interpretation of the reactions is incomplete in that it does not explain the profound influence exerted by the metal concerned on both reaction rates and yields. It should be noted that the solution of a metal nitrate hydrate in acetic anhydride will tend to produce the anhydrous metal nitrate in solution. In view of the reactivity of copper nitrate discussed above, it seems possible that the anhydrous nitrates themselves (or derivatives containing at least

TABLE XIV
NITRATION OF BENZYLIDENE DIACETATE BY METAL NITRATES IN ACETIC ACID

Nitrate used	Type of bond in anhydrous nitrate	% Yield of <i>p</i> -nitro-benzylidene diacetate
$\text{Cu}(\text{NO}_3)_2$ hydrate	strongly covalent	79
$\text{Zn}(\text{NO}_3)_2$ hydrate	covalent	23
$\text{Fe}(\text{NO}_3)_3$ hydrate	covalent	19
$\text{Bi}(\text{NO}_3)_3$ hydrate	covalent	19
$\text{Ni}(\text{NO}_3)_2$ hydrate	covalent	12
$\text{Mg}(\text{NO}_3)_2$ hydrate	ionic	8
$\text{Co}(\text{NO}_3)_2$ hydrate	ionic and covalent	4
$\text{Ca}(\text{NO}_3)_2$	ionic	0
$\text{Pb}(\text{NO}_3)_2$	ionic	0

one metal-nitrate bond, such as a covalent metal nitrate-acetate) may play an important part in the mechanism. There are at least two pieces of evidence in support of this. Firstly, anhydrous uranyl nitrate reacts rapidly with toluene to give a red solution from which nitrotoluenes can be sepa-

rated (83); zirconium tetranitrate behaves similarly (32). Secondly, Davey and Gwilt (190) compared the efficiency of a series of metal nitrates in the nitration of benzylidene diacetate; 21 gm of this compound was dissolved in 100 ml acetic acid, the metal nitrate (25–50 gm) added, and the mixture refluxed for several hours. The yields of the *p*-nitro derivative obtained are given in Table XIV.

There is a direct correlation between the covalency of the metal nitrates and the efficiency of their solutions as nitrating agents; the efficiency of copper nitrate far exceeds that of the other nitrates tested, and further study of the species present in these solutions would seem to be desirable.

VII. Decomposition of Metal Nitrates

Apart from the decomposition of the nitrate group which inevitably occurs when metal nitrates act as oxidizing agents in mixtures with metals (e.g., aluminum) or nonmetals (e.g., carbon, sulfur), the main types of decomposition can be discussed under three headings: (1) decomposition by water or organic solvents; (2) decomposition by irradiation; (3) thermal decomposition. The first type of decomposition has already been discussed in Section VI; the general principles governing the second and third types will be considered at this stage.

A. DECOMPOSITION ON IRRADIATION

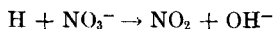
Irradiation experiments have been concerned almost entirely with ionic nitrates. These salts, usually in the solid state, have been irradiated by fast electrons (191, 192), γ -rays (191, 193), X-rays (194), or ultraviolet light (191, 195). A Co^{60} source has usually been used as the source of γ -radiation, and ultraviolet radiation is provided by a high pressure mercury arc. Maddock and Mohanty (191) carried out electron irradiations using 2-Mev electrons accelerated by a Van der Graaff machine, and the samples were so distributed that their thickness in the direction of the beam was less than half the range of the electrons in the compound concerned.

Although the mode of decomposition is similar in each case, there still appears to be a little doubt as to whether the primary radiolytic fragments produced on breakdown of the NO_3^- group by irradiation are NO_2^- and O, or NO_2 and O^- . The production of nitrite ion is generally favored:



and is supported by the infrared spectra (194), ultraviolet spectra (196), and X-ray diffraction data (194) for irradiated nitrate crystals. Magnetic susceptibility measurements on extensively radiolyzed potassium nitrate crystals indicate the presence of molecular oxygen in the crystals, together with nitrite ions (197). In this connection it is important to distinguish

between the anhydrous and hydrated salts. When an aqueous solution of a metal nitrate is irradiated, it is generally accepted (198) that the first stage of the reduction of nitrate to nitrite involves the H atoms formed during the radiolysis of water:

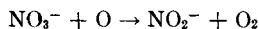


and that the formation of NO_2^- from NO_2 is a second stage in the process.

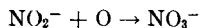
The paramagnetic absorption spectrum of crystals of lanthanum magnesium nitrate hydrate incorporating americium showed three kinds of magnetic centers, all of which could be attributed to NO_2 molecules (199). Measurements of the absorption spectrum of an extensively irradiated sample of lead nitrate failed to show any such absorptions (191), so that the radiolytic behavior of nitrate hydrates may well be quite different from that of the anhydrous nitrates. On solution in water, and in some cases fusion, irradiated anhydrous nitrates release gaseous oxygen, and nitrite can be determined spectrophotometrically in the solutions. The yields of NO_2^- and O_2 , as determined by analysis of an irradiated sample of sodium nitrate, were found to be precisely in the ratio $\text{NO}_2^-:\text{O}_2 = 2:1$ (193).

The photochemical decomposition of a number of solid nitrates under the influence of light from a mercury arc (195) produces nitrite and oxygen. The approximate quantum yields vary from 0.002 for lithium nitrate to 0.19 for caesium nitrate, in the order LiNO_3 , $\text{Sr}(\text{NO}_3)_2$, NH_4NO_3 , AgNO_3 , $\text{Pb}(\text{NO}_3)_2$, $\text{La}(\text{NO}_3)_3$, $\text{Ba}(\text{NO}_3)_2$, KNO_3 , $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and CsNO_3 . Water of hydration increases the sensitivity to radiation, and the rate of decomposition of the anhydrous nitrates varies in roughly the same manner as the polarizing power of the cations. Decomposition of barium nitrate by fast electrons also yields nitrite and oxygen (192).

The mechanism for the radiation-induced decomposition of the nitrates is a complex one. Following initial rupture into NO_2^- and O fragments, the reactions



and



take place. Experimental results for sodium, potassium, caesium, barium, and lead nitrates are compatible with this scheme. Silver nitrate does not follow the same kinetics; the rate of production of nitrite falls off rapidly as dose is increased, and some silver oxide is found in the products (200). It is relevant that the *G* value (compare Table XV) for nitrite production in the radiolysis of aqueous silver nitrate solutions is negligible, the main product being metallic silver (198, 201). With the other nitrates (excluding silver) the complexity arises partly from the fact that lattice changes

occur during irradiation, which affect the relative importance of these reactions. Using 240-curie Co^{60} as a source of γ -radiation, Johnson and Forten (193) have produced some interesting correlations in support of this. The variations in density, heat of solution, and nitrite yield for various nitrates were studied as irradiation proceeded. The change in nitrite yield coincided with changes in heat of solution and density, and the parameter which accounts best for the variations is the closeness of packing of the crystal structure. With potassium nitrate, for example, there is an abrupt decrease in the density at a dose of about 34×10^{20} ev/gm, and this coincides with a sharp break in the nitrite-yield curve. The results in Table XV compare the sensitivity of different metal nitrates to γ -radiation.

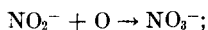
TABLE XV
DECOMPOSITION OF SOME METAL NITRATES UNDER γ -RADIATION

Compound	<i>G</i> value (molecules decomposed per 100 ev absorbed)			
NaNO_3	0.16 (193)	0.25 (202)	0.37 (194)	0.2 (203)
KNO_3	1.38 (204)	1.38 (193)	1.46 (203)	
CsNO_3	1.44 (193)	1.68 (202)	1.37 (194)	1.72 (203)
$\text{Pb}(\text{NO}_3)_2$	0.48 (193)	0.44 (202)	0.43 (204)	

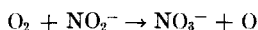
The *G* values quoted in Table XV represent the initial decomposition rates before the change in density occurs. The values decrease as irradiation proceeds; with potassium nitrate, the value of *G* falls abruptly from 1.38 to 0.93 after the change in density has occurred. Of the nitrates tested, sodium nitrate has the smallest "free space" (i.e., the most closely packed structure) and the low *G* value is in accord with the view that the initial *G* values are proportional to the free space. The extent of decomposition has also been calculated. For potassium nitrate, a dose of 120×10^{20} ev/gm gives 3 mole % decomposition; corresponding values for caesium nitrate are 1.6 mole % (99×10^{20} ev/gm) and for lead nitrate 0.73 mole % (27×10^{20} ev/gm).

The fragments generated by irradiation of metal nitrates can recombine under the influence of heat, and this "annealing" process gives valuable information on the decomposition mechanism. Gamma irradiation of lead nitrate crystals (191) produces a yellow-brown coloration which fades on heating the crystals, the rate of fading increasing with temperature in the range 100–200°. The data may be interpreted in terms of a unimolecular recombination affecting only a proportion of the fragments, and a bimolecular process, with a higher energy of activation, governing the behavior of the remainder. On radiolysis, decomposition takes place at normal lattice sites and is not primarily associated with the original lattice defects

(194). The first annealing process is explained (191) by recombination of the primary fragments, i.e.,



it involves only those fragments which have separated a very short distance in the lattice, and thus have a small energy barrier to recombination. The second recombination process involves the remainder of the fragments. The oxygen atoms penetrate into the lattice, where they combine to produce molecular oxygen. This oxygen remains dissolved (except under extensive radiolysis, when gas bubbles may appear) and the second-order annealing reaction may be represented by the equation:



followed by the rapid reaction



Since the covalent metal nitrates are more readily decomposed than the ionic nitrates, study of their radiolysis has fascinating possibilities.

B. THERMAL DECOMPOSITION

Present knowledge of the mechanism of thermal decomposition of metal nitrates is very limited indeed. It is known, however, that a distinction can be drawn between the decomposition of the hydrates and that of the anhydrous compounds. Some hydrates [e.g., $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$] first lose water of crystallization, followed by decomposition of the anhydrous nitrate, but with many hydrated nitrates of heavy metals the water present plays a major part in the decomposition. Both water molecules and nitrate groups are in the coordination sphere of the metal atom and react with one another to produce nitric acid as the main decomposition product; these reactions are not relevant to the present review. With the anhydrous compounds, we are concerned with the readiness with which the NO_3 group disintegrates and the various ways in which this can occur, but the scope of the work has been limited severely in the past by the very few such compounds available. Even so, investigations have concentrated almost exclusively on the solid phases involved. For example, in the well-known decomposition



one might ask whether the ratio of nitrogen dioxide and oxygen evolved is constant throughout the decomposition. Are these gases primary products, or is some nitric oxide first produced and subsequently oxidized to nitrogen dioxide? Answers to these questions, together with thermogravimetric

analysis, would give a useful indication of the decomposition mechanism, but the problem has been approached only recently from the point of view of the gas phase (254).

The more important factors influencing thermal stability include the following:

- (1) The physical state of the nitrate (i.e., solid, liquid, or gas).
- (2) The polarizing power of the cation.
- (3) The type of metal-nitrate bond.
- (4) The valency of the metal.
- (5) The availability of higher valency states of the metal.
- (6) The stability of intermediate decomposition products.
- (7) Lattice energy.

In most instances several of these factors are operating together, and it is seldom that one factor can be isolated. The decomposition of the alkali metal nitrates is simplest to interpret. Each compound is ionic; each gives the metal nitrite as a first step in the decomposition (though lithium nitrite is by far the least stable), so that the polarizing power of the cation is the major variable. The alkali metal nitrate decomposition temperatures in Table XVI are those at which the decomposition vapor pressure of oxygen

TABLE XVI
CATION POLARIZING POWER AND DECOMPOSITION TEMPERATURES
FOR THE ANHYDROUS NITRATES OF METALS OF GROUPS I AND II

Metal	e/r^2	Decomposition temperature of nitrate (°C)
Li	2.2	474
Na	1.0	529
K	0.57	533
Rb	0.46	549
Cs	0.36	584
Be	17	125 (48)
Mg	3.3	450 (48)
Ca	1.8	575 (128)
Sr	1.2	635 (128)
Ba	1.0	675 (128)

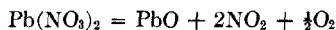
reaches 1 atmosphere, and polarizing power is defined as the ionic charge e divided by the square of the ionic radius r , following Goldschmidt (205). The stronger the polarizing power, the more is the electron distribution in the free nitrate ion distorted, and the lower is the thermal decomposition temperature. There is an obvious correlation between the two properties. With the nitrates of Group II, other factors must be considered also. The

polarizing powers of Ba^{2+} , Sr^{2+} , and Ca^{2+} are comparable with those of Li^+ and Na^+ ; these nitrates are ionic and give nitrite as the first decomposition stage, and high decomposition temperatures are again observed. The increased polarizing power of Mg^{2+} is reflected in the lower decomposition temperature; on rapid heating, anhydrous magnesium nitrate can be induced to melt, but it then decomposes immediately. It is in the case of anhydrous beryllium nitrate that the most marked decrease occurs (Table XVI). The very high polarizing power of Be^{2+} should in itself lower the decomposition temperature; added to this, however, is the covalent nature of the metal-nitrate bond (as shown by its infrared spectrum) and the high thermal stability of the first decomposition product $\text{Be}_4\text{O}(\text{NO}_3)_6$, which has been described earlier.

The decomposition temperatures given in Table XVI for barium, strontium, and calcium nitrates are those at which decomposition becomes visible; where melts are concerned, the onset of decomposition can usually be recognized to within about 20° , and the temperatures quoted are sufficiently accurate to illustrate the arguments outlined above. Where detailed comparisons of thermal behavior are required, it is necessary to define experimental conditions more precisely. This results from the fact that it is usually difficult to select the exact temperature at which thermal decomposition first begins, and this is particularly the case where solid nitrates are concerned. In a typical experiment, a stream of dry oxygen was passed over anhydrous zinc nitrate controlled at various temperatures, and oxides of nitrogen produced by decomposition were carried over with the gas stream into a trap containing sodium hydroxide, which was titrated at intervals (68). The following results were obtained:

Temperature ($^\circ\text{C}$):	100	150	240	285	310
Decomposed per minute (%):	0	(just detectable)	0.033	0.33	0.66

The decomposition rate approaches zero asymptotically as temperature decreases. Baekeland (206) studied the same effect with lead nitrate. The reaction



is reversible, and a sample of lead nitrate heated at various temperatures in an evacuated vessel gave the following equilibrium dissociation pressures (p):

Temperature ($^\circ\text{C}$):	223	230	250	274	297	357	448
p (mm Hg):	6.2	6.9	11.8	32.6	78.4	514	1180

This behavior is typical of the decomposition of all solid nitrates, and it is obvious that the term "decomposition temperature" has no significance

unless the experimental conditions under which it was determined are defined. Decomposition temperatures are usually determined by thermogravimetric analysis, in which the solid is heated at a constant rate of about $0.5\text{--}3^\circ$ per minute; the decomposition temperature is then defined as that temperature at which change in weight is first detected.

Using this technique, Wendlandt (1) determined decomposition temperatures for the anhydrous nitrates of lanthanum, praseodymium, and neodymium (Table XVII). These nitrates give intermediate decomposition products of composition MONO_3 , and their decomposition temperatures are also recorded. The hydrated nitrate of each of the lanthanide elements has been studied by thermogravimetric analysis (6, 207), but the lanthanum, praseodymium, and neodymium compounds were the only cases in which a plateau corresponding to the anhydrous trinitrate was

TABLE XVII
DECOMPOSITION TEMPERATURES ($^\circ\text{C}$) FOR ANHYDROUS NITRATES
OF SOME LANTHANIDE ELEMENTS

Metal (M)	T for $\text{M}(\text{NO}_3)_3$	T for MONO_3	Final product
Lanthanum	420	575	La_2O_3
Cerium	—	—	CeO_2
Praseodymium	375	480	Pr_6O_{11}
Neodymium	380	475	Nd_2O_3

obtained (1). These nitrates are essentially ionic; the infrared spectrum of praseodymium trinitrate indicates the presence of symmetrical D_{3h} nitrate ions (208). The infrared spectra of solid decomposition products suggest that the decomposition proceeds via an intermediate nitrite structure (208). This is not necessarily in conflict with thermogravimetric analysis (which indicated the intermediate PrONO_3) since praseodymium nitrite may have only transitory existence, in which case it would not be recognized on the thermobalance. This is another instance in which a study of the gaseous products also would be desirable. Table XVII shows that the thermal stability of lanthanum, praseodymium, and neodymium nitrates is quite high, as would be expected from their ionic character. The polarizing power (e/r^2) of the M^{3+} cations is 2.27 (i.e., between lithium and magnesium) and the decomposition temperatures also lie between those for lithium and magnesium nitrates. However, a direct comparison of this nature is not fully justifiable since the lanthanide nitrates decompose in the solid state.

The fact that anhydrous cerium(III) nitrate is not obtained on heating the hexahydrate has special interest. The thermogravimetric curve shows a steady loss in weight, with no plateau corresponding to either $\text{Ce}(\text{NO}_3)_3$

or CeONO_3 . Since cerium falls in the series La, Ce, Pr, Nd, it might have been expected to show a behavior resembling that of its congeners. The difference is attributed to the higher valency, Ce(IV), which is available in cerium, and to which Ce(III) can readily be oxidized on breakdown of the nitrate group; the final decomposition product is the oxide CeO_2 (1, 209).

As examples of covalent nitrates we may refer to the anhydrous compounds of general formula $\text{M}(\text{NO}_3)_2$ which are now known for manganese (75), cobalt (103), nickel (77), copper (171), and zinc (58, 68). The decomposition temperatures of these nitrates do not differ greatly from one another, and it is therefore necessary to define precisely the stage of decomposition at which comparison is to be made. Each compound was therefore heated in a thermobalance, in an atmosphere of dry nitrogen at a heating rate of 0.7° per minute, and an accurate weight-temperature curve obtained. The variation in the decomposition rate with temperature was then derived from the slope of the curve, and the results are given in Fig. 11.

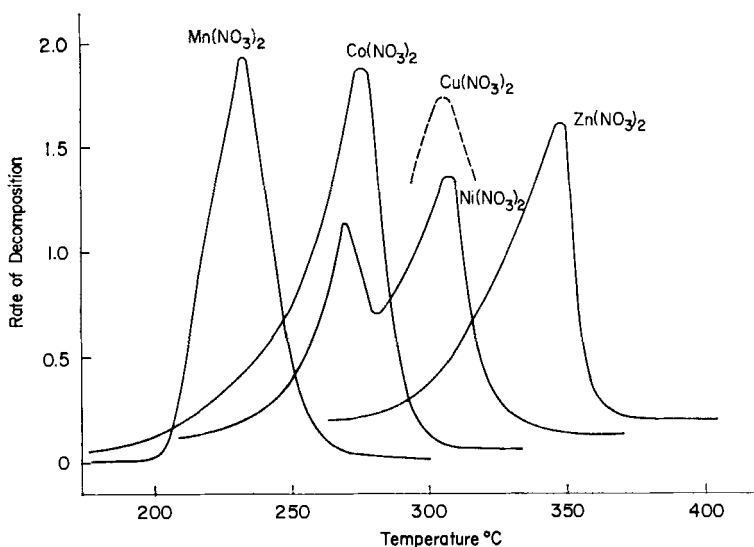


FIG. 11. Rates of thermal decomposition of some transition metal nitrates. (Rates of decomposition are expressed in molecular weight units lost per minute, assuming each experiment began with 1 gram mole of metal nitrate; for clarity, the values for cobalt, nickel, and zinc nitrates are raised progressively by 0.07 unit on the rate axis.)

Inspection of any particular curve shows that there is the usual difficulty in deciding, with any accuracy, the temperature at which decomposition commences, but the temperature corresponding to maximum rate of decomposition is clearly defined and forms an excellent basis on which to compare the thermal properties of the compounds. Nickel nitrite has an unusually

high thermal stability for a transition metal nitrite (78), and the formation of nickel nitrite on thermal decomposition of the nitrate is shown by the double peak for this compound in Fig. 11. The curve for copper nitrate could not be determined by thermogravimetric analysis since the compound sublimates. The broken curve in Fig. 11 was determined by differential thermal analysis (194) and is placed at an arbitrary position on the rate axis. There is satisfactory agreement between the two techniques; the maximum decomposition rate for cobalt(II) nitrate was found to occur at 270° by each method (70, 76).

We have already mentioned that the temperature at which decomposition occurs can be defined much more sharply for a molten nitrate than for a solid nitrate. This is presumably because in a melt the ions are kinetically more free, so that their response to increase in temperature is more nearly the same. In a solid, the lattice environment may not be the same for all ions; ions in different environments are subject to different lattice forces and will decompose at different temperatures. The influence of physical state should be even more marked when a metal nitrate is decomposed in the vapor and in the solid state, and this is illustrated clearly by the behavior of copper nitrate. In the absence of other gases there is no evidence for decomposition of the vapor below 226°. At this temperature decomposition occurs suddenly; all the vapor decomposes within a temperature range of a few degrees, and the walls of the containing vessel are covered by a dark-colored deposit. In contrast, decomposition of the solid occurs at a maximum rate at 305° (Fig. 11), is measurable at 190° (171), and is detectable at temperatures as low as 100°.

Infrared and ultraviolet spectra show that in each of the compounds referred to in Fig. 11 the nitrate groups are covalently bonded to a greater or lesser extent. It is consistent with this that thermal decomposition should occur over a lower temperature range than that for the ionic nitrates discussed earlier. In this connection the temperature of maximum decomposition rate for zinc nitrate, 350°, may be compared with the 420° found for cadmium nitrate (210), which is fully ionic (211). The 4-valent state of manganese is readily available, and for this reason it is understandable that manganese(II) nitrate, which decomposes according to the equation:



should have the lowest decomposition temperature. The oxide Co_3O_4 is obtained on decomposition of cobalt(II) nitrate (76), which also decomposes at a lower temperature than do the nitrates of nickel, copper, or zinc; the latter have no higher valency which is readily accessible under these conditions. However, in the present state of our knowledge it is somewhat surprising that such factors as variable valency and the pronounced differences in

The anhydrous nitrates of chromium(II) and iron(II) have not been isolated. The thermal stability of the simple Cr(III) nitrate, which is strongly covalent, is much lower than that of any other anhydrous nitrate studied; sudden decomposition occurs at 60°, and decomposition rate is maximum at 100° (248). In view of the high stability of the ionic nitrates of La(III), Pr(III), and Nd(III), it would seem that the ionic or covalent character of the bond has a pronounced influence on stability so far as the trivalent metals are concerned.

All relevant aspects have been discussed in Sections II, III, IV, and VII.

Group II

Following the recent isolation of anhydrous beryllium nitrate, it is now possible to view the nitrates of this group as a whole, and a comparative account has been recently published (48). The preparation of the ionic nitrates of barium, strontium, calcium (Section II,B), and magnesium (Section II,F,H,I) has been discussed. Only beryllium nitrate is covalent; its preparation (Sections II,I and V,D), its decomposition to the basic nitrate (Section V,D), and its solution properties in water (Section VI,C) have already been treated in detail.

Group III

In view of the preparation of a compound $B(\text{HSO}_4)_3$ from boron tetrachloride and anhydrous sulfuric acid (212), the existence of boron trinitrate is an attractive possibility. However, reaction of boron trichloride with dinitrogen pentoxide (27), dinitrogen tetroxide (50), or absolute nitric acid (17) gave only boric oxide or addition compounds of boron trichloride. The formation of $B(\text{NO}_3)_3$ by the $\text{BCl}_3\text{—ClNO}_3$ reaction has been mentioned, but no confirmatory evidence is available. It decomposes even at -78° to give $\text{BO}(\text{NO}_3)$ (37). A similar reaction carried out at -7° , using aluminum bromide in liquid bromine as reaction medium, is said to give anhydrous aluminum trinitrate, which sublimates with some decomposition, when heated above room temperature in vacuum. Solvolysis of aluminum chloride in dinitrogen tetroxide does not give the simple nitrate. A product $\text{Al}(\text{NO}_3)_3 \cdot 0.38\text{N}_2\text{O}_4$ has been described (60); the simple nitrate cannot be isolated from this product, which may in fact be an oxide-nitrate. Using the same reaction, Addison *et al.* (175) isolated a product of composition $\text{Al}(\text{NO}_3)_3 \cdot \text{AlO}(\text{NO}_3) \cdot 2\text{N}_2\text{O}_4$, which could not be converted to the simple nitrate. The preparation of the compounds $\text{Ga}(\text{NO}_3)_3$ (Section II,B) and $\text{In}(\text{NO}_3)_3$ (Section II,I) has already been mentioned.

In view of the similarity in the behavior of Tl^+ to Ag^+ and the alkali metal cations, the isolation of anhydrous thallium(I) nitrate from aqueous solution is not surprising. The salt melts at 206° , and decomposition sets in rapidly at 450° ; according to Thomas (213), a little thallium(I) nitrate may be volatilized unchanged. Anhydrous thallium(III) nitrate is unknown, but an anhydrous double salt $\text{Tl}(\text{NO}_3)_3 \cdot 2\text{TlNO}_3$ has been described (214).

Group IV

The action of dinitrogen pentoxide (27), chlorine nitrate (37), or nitric acid (17) on silicon tetrachloride produces only silica. Silicon tetranitrate may well be the primary product in these reactions, but decomposes immediately. However, an addition compound of the tetranitrate with

pyridine was obtained by first mixing solutions of silver nitrate in methyl cyanide and silicon tetrachloride in ether at -40° ; on addition of pyridine to the supernatant liquor, a white precipitate of the compound $\text{Si}(\text{NO}_3)_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ was obtained which evolved oxides of nitrogen at room temperature (215). Oxy-acid salts of germanium are rare, and no nitrate has yet been described; moderately concentrated nitric acid converts germanium to hydrated germanium dioxide. The reactions of germanium compounds with the nitrogen oxides and their derivatives do not appear to have been studied, and may well prove fruitful. The preparation of tin tetranitrate has been discussed (Section II,G). It can also be prepared by reaction of tin tetrachloride with dinitrogen pentoxide (27). Tin(II) nitrate has not yet been prepared; its instability is probably due to the ready oxidation of Sn(II) to Sn(IV), especially in the presence of nitrate groups, and it is relevant that even the basic tin(II) nitrate $\text{Sn}_3(\text{OH})_4(\text{NO}_3)_2$ explodes on heating (216). With lead, the higher stability is in the +2 oxidation state; the tetranitrate has not been prepared.

Group V

In this group, only antimony and bismuth are sufficiently electropositive to form salts with oxy-acids. A simple nitrate of antimony has not been obtained, though some oxide-nitrates are known. The basic salt SbONO_3 separates from solutions in nitric acid on dilution with water; the same product is obtained as the addition compound $\text{SbONO}_3 \cdot (\text{CH}_3)_2\text{SO}$ from the reaction of metallic antimony with a mixture of dinitrogen tetroxide and dimethyl sulfoxide (102). The oxide-nitrate of Sb(V), $\text{SbO}(\text{NO}_3)_3$, is the product of the reaction between antimony pentachloride and dinitrogen pentoxide (27), and is highly unstable at room temperature. In contrast to antimony, bismuth forms an oxide-nitrate and a simple nitrate. The action of heat on the hydrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ gives the oxide-nitrate $\text{BiO}(\text{NO}_3)_3$, whereas slow dehydration at room temperature (Section II,B) gives $\text{Bi}(\text{NO}_3)_3$. Bismuth metal also reacts with a mixture of methyl cyanide and excess dinitrogen tetroxide to give an adduct $\text{Bi}(\text{NO}_3)_3 \cdot 0.25\text{N}_2\text{O}_4 \cdot 0.25\text{MeCN}$, which can be thermally decomposed in vacuum to give the anhydrous nitrate (102). From the infrared spectrum, the nitrate groups would appear to be covalently bonded.

Group VI

The formation of a compound $\text{Te}(\text{NO}_3)_2$ by reaction of silver nitrate and tellurium tetrabromide in boiling benzene has been claimed (250). The only other known nitrate compound of tellurium has the empirical formula $2\text{TeO}_2 \cdot \text{HNO}_3$ (249); its structure is unknown.

The preparation of anhydrous polonium(IV) nitrate (217, 218) is of

considerable interest. Treatment of polonium(IV) chloride or hydroxide with dilute nitric acid gives rise to basic salts, one of which is the analogue of $2\text{TeO}_2 \cdot \text{HNO}_3$. A basic salt is also obtained on keeping polonium metal in a gaseous mixture of nitrogen dioxide and oxygen. Polonium metal is not attacked by either pure liquid dinitrogen tetroxide or its mixture with ethyl acetate; however, both polonium dioxide and polonium tetrachloride react with liquid dinitrogen tetroxide to give the white crystalline addition compound $\text{Po}(\text{NO}_3)_4 \cdot \text{N}_2\text{O}_4$, from which dinitrogen tetroxide is easily removed to give polonium(IV) nitrate. This decomposes to give a basic salt slowly in air at room temperature, or more rapidly (1.5–2 hours) under vacuum.

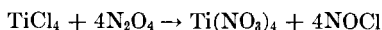
B. TRANSITION ELEMENTS

Scandium Group and Lanthanides

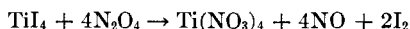
The preparation of anhydrous nitrates of scandium, yttrium, and lanthanum has been referred to in Section II,B,I,J, and the thermal decomposition of lanthanum nitrate in Section VII,B. No anhydrous nitrate of actinium has been described. So far as the lanthanides are concerned, the position is indicated in Fig. 12. The earlier members form anhydrous nitrates; thermogravimetric analysis of the 4-hydrates of europium, holmium, erbium, thulium, ytterbium, and lutecium indicates that these metals form only oxide-nitrates (6). It seems quite likely, however, that the simple nitrates could be prepared by appropriate methods. The nitrate chemistry of promethium and terbium does not appear to have been studied.

Titanium Group

All the elements of this group form anhydrous nitrates $\text{M}(\text{NO}_3)_4$. The titanium compound has been prepared (a) by reaction of the tetrachloride with chlorine nitrate (Section II,G) or with dinitrogen pentoxide in carbon tetrachloride solution (27), and (b) by reaction of hydrated titanium nitrate with dinitrogen pentoxide (26). The compound melts at 58.5° , sublimes in high vacuum, and decomposes at about 100° to the nonvolatile oxide-nitrate $\text{TiO}(\text{NO}_3)_2$. Titanium tetrachloride reacts in a different way with dinitrogen tetroxide. The reaction:



does not go to completion, since the nitrosyl chloride formed reacts with the remaining tetrachloride to give the stable complex $(\text{NO})_2[\text{TiCl}_6]$ (54). Reaction with titanium tetraiodide,



is more satisfactory. There is a vigorous reaction on addition of the tetraiodide to liquid dinitrogen tetroxide in carbon tetrachloride at -17° . Zirconium tetraiodide reacts in the same way. The tetranitrates are no doubt present in the solution, but were not isolated since at temperatures above 10° brown fumes were evolved, and the only compounds which could be isolated were the oxide-nitrates $\text{TiO}(\text{NO}_3)_2$ and $\text{ZrO}(\text{NO}_3)_2$.

Anhydrous zirconium tetranitrate has now been prepared by reaction of zirconium tetrachloride with dinitrogen pentoxide (32). The initial product had the composition $\text{Zr}(\text{NO}_3)_4 \cdot 0.4\text{N}_2\text{O}_5 \cdot 0.6\text{N}_2\text{O}_4$, but the nitrogen oxides could be removed by heating at 100° for 4 hours under vacuum (0.01 mm). On continued heating, the tetranitrate slowly sublimed onto a cold finger in the form of colorless crystals. The compound has a high solubility in water and in polar aliphatic solvents; it is insoluble in toluene, with which it reacts rapidly to produce nitro compounds. The infrared spectrum of the solid includes bands in the ranges 1224–1284 (ν_1), 1575–1631 (ν_4), and 983–1015 (ν_2) cm^{-1} . The high ν_4 frequency suggests that the metal-nitrate bonds are strongly covalent, and that the nitrate groups are bidentate or bridging (Section V,C,D). This would also be consistent with the high reactivity towards aromatic solvents (Section VI,D). If all nitrate groups are bidentate, a structure represented by a cubic arrangement of eight oxygen atoms, with the zirconium atom at the center, is attractive. The corresponding hafnium compound $\text{Hf}(\text{NO}_3)_4$ has been prepared by the reaction of dinitrogen pentoxide with hydrated hafnium nitrate. Its properties resemble those of the zirconium compound (30).

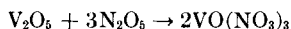
The preparation of the thorium compound $\text{Th}(\text{NO}_3)_4$ has been described (Section II,E). The covalent bonding must again be strong, since it persists even in the tetrahydrate. The infrared spectrum of the latter compound includes bands at 1292, 1323 (ν_1), 1506, 1520 (ν_4), and 1030, 1036 (ν_2) cm^{-1} , but no frequency corresponding to an ionic nitrate (211).

Vanadium Group

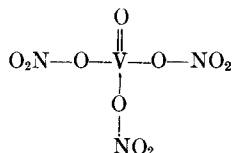
At this position in the Periodic Table it is to be expected that nitrate groups will again be covalently bonded. In view of the oxidizing properties of such groups, it is also to be expected that the metals concerned will normally be present, in covalent nitrates, in their highest oxidation states. However, with the metals of the vanadium group this would involve either the unfavorable coordination number of 5 (if all nitrate groups were unidentate) or a coordination number too high to be acceptable on steric grounds (if nitrate groups were bonded in bidentate fashion). It is not surprising, therefore, that no simple nitrates $\text{M}(\text{NO}_3)_5$ are known for the metals of this group. This is the hypothetical initial product in a number of reactions, but we may consider that decomposition to oxide-nitrates then

occurs; this reduces the coordination number while retaining the maximum oxidation state.

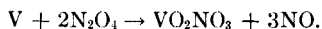
Dinitrogen pentoxide reacts with vanadium pentoxide according to the equation



and reaction with VOCl_3 gives the same product (27, 219). Vanadium oxide trinitrate is yellow, melts at 2° , and boils at $68\text{--}70^\circ$ in high vacuum. Further study of the physical and chemical properties of this compound should be rewarding. The fact that it is a liquid at room temperature indicates a covalent molecule. If the nitrate groups are monodentate, the structure would then be

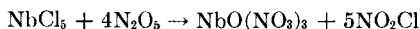


Rupture of the molecule may occur either at the $\text{V}-\text{O}$ or the $\text{O}-\text{N}$ bonds in the $\text{V}-\text{O}-\text{N}$ links, as discussed in Section VI. Depending on the reaction conditions, the compound may therefore behave as vanadyl nitrate, $\text{VO}^{3+}(\text{NO}_3^-)_3$, or as nitronium vanadate, $(\text{NO}_2^+)_3\text{VO}_4^{3-}$. Reactions with dinitrogen tetroxide give a different product (220). Chips of electrolytic vanadium metal react readily with a mixture of liquid dinitrogen tetroxide and methyl cyanide at 0° :



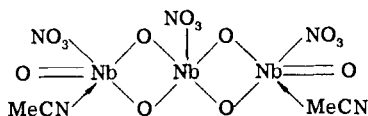
The mononitrate was obtained as a brick-red free-flowing powder; it is highly soluble in water to give an orange-colored solution, but is insoluble in common organic solvents.

The particular oxide-nitrate of niobium obtained again depends upon the oxide of nitrogen used. Reaction of anhydrous niobium pentachloride with liquid dinitrogen pentoxide at 30°



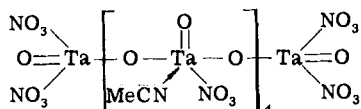
gives the oxide trinitrate as a white powder which is immediately hydrolyzed by water to nitric acid and hydrated niobium pentoxide (29). It is slightly soluble in some organic solvents. It is not volatile, and decomposes in vacuum at about 120° . These properties, together with the infrared spectrum, are considered to indicate that the complex contains a niobium-oxygen double bond, and that the monomeric units are linked together by bridging nitrate groups (29). From the reaction of niobium pentachloride

with dinitrogen tetroxide in methyl cyanide solution, a complex is obtained which has a higher oxide: nitrate ratio, and is believed to have the structure



This compound is stable at 70°, is insoluble in organic solvents, and takes up one molecule of water (for each trimer unit) in moist air (221). The reaction has an induction period, and probably proceeds via intermediate species such as $\text{Nb}(\text{NO}_3)_5$ and $\text{NbO}(\text{NO}_3)_3$ (222). The analogous complex with *N,N*-dimethylacetamide is polymeric. Using ethyl acetate or nitrobenzene as solvent, products are isolated which by analysis appear to be $\text{NbO}_2(\text{NO}_3)$ with varying amounts of combined solvent. These products are much less stable, and probably contain monomeric $\text{NbO}_2(\text{NO}_3)$ units.

A complex of the tantalum oxide-nitrate $\text{TaO}(\text{NO}_3)_3$ with methyl cyanide is prepared by the same reaction as for the niobium complex (221). The structure



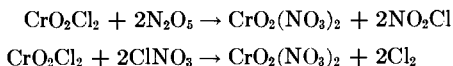
has been proposed. No anhydrous nitrates or oxide-nitrates of protactinium have been described.

Chromium Group

Under this heading we shall treat the nitrate chemistry of chromium, molybdenum, tungsten, and uranium. Simple chromium(III) nitrate $\text{Cr}(\text{NO}_3)_3$ has recently been isolated by reaction of chromium carbonyl with dinitrogen pentoxide in carbon tetrachloride solution (248). The addition compound $\text{Cr}(\text{NO}_3)_3 \cdot 2\text{N}_2\text{O}_4$ is formed when dinitrogen tetroxide reacts with chromium carbonyl (Section II,I) or with chromyl chloride. The latter reaction is of particular interest, both in comparison with the corresponding reaction with dinitrogen pentoxide and because it is one of the few instances in which liquid dinitrogen tetroxide acts as a reducing agent. When chromyl chloride vapor is passed into a N_2O_4 — CH_3NO_2 mixture, reaction is vigorous, and green crystals of the compound $\text{Cr}(\text{NO}_3)_3 \cdot 2\text{N}_2\text{O}_4$ separate (51). The infrared spectrum of the solid is highly complex, indicating the presence of unidentate, bidentate, and (possibly) bridging nitrate groups; frequencies assignable to the NO^+ ion as well as the coordinated N_2O_4 molecule are also present. The fact that the simple nitrate cannot

be obtained by thermal decomposition of the N_2O_4 addition compound is to be related to the complex nature of the latter.

Each of the four metals forms a compound of formula $\text{MO}_2(\text{NO}_3)_2$. Reaction of chromyl chloride with dinitrogen pentoxide (Section II,F) or chlorine nitrate (Section II,G)



gives chromyl nitrate as a brown volatile liquid which melts at -70° , boils at $28-30^\circ$ at a pressure of 10^{-3} mm, and can be distilled unchanged. It is a violent oxidizing and nitrating agent, and inflames on contact with benzene (219, 246). Like vanadium oxide trinitrate, this compound merits further detailed study, since it may behave either as chromyl nitrate or as nitryl chromate $(\text{NO}_2)_2\text{CrO}_4$. By similar preparative methods, the corresponding molybdenum and tungsten compounds $\text{MoO}_2(\text{NO}_3)_2$ and $\text{WO}_2(\text{NO}_3)_2$ are believed to be formed (27). These appear to be much less stable than the chromium compound, and have not been fully characterized. Reaction of molybdenum and tungsten hexacarbonyls with dinitrogen tetroxide results in the formation of amorphous yellow powders having the empirical formulas MoNO_5 and $\text{W}_2\text{N}_3\text{O}_{11}$, respectively. These products contain nitrate groups, but are probably polymeric; they begin to decompose at 95° and 67° , respectively (70).

The existence of anhydrous uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2$, as a distinct compound is now well established. Section II,E,F,I deals with its preparation, and Section VI,E with some of its chemical properties. Its infrared spectrum shows that the nitrate groups are bonded covalently (51), and its thermal stability is much higher than that of the corresponding chromium, molybdenum, or tungsten compounds. When the addition compound $\text{UO}_2(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$ is heated in a thermobalance at a heating rate of 1° per minute, a plateau corresponding to $\text{UO}_2(\text{NO}_3)_2$ is obtained, and decomposition is not apparent, under these conditions, below 240° (51). The ultraviolet absorption spectrum of solutions of anhydrous uranyl nitrate in a number of organic solvents has been measured. The spectrum retains the vibrational band structure in acetone, 2-heptanone, dioxan, formamide (223), nitromethane (83), ethyl acetate, and methyl cyanide (70). The compound forms a very large number of adducts with organic compounds containing oxygen, sulfur, or nitrogen donor atoms (224); essential features in the structure of such compounds have been discussed in Section V,C.

The spontaneous decomposition of uranium tetranitrate has been referred to in Section II,C; it is known in the form of the *N,N*-dimethylacetamide complex $\text{U}(\text{NO}_3)_4 \cdot 2.5\text{AcNMe}_2$ (15).

Transuranium Elements

The preparation of simple anhydrous nitrates of the transuranium series is still awaited. The nitrate group decomposes under irradiation (Section VII,A), and for this reason the simple nitrates of the higher members of this series may not be available. The nitrates of neptunium are known only in solution, but the plutonium compounds $\text{Pu}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ and $\text{PuO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ have been isolated (225). All the plutonium(IV) present in nitrate solutions above 1 *M* concentration or in 1–4 *M* nitric acid, is in the form of undissociated $\text{Pu}(\text{NO}_3)_4$, and the only Pu(IV) species present in concentrated nitric acid is $\text{H}_2[\text{Pu}(\text{NO}_3)_6]$ (226). The americium(VI) nitrate $\text{AmO}_2(\text{NO}_3)_2$ is extracted from aqueous solution by ether (225) [compare hydrated $\text{UO}_2(\text{NO}_3)_2$] and the heavier transuranium elements no doubt behave similarly; americium(III) nitrate, presumably hydrated, is known (227). Tri-*n*-butyl phosphate has, of course, one of its most extensive applications in separations of the transuranium elements. Disolvates are formed with plutonium(VI) and plutonium(IV) nitrates, and with neptunium(VI) and neptunium(IV) nitrates (228). Plutonium(III) (229, 230) and americium(III) (231) nitrates form trisolvates. Trivalent curium forms a nitrate which has properties similar to americium(III) nitrate (232).

Manganese Group

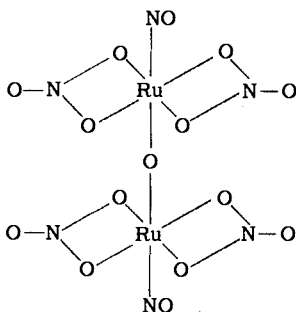
In discussing nitrates of the vanadium and chromium group metals, it was seen that where the metal readily assumes a high oxidation state, oxide-nitrates rather than simple nitrates are usually produced, and that the higher the available valency state the more readily does complete decomposition to oxide occur. Thus, the oxide-nitrates of molybdenum and tungsten are less stable than those of niobium and tantalum. No nitrates or oxide-nitrates of technetium or rhenium are known, and this is now seen to be in accord with the general pattern. However, the manganese(II) oxidation state is stable because of its $3d^5$ electronic structure, and the anhydrous nitrate $\text{Mn}(\text{NO}_3)_2$ is well established. Its preparation has been mentioned in Section II(B,C,D,E,I) and its thermal decomposition has been discussed in Section VII,B. The compound $\text{Mn}(\text{CO})_5\text{NO}_3$ is a key compound in connection with the infrared spectrum of the unidentate nitrate group (Section V,B), and the infrared spectrum of $\text{Mn}(\text{NO}_3)_2$ shows that in this compound also the nitrate groups are covalently bonded (211).

Iron Group

When ferric chloride is treated with a mixture of liquid dinitrogen tetroxide and ethyl acetate, the addition compound $\text{Fe}(\text{NO}_3)_3 \cdot \text{N}_2\text{O}_4$ is

obtained in the form of pale brown crystals (49). The same product is obtained by reaction of iron pentacarbonyl with excess liquid dinitrogen tetroxide (Section II,I) or by the action of dinitrogen pentoxide on metallic iron (30). Attempts to obtain the simple nitrate from this adduct have so far been unsuccessful. On heating at 80° in vacuum the compound vaporizes (Section VI,A); the first stage in the thermal decomposition under atmospheric pressure is the oxide-nitrate $\text{FeO}(\text{NO}_3)$ (67), which is also produced by reaction of iron pentacarbonyl and nitrogen dioxide vapors.

Ruthenium and osmium are known to form neither simple anhydrous nitrates nor oxide-nitrates, although a number of derivatives of these compounds are known. Ruthenium, in particular, forms a large number of nitrate-nitrosyl ruthenium complexes (233, 234). For example, reduction of a nitric acid solution of ruthenium tetroxide with nitric oxide gives the dark red compound $\text{Ru}(\text{NO})(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ (235). When this is held in vacuum at 50° for 12 hours, the dihydrate is obtained as the 6-coordinate complex $[\text{Ru}(\text{NO})(\text{NO}_3)_3(\text{H}_2\text{O})_2]$; the infrared spectrum of this compound shows that the nitrate groups are covalently bonded to the metal. A corresponding compound $\text{Ru}(\text{NO})(\text{NO}_3)_3 \cdot (\text{Bu}_3\text{PO}_4)_2$ has also been isolated. The anhydrous compound $\text{Ru}(\text{NO})(\text{NO}_3)_3$ cannot be obtained; the dihydrate decomposes to RuO_2 on heating to 150° in vacuum (236). Again, when the $\text{RuO}_4\text{--NO}$ reaction is carried out in carbon tetrachloride, an anhydrous product of composition $\text{Ru}_2\text{N}_6\text{O}_{15}$ is obtained in the form of a brown powder. The infrared spectrum indicates that the nitrate groups may well be bidentate, and the compound is believed to have the binuclear structure (233, 236)



The known nitrate chemistry of osmium is negligible, but this is more likely to be the result of limited investigation than of any inherent reluctance of osmium to form such compounds. Osmium trinitrate is said to be deep brown, and sufficiently stable to be dried at 100° (237). However, these properties are actually those of a compound $\text{Os}(\text{NO}_2)_3$ described by Wintrebort (238), which has not itself been properly characterized. The

only other nitrates described are those where the nitrate is the anion in salts in which coordination complexes of osmium form the cation.

Cobalt Group

The preparation of cobalt(II) nitrate has already been mentioned (Section II,E,I); in spite of the fact that dinitrogen tetroxide or dinitrogen pentoxide are used as reagents, it is the nitrate of Co(II) which is obtained. When isolated from dinitrogen tetroxide medium, the adduct $\text{Co}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$ is first obtained as deep purple crystals. This decomposes in vacuum at about 50° to the 1:1 adduct $\text{Co}(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$. In this compound the infrared bands of dinitrogen tetroxide are no longer observed, but an NO^+ band remains (76). The compound may be represented in the form $\text{NO}^+[\text{Co}(\text{NO}_3)_2]^-$, though its structure has not been studied. Further heating in vacuum gives the pale purple anhydrous $\text{Co}(\text{NO}_3)_2$. The electrical conductivity (67, 76) and ultraviolet spectrum (76) of solutions of this compound in nitromethane and methyl cyanide and its thermal decomposition (Section VII,B), suggest predominantly covalent bonding of the nitrate groups. The infrared spectrum of the solid (211) has been interpreted as indicating ionic bonding. However, on re-examination (76) the spectrum has been found to be compatible with the presence of both ionic and covalent nitrate groups.

No anhydrous nitrates or oxide-nitrates of rhodium or iridium appear to have been described; a hydrate of rhodium(III) nitrate is said to be formed on evaporation of a solution of the oxide Rh_2O_3 in nitric acid (239).

Nickel Group

The infrared spectrum of the anhydrous compound $\text{Ni}(\text{NO}_3)_2$ shows it to be a typical covalent nitrate. It can be prepared as a pale green powder by dehydration of the hydrate in an N_2O_5 - HNO_3 mixture (Section II,E) or by reaction of nickel carbonyl with dinitrogen tetroxide (Section II,I). When the latter reaction was carried out with heptane, cyclohexane, or methyleyclohexane as diluent, the product always contained a small amount of an impurity containing carbon. This is attributed to attack of the covalent nitrate (or an intermediate carbonyl-nitrate) on the hydrocarbon (see Section VI,D); similar attack occurred during the preparation of cobalt nitrate from cobalt carbonyl. Anhydrous nickel nitrate may also be prepared by the solvolysis of nickel chloride in an ethyl acetate-dinitrogen tetroxide mixture; it is unique among transition metal nitrates in giving the metal nitrite on thermal decomposition (Section VII,B), and it is prepared from the nitrite by oxidation with liquid dinitrogen tetroxide (78). Anhydrous nickel nitrate is not volatile.

Palladium metal and palladium oxide dissolve in nitric acid solution;

it is stated in a number of textbooks that the compound $\text{Pd}(\text{NO}_3)_2$ separates as yellow-brown crystals from concentrated nitric acid, but this is now subject to considerable doubt. In contrast to nickel nitrate, palladium nitrate is readily volatile. When the dihydrate $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ is mixed with dinitrogen pentoxide and heated to 110° under a pressure of 0.1 mm, anhydrous palladium nitrate sublimes onto a cold finger (30). Manchot and Waldmuller (240) report the formation of palladium nitrite by reaction of the anhydrous nitrate with nitric oxide.

Consistent with the general reluctance of platinum to form simple salts of the oxy-acids, the nitrates of platinum are not so well characterized as is palladium nitrate. There are early references (241) to the existence of both $\text{Pt}(\text{NO}_3)_2$ and $\text{Pt}(\text{NO}_3)_4$, but further study is necessary to determine whether the products are correctly represented by these formulas.

Copper Group

The many unusual features in the chemistry of anhydrous copper(II) nitrate have already been discussed in some detail in various sections of this review. Copper(I) nitrate is unknown as the simple salt (Section II, C). In contrast, silver(I) nitrate is of course well known, but silver(II) nitrate has not yet been isolated as the simple salt; on the basis of calculated values for the free energy of formation, Morris (242) has predicted that $\text{Ag}(\text{NO}_3)_2$, if formed, would be thermodynamically unstable. If the Ag^{2+} cation is coordinated, as in the orange-red compound $[\text{Ag}(\text{py})_4](\text{NO}_3)_2$, then the nitrate is stable (243). The dark brown solution obtained by dissolving the oxide AgO in concentrated nitric acid may contain silver(II) nitrate or nitrate complexes of silver(II), but no corresponding solid has been isolated from the solution (244). In an attempt to achieve this, dinitrogen tetroxide was added to this solution, but mutual decomposition occurred and silver(I) nitrate was deposited (67). The simple nitrate of Au(I) is not known, but $\text{Au}(\text{NO}_3)_3$ has recently been prepared (30). When a solution of gold(III) nitrate in concentrated nitric acid is diluted with water, immediate hydrolysis occurs with deposition of hydrated gold(III) oxide. The nitrates $[\text{Au}\{(\text{CH}_2\text{NH})_2\text{CS}\}_2]\text{NO}_3$ (245) and $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$ have been isolated; the complex acid $\text{H}[\text{Au}(\text{NO}_3)_4] \cdot 3\text{H}_2\text{O}$ and its salts with K^+ , Rb^+ , and NH_4^+ are known, as well as salts of hexanitratogold(III) acid, e.g., $\text{K}_2\text{H}[\text{Au}(\text{NO}_3)_6]$.

Zinc Group

Anhydrous nitrates $\text{M}(\text{NO}_3)_2$ are known for each of the metals zinc, cadmium, and mercury. Their preparation has been referred to (Section II), and the thermal decomposition of zinc and cadmium nitrates compared (Section VII). Anhydrous mercurous nitrate, $\text{Hg}_2(\text{NO}_3)_2$, is unknown. There are some pronounced differences in the chemistry of the nitrates of these

three metals for which no fully satisfactory reason exists at present. For example, their infrared spectra show zinc and mercury(II) nitrates to contain coordinated nitrate groups, whereas cadmium nitrate gives a typically ionic nitrate spectrum (211). Again, the readiness with which these nitrates form N_2O_4 adducts is quite different. The compound $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$ decomposes slowly at 100° , $\text{Hg}(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$ decomposes rapidly even at room temperature, while $\text{Cd}(\text{NO}_3)_2$ separates as the simple salt from media containing dinitrogen tetroxide. Zinc nitrate (30) and mercury(II) nitrate (70) show slight volatility in vacuum.

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CHEMICAL REACTIONS IN ELECTRIC DISCHARGES

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I. Plasma Generators and the Nature of Electric Discharge Reactions

A. INTRODUCTION

The existence of unusual species in electric discharges has been known for many years and scientists have traditionally sought atomic and molecular spectra from arcs and sparks for analytical purposes. Recently there has been a new concern with electric discharges as devices for chemical syn-

thesis, and it is this latter development which is to be emphasized in this chapter.

It is not the purpose of this chapter to trace the history of chemical reactions in electric discharges or to cover extensively all the investigations of discharge reactions reported. An extensive review on the subject was prepared 20 years ago by Glockler and Lind (84) and a more recent review appeared as a technical report by Jolly (109) in 1960. Rather it is intended here to point out the available devices and special techniques being used in modern studies of discharge reactions, and to cite some of the more recent work in the field illustrative of the importance of such studies. For example, an electric discharge synthesis is often the only convenient way to prepare compounds thermodynamically unstable at room temperature.

B. PLASMA GENERATION DEVICES

An electric discharge is observed when a gas or vapor, across which a voltage gradient exists, becomes electrically conducting by transition to the plasma state. The condition necessary for the development of a plasma in any discharge is that the rate of generation of ions shall be sufficient to produce a potential maximum in the discharge container.

The fundamental types of continuous electric discharge are (1) the glow discharge, and (2) the arc discharge. These are self-sustained and can be maintained without the support of an external ionizing agency. On the other hand, excitation and thermal ionization of an isolated gas at a given reduced pressure can be obtained by application of an external source of energy.

1. *The Glow Discharge*

A glow discharge is maintained by electrons produced at the cathode by bombardment of particles and light quanta from the gas. The direct-current glow discharge is established in a tube containing gas at a pressure of a few millimeters of mercury. The appearance of the discharge depends on the operating conditions (35). The a.c. discharge does not differ significantly from the d.c. discharge. At low frequency and relatively short gaps, the time required for an electron to cross the gap is very short compared with the time of a half-cycle. Negative ions, formed by electron attachment, and positive ions cross the gap more slowly, but removal of ions and electrons from the gap occurs before the succeeding half-cycle. In long gaps ions oscillate only about a mean position near the point of their formation, and are subject to diffusion and recombination during the periods of low voltage. A discharge powered by an a.c. power supply is normally stabilized by an autotransformer which permits adjustment of the voltage applied to the primary. A resistance in series with the discharge tube is not necessary for stabilization as is the case in a d.c. discharge.

2. Electrodeless Discharges

The development of efficient high-frequency power sources has resulted in the wide use of electrodeless radiofrequency and microwave discharges and decreased interest in discharges between electrodes. Adoption of the electrodeless discharges can be attributed to a combination of factors such as ease of control, simplicity of construction of the discharge tube, greater stability, and, probably most important, greater purity of the discharge products since metallic electrodes, in contact with the discharge gases, are not required.

The transfer of radiofrequency energy into a discharge tube can be accomplished by inductance or capacitance. Also, efficient coupling can be accomplished with a microwave generator coupled to the discharge tube by various types of resonance cavities. Small amounts of radiofrequency power may be obtained from conventional power supplies and amplifiers. The three main types of high frequency-generating equipment for large power jobs (5–100 kw) are the spark gap converter, the vacuum-tube oscillator, and the motor generator set. A detailed discussion of high frequency generators is presented by Jordan (112).

In inductive coupling a metal solenoid surrounding the discharge tube can be used to induce an alternating current in the tube and create a plasma. At sufficiently high frequencies, a thin layer near the surface of the tube

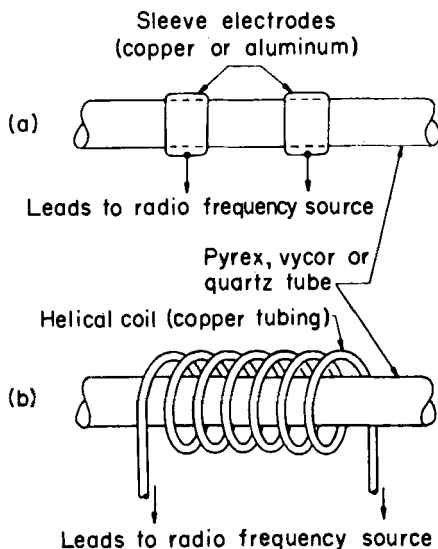


FIG. 1. Coupling arrangements for use with radiofrequency discharge; (a) capacitive coupling, (b) inductive coupling (195).

will carry nearly all of the current as required by the "skin effect" (151). Figure 1b shows a general arrangement of a high frequency discharge formed by inductive coupling.

Capacitive coupling (Fig. 1a) is accomplished by placing the discharge electrodes on the outside of the tube. This amounts to adding capacitors in series with the discharge circuit. A metal foil, a thin coat of aquadag, mercury, or an electrolytic solution of 1% HCl in acetone (f. p. = -95°) can be used as external electrodes. The tube can be powered by the regular line frequency of 50–60 cps (146).

Microwave coupling through a resonance cavity gives standing waves whose pattern depends on the shape and dimensions of the cavity (6, 83, 171). Shaw (195) has described conventional microwave coupling systems and a variety of microwave circuitry and components. The main critical point in the choice of the microwave discharge arrangement is that an impedance match between the discharge tube and the microwave power source is attained. Designs for microwave cavities are described in the literature (33), and microwave discharge sources are commercially available at various frequencies, e.g., the microthermic unit made by Raytheon has a frequency of 2400–2500 megacycles and a power output of 120 watts.

3. The Arc Discharge

The electric arc is a self-sustaining discharge of low voltage and high current. The arc is usually established by separation of contacts or by transition from a higher voltage discharge. It differs from the glow discharge by its low cathode fall of about 10 volts and its high current density. The transition from the relatively low current density and high voltage of the glow discharge requires an important change in the electron-emission processes at the cathode (35). Arcs are classified as low and high intensity arcs. The voltage drop across the plasma region in the low intensity arc accounts for the major portion of the arc voltage. As the current is increased, very little change will be noticed in the appearance of the arc and the current density remains the same. Further increase of the current results in a spread of the arc crater over the entire area of the anode tip. Figure 2 shows the appearance of a carbon arc as the total current is increased through the transition point from a low intensity to a high intensity arc (196, 225). The high intensity arc is characterized by a jet of gaseous material that proceeds from the anode surface known as the "tail flame." The jet comprises a mixture of vaporized anode components and infused ambient material.

The so-called Beck arc is an example of a high intensity arc characterized by an anode containing oxides and fluorides of cerium. The high current density at the anode leads to very rapid evaporation from the anode sur-

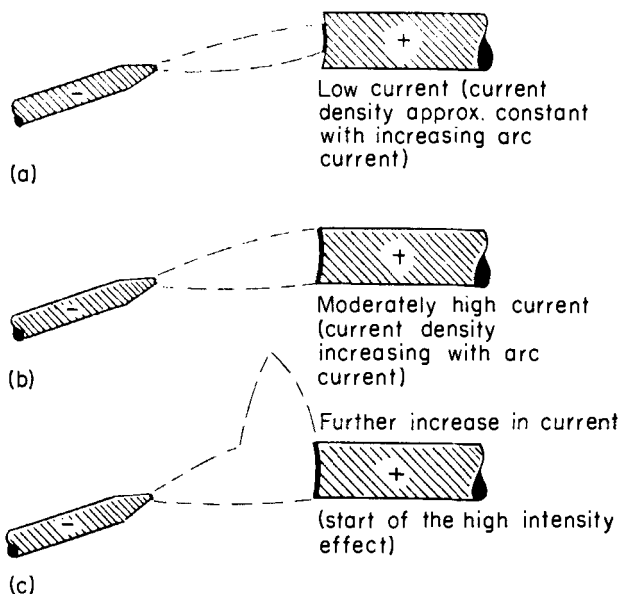


FIG. 2. Appearance of a carbon arc as the total current is increased through transition to the high intensity arc: (a) low intensity region, (b) just below transition point, (c) just above transition point (225).

face, and a plasma temperature of the order of 9000–10,000°K is attained. The possibility of introducing a variety of elements into the arc by placing the substances to be studied in the core of the carbon anode is convenient and unique. The rapid evaporation results in a high temperature jet at an initial velocity of 10^3 – 10^4 cm sec⁻¹ (137).

4. Plasma Jet Generators

Besides the above mentioned form of the high intensity arc, the constricted arc is a well-developed device for producing high temperature plasmas. Whenever an arc is forced to burn through a narrow hole, the increased current density results in an increased magnetic force directed in such a way as to produce confinement of the arc. The magnetic pressure directed radially results in pressure release in both axial directions from the confining hole. The mechanism may be described as a kind of pump, which sucks gas sideways into a constriction and blows it out in an axial jet after heating the gas and transforming it into plasma.

The term plasma jet applies to any high current arc in which plasma is jetted through a nozzle. The plasma jet generator is an electric arc contained within a small tube through which the gas is also blown. The significant characteristic of this device is that it incorporates an ingenious cooling

system, which keeps the electrodes from evaporating and helps to elevate the temperature of the plasma. The concept of increasing the plasma temperature depends on the "pinch effect" caused by the self-induced magnetic field, i.e., the "magnetic pinch," and on the "thermal pinch" resulting from the increased current density. By means of such techniques the plasma jet ejected from an orifice in one of the electrodes consists of a beam of highly excited particles with temperatures in the range 10,000–100,000°K.

The Gerdien arc (80) is the prototype of modern plasma jet generators.

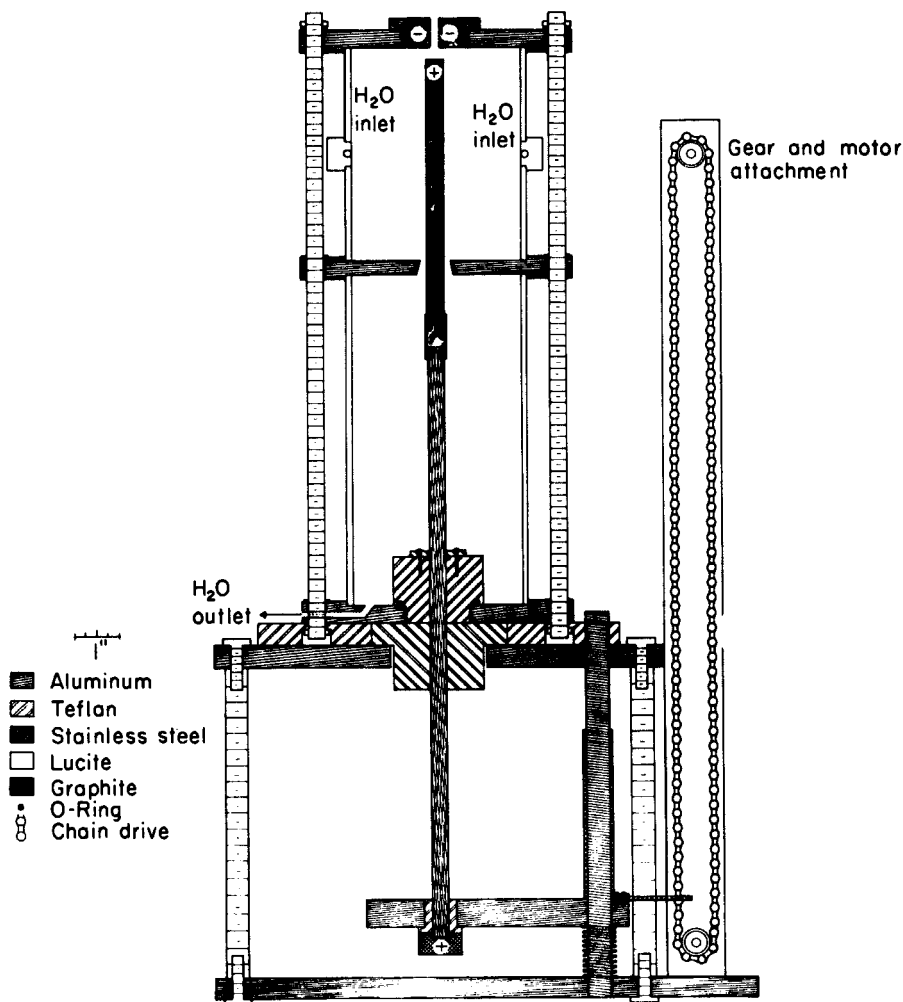


FIG. 3. Water-constricted plasma generator (114).

The arc is forced to pass through a narrow water-cooled constriction established by a copper diaphragm. The cooling effect of running water (or some other fluid) in direct contact with the arc column has proved to be of high efficiency. A cooling water column may be established by introducing water tangentially with enough energy to form a hollow vortex with almost parallel walls. Improvements of the Gerdien arc were reported by Maecker (140) and Weiss (237). A diagram of a water-constricted plasma generator based on the one constructed by Weiss is shown in Fig. 3.

Stabilization of the plasma jet generator is also possible by the use of a rare gas like argon or helium or a diatomic gas such as hydrogen or nitrogen. Stabilization in this case is either by vortex flow and formation of a gas sheath or by wall stabilization. Examples of these generators are presented in Figs. 4-6.

The distinction between the arc and the plasma jet is arbitrary. Usually the arc is considered as the portion of the discharge between the electrodes and carries current due to the excess supply of electrons. On the other hand, the plasma jet does not carry excess electrons from the external circuit. In

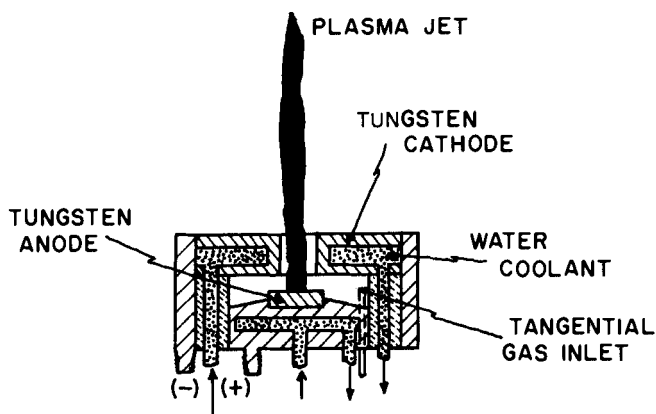


Fig. 4. Vortex-stabilized plasma generator (222b).

a sense the plasma jet resembles a chemical flame in appearance, but differs from the flame by its high ionization and its almost unlimited supply of energy. In the plasma jet the source of energy is the electric power supplied to the arc generating the plasma jet. The plasma jet heated by the arc energy may be used as a heat source and to provide an environment for chemical reactions at temperatures higher than flame temperatures. On the other hand, direct contact of the reagent with the electric arc is avoided. Endothermic reactions are expected to take place when a reagent contacts the plasma stream outside the arc chamber. The rapid heating and fast

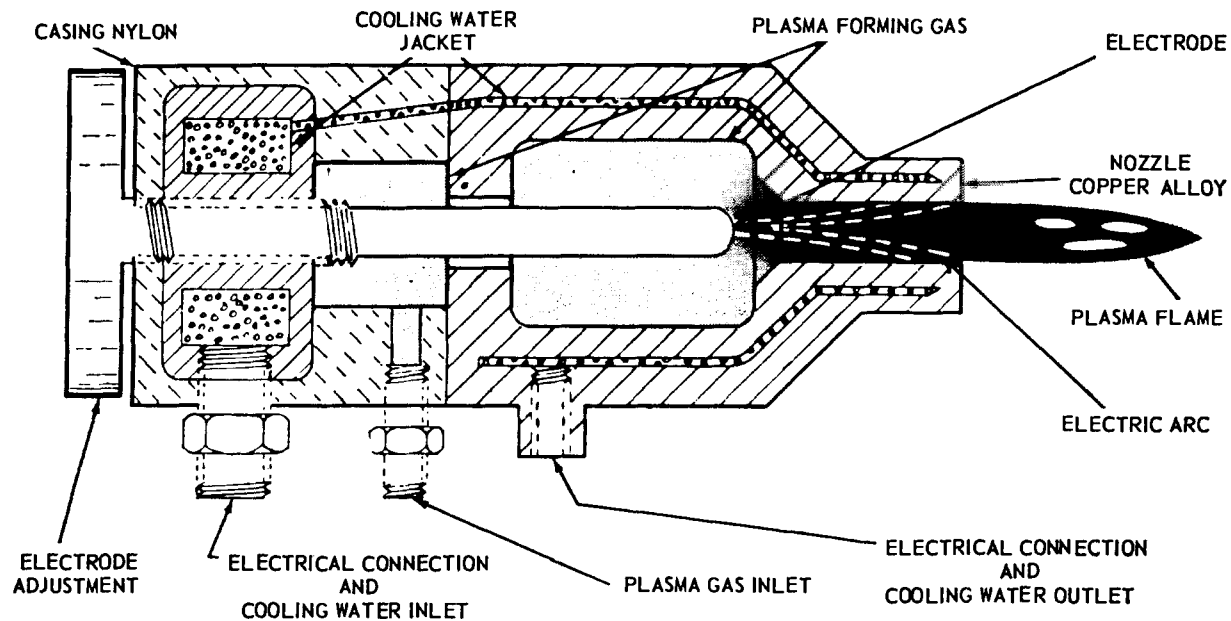


FIG. 5. Gas sheath-stabilized plasma generator (222b).

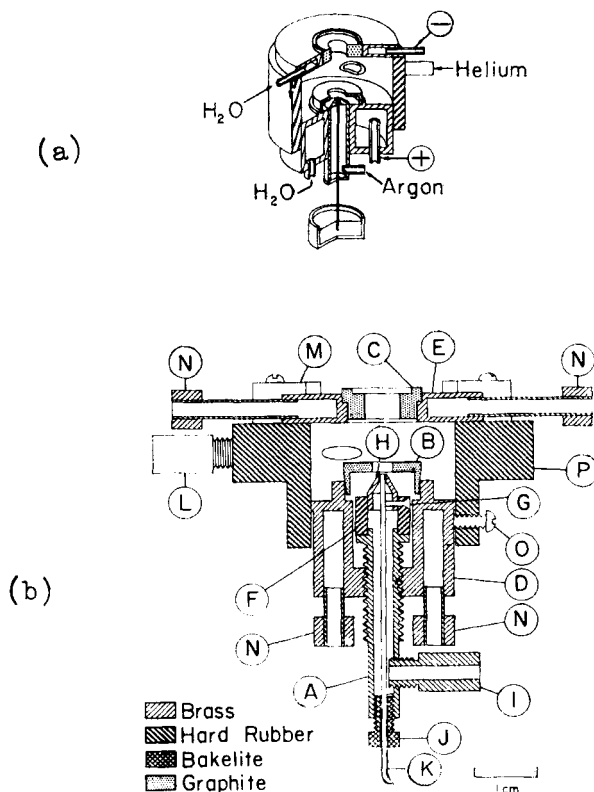


FIG. 6. The plasma jet as modified for a spectroscopic source: (a) schematic drawing, (b) detailed drawing: A, atomizer; B, anode; C, cathode; D, chamber holding atomizer and anode; E, cathode holder; F, hard rubber insulator; G, set screws for positioning capillary; H, atomizer tip; I, argon inlet; J, plastic screw holding capillary; K, capillary tube; L, helium inlet; M, cathode holder clamps; N, water connections; O, set screws; P, outer case (162).

quenching of the reagents in the plasma stream are important factors in the utilization of the plasma jet in chemical processes.

5. Induction-Heated Plasma Torches

This type of plasma torch uses a radiofrequency field to maintain a thermal plasma, without the consumption of electrodes. The energy of the high-frequency electromagnetic field is transferred to a gas by interactions with the ionized gaseous molecules, atoms, and electrons and thus maintains a high degree of dissociation and excitation. By allowing recombination among these species, the absorbed energy is given off in the form of heat and light. This method of heating gases can best be understood in the

same terms as general heating by induction. The plasma generation is started by forming a small volume of plasma by induction heating of a tantalum wire or a carbon or tungsten rod placed in the center of the coil. This, in turn, heats the gas around it, lowering its breakdown potential

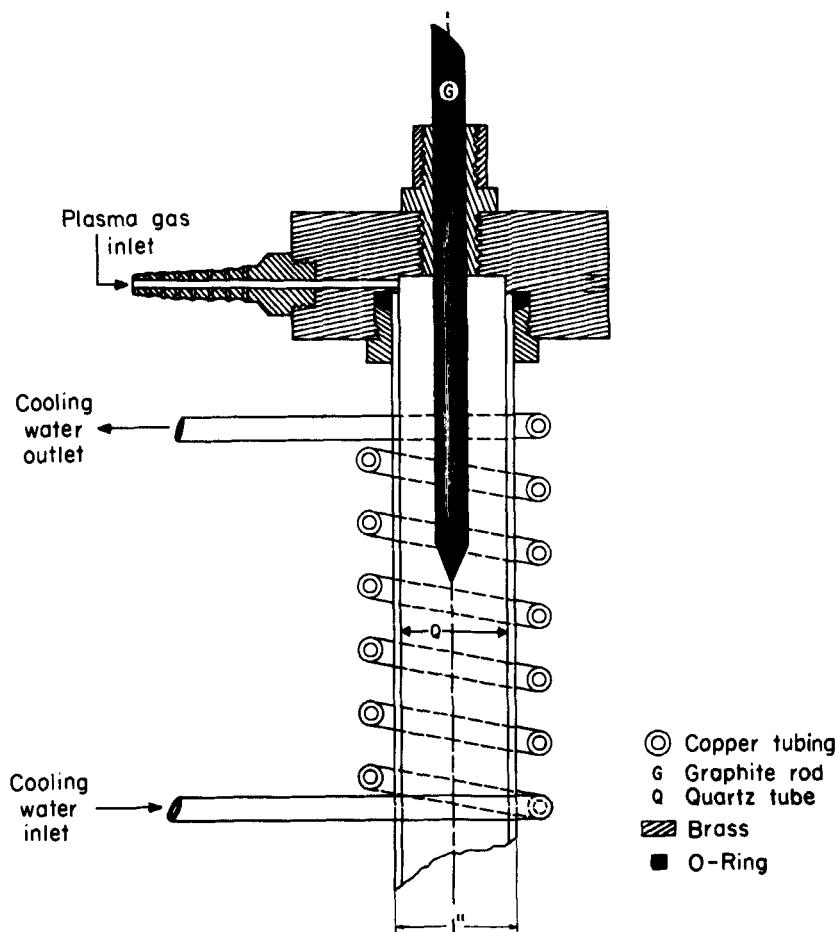


FIG. 7. Thermal induction plasma torch (114).

and giving rise to ionization of the gas and establishment of the plasma in the high radiofrequency field. As in other plasma jet generators, the plasma has to be stabilized to maintain itself against the gas flow. Vortex stabilization has proved to be convenient. A tangentially fed gas flows spirally down the walls of the torch tube, creating a low pressure area in the center of the tube. This causes some of the plasma to flow up the tube

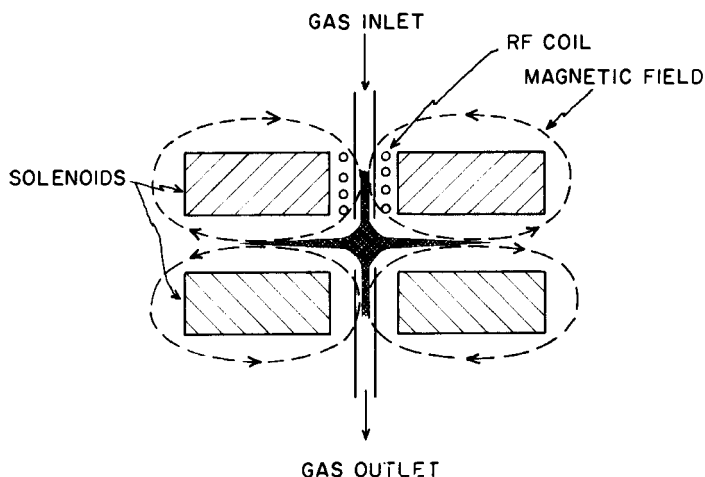


FIG. 8a. Plasma torch trapped in a cusp-shaped magnetic field (85).

countercurrent to the main flow. The flow along the walls tends to keep the plasma centered and away from the walls, thus keeping the tube walls cool and making it possible to operate at higher power levels (88, 175, 177). The field producing the energy may be from either an ordinary high-frequency or microwave transmitter. A frequency of 4 megacycles was used by Reed (175) and in this laboratory. Frequencies of the order of 25–28

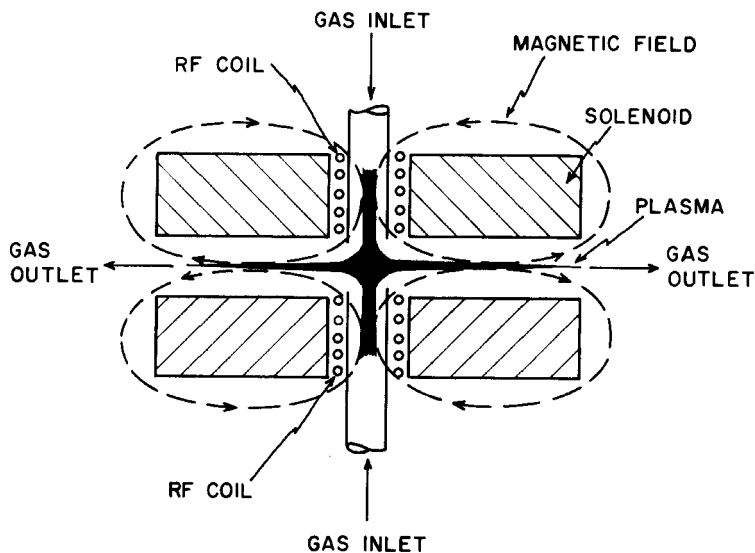


FIG. 8b. Plasma torch confined by a steady magnetic field (85).

megacycles were used by Grosse (88), and a 5-kw source at 915 megacycles was utilized by Friedman (76). Figure 7 shows a sketch of an induction-heated torch.

Magnetic confinement of the plasma generated in a radiofrequency torch has been reported by the Plasmadyne Corporation (85). A diagram of such a torch is shown in Fig. 8. Figure 8b shows a design expected to be

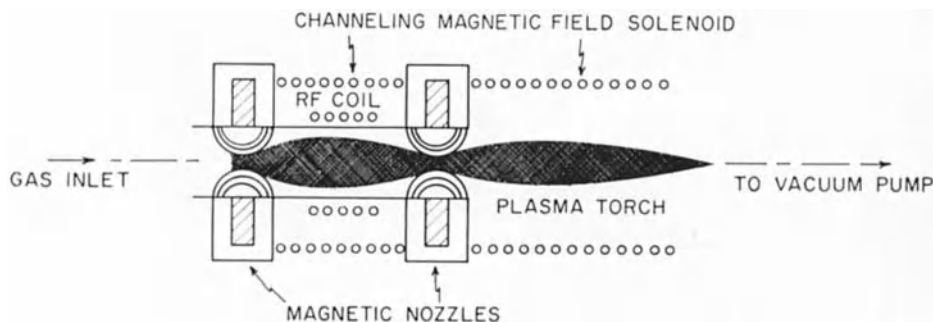


Fig. 8c. Plasma torch with a magnetic nozzle (85).

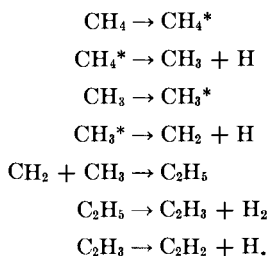
of use in chemical studies, while the torch configuration of Fig. 8c has the advantage of jet formation where a high velocity plasma is desired.

C. IONIZATION- AND EXCITATION-ACTIVATED REACTIONS

Chemical reactions of substances in an electric discharge are widely varied. Decomposition, formation, and/or transformation of a given substance may take place according to the nature of the substance and the discharge parameters. The reactions which may take place vary in complexity, depending on the number of highly active species which are produced as intermediate fragments, and their lifetimes.

The main activating processes which may induce chemical reactions in an electric discharge reactor may be categorized as thermal-, excitation-, or ionization-activation processes. Considerations of the mechanism of a given reaction involve the energy of the electrons produced in the discharge and the site of the reaction in the reactor. One of the first general attempts to explain the mechanism of electric discharge reactions was that of Lind (135), where an ion-cluster theory was proposed to explain the high yield of chemical reactions in a discharge. Brewer and Westhaver (28-31) explained the formation of NH_3 , O_3 , and the oxidation of hydrogen in electric discharges on the basis of ion-activation processes. On the other hand, Lunt and Mills (138) and Emeleus and Lunt (60) denounced the ionic mechanism and interpreted the reactions on the basis of a free radical mechanism. In support of the free radical mechanism, Bradford and Finch

(27) considered the production of free radicals by electronic excitation processes as opposed to thermal ones. Burton and Magee (38, 39) suggested that electronic excitation may be perceived by considering the role of low energy electrons (0.5–4 eV) in electric discharges, and argued that molecular electronic states of very high energies can be excited by moving the molecule up a succession of closely spaced electronic energy steps. They favor electron impacts, rather than radiation, as responsible for the excitation on account of the rapid mechanism of the first. In support of this view Wiener and Burton (238) cited the decomposition of methane in an electric discharge. They suggested the excitation of CH_4 where the initial excitation furnishes sufficient CH_3 radicals to start the process. CH_2 radicals are then formed in high concentration as evidenced by the formation of CH_2D_2 in presence of D_2 , while CHD_3 and CH_3D are formed in small amounts. The formation of C_2H_2 in this process was assumed to follow the steps:



Reddy and Burton (174) used the same argument in explaining the decomposition of C_2H_4 in an electric discharge to give C_2H_2 .

In the event that ionization serves as the rate-determining step in electric discharge reactions, one would predict that a given reaction would set in at the ionization potential of the reactant involved. This still does not exclude the possibility of excited species also acting as reactive centers. Metastable states, on account of their relatively long lives, may be effective in the activation of certain reactions. Further, one has to take into account the effect of thermal activation, especially in high temperature plasmas. Although support for various views can be deduced from experimental data on a specific reaction, it is clear that the mechanisms of chemical reactions in discharges do not all follow the same path.

D. PRODUCT COLLECTION AND IDENTIFICATION

The occurrence of a given chemical reaction depends on activation of the appropriate species, and this explains the unique role which an electric discharge might play in producing a particular product molecule. In certain cases the electric discharge may be needed to activate a single species, which contacts a second reactant at lower temperature outside the discharge zone.

In other instances both reactants may be found in the discharge zone where contact and interaction take place under the activating condition of the discharge. In any case, the nature of the products determines the kind of discharge and the system to be used in the synthesis. For example, if rather unstable products are of interest they should be removed from the discharge zone as rapidly as possible, and a flow discharge system is used. If stable products of low volatilities, which condense out on the walls of the reactor and do not undergo further reactions, are synthesized, a static discharge system may be used. In certain cases where intermediates or by-products are undesirable, the discharge reactors may be immersed in a low temperature bath. This can also be done when the products are volatile to provide for their continuous condensation by such cooling.

The uses of the plasma jet devices for studies of chemical reactions differ from those of other electric discharge devices, in that the hot gas stream may be utilized either as a heat source or as the source of chemical species which participate in a chemical reaction. In the first case the plasma gas is a relatively inert gas, such as argon or helium, and serves as a source of heat by heat exchange. Of course, the electrons and excited species of the plasma may also participate in some chemical reactions with other substances present in the plasma reactor. In the case of other plasma gases, such as nitrogen, hydrogen, or oxygen, one has introduced into the system species which can take a more active part in the chemical reaction. When these substances are present in the plasma stream, they either react (after being activated to the right energy state or decomposed into the appropriate intermediate fragments) among themselves or form new compounds by combination and transformation with other materials introduced into the plasma gas stream. In many cases, a well-known gas cannot be used as a plasma gas directly. Maintenance of the discharge requires a critical temperature to perpetuate the electric conductivity, and, in addition, corrosive decomposition products may react with the electrodes and change the discharge characteristics, leading to instability and extinction of the arc.

Various techniques can be used to inject materials of interest into a plasma stream. The nature of such substances, their state, and the best predicted conditions under which a reaction is expected to take place, help determine which one to use. A description of some typical reactors is given below.

A general arrangement for a plasma jet reaction chamber is given in Fig. 9. The reaction chamber is fitted with an opening through which variously shaped "cold fingers" may be inserted. For collecting solids the cold finger is set close to the feed ring to quench the products. The same

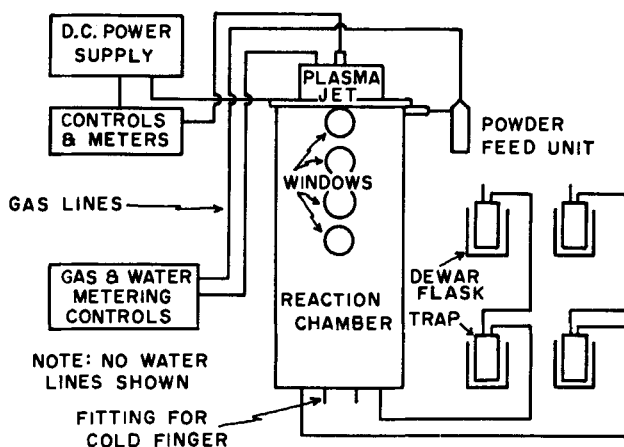


FIG. 9. Plasma jet reaction chamber and collection system (204).

setup can be used to quench the reaction products when gaseous compounds are prepared. In this latter case, cold traps are used with either liquid nitrogen or dry ice. A somewhat similar arrangement by Grosse *et al.* (88) allowed for passage of the gas from the quenching chamber through a glass tube packed with glass wool (intended to retain finely divided soot which is found in $(\text{CN})_2$ preparation) (Fig. 10).

In those cases where the reactant gas is heated by the stream of hot plasma outside the discharge chamber, the reactor may consist of two sections: the first for mixing the reactant gas with the plasma and initiating reaction, and the second to provide for cooling and quenching the products. A reactor-quencher combination is shown schematically in Fig. 11. The quenching chamber consists basically of a water-cooled double-walled tube to which the plasma generator is bolted by means of flanges and the joint is made gastight with O-ring seals.

Due to the variety of reactions and their needs for different environmental conditions, one cannot give a general account of all the possibilities for product and reactant handling. Figure 12 gives a general idea of several of the different methods by which a plasma torch can be utilized for chemical reactions. Grosse *et al.* (90) reported the feasibility of liquid-phase chemical reactions in a plasma reactor at temperatures above 4000°K . Their reactor consisted of a centrifugal furnace with a reaction section of three concentric tubes: (1) oxides, carbides, nitrides, or graphite, (2) insulating material, and (3) the water-cooled external metal cylinder. Using aluminum as a test material, and alumina as the internal tube of the reactor, the alumina tube partially melted and by rotation of the furnace served

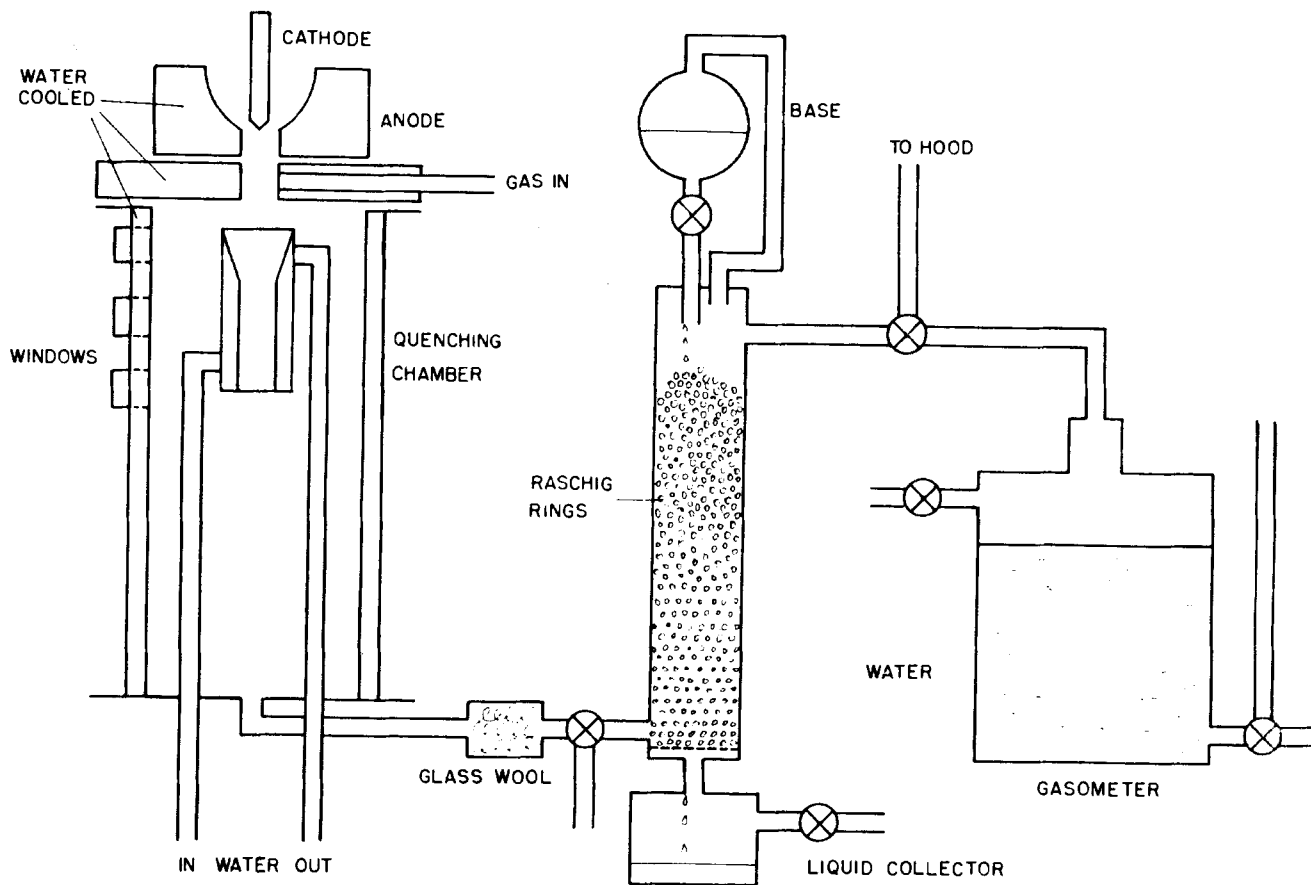


FIG. 10. Plasma jet reaction chamber and product collection system (88).

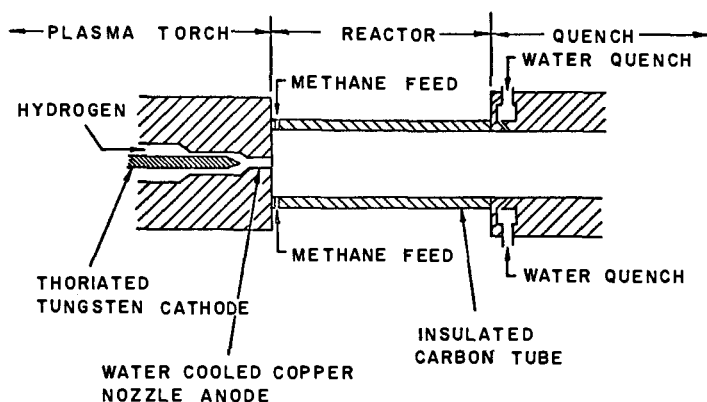


Fig. 11. Plasma reactor and quencher combination (7).

as a liquid crucible. Other refractories were also used as liquid containers in such a reactor.

For product analysis one utilizes all of the conventional analytical techniques along with gas chromatography, optical spectroscopy, and mass spectrometry in identifying the products. In certain cases, intermediate fragments can also be detected by spectroscopic techniques, and such identification of intermediate free radicals should aid in establishing the steps of a given reaction mechanism.

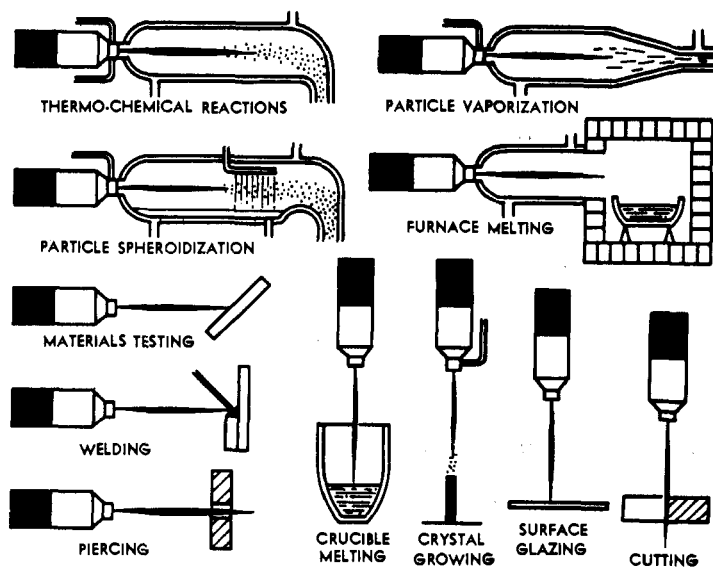


Fig. 12. Various arrangements for plasma jet reactors (222a).

II. Chemical Reactions in Glow and Arc Discharges

The current state of knowledge of chemical reactions in glow and arc discharges will be elucidated in this section by fairly comprehensive reviews of research covering reactions of boron, silicon, sulfur, titanium, phosphorus, oxygen, nitrogen, hydrogen, various halides, and inorganic and organic carbon compounds.

A. BORON AND ITS COMPOUNDS

1. Boron Halides

Diboron tetrachloride, B_2Cl_4 , was first prepared by Stock *et al.* (202) in 1925 by striking an arc between two Zn electrodes immersed in liquid boron trichloride. Wartik *et al.* (234) synthesized the same compound by passing BCl_3 at a pressure of 1–2 mm Hg through a glow discharge between Hg electrodes, as described schematically in Fig. 13. The volatile products

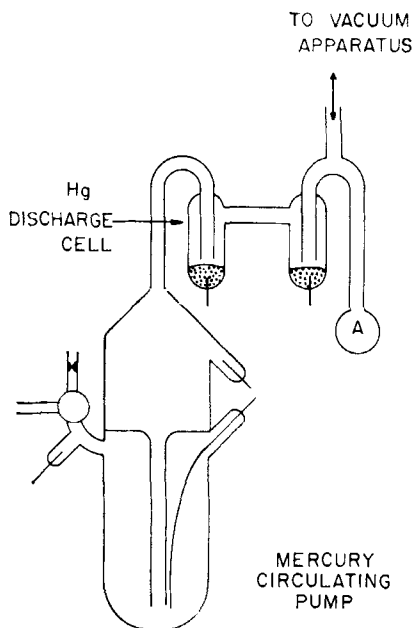
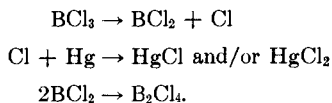
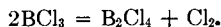


FIG. 13. Mercury discharge tube for preparation of B_2Cl_4 and B_4Cl_4 (223).

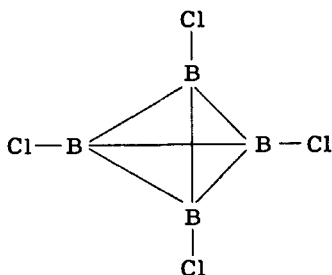
of the reaction were passed through a trap at $-78^\circ C$ where the B_2Cl_4 was retained. Urry *et al.* (223) suggested the following step mechanism for the reactions in the discharge:



The interference of metallic electrodes was eliminated by Frazer and Holzman (74, 75), who used microwave radiation to excite BCl_3 vapor under a pressure of 44 mm Hg as it passed through a resonating cylindrical cavity maintained at a temperature below 0°C . The microwave exciter unit operated at a wavelength of 12.2 cm with a power of 30–40 watts, and B_2Cl_4 was condensed in a trap at -111°C . Free chlorine produced in the reaction was removed from the trap, along with small amounts of BCl_3 , by fractional distillation. Investigation of the spectra of the emitted light in the process suggested the presence of the BCl molecule as an intermediate species in the reaction (102):



The absence of spectroscopic evidence for the species BCl_2 shows that either the location of the spectrum of BCl_2 lies outside the investigated region (2000–7000 Å) or the energy absorbed is higher than the dissociation energy of BCl_2 , resulting in immediate rupture. Other investigations of the preparation of B_2Cl_4 and similar compounds, in electric discharges of various types, were reported by Wartik (234). Two other boron subchlorides were reported by Schlesinger *et al.* (189). B_4Cl_4 was formed as a by-product in the reaction of BCl_3 in an electric discharge, while the main product was B_2Cl_4 . The structure of B_4Cl_4 is believed to consist of a tetrahedron of boron atoms with chlorines at each apex:



The second by-product was $(\text{BCl})_x$, which appeared as a coating on the walls of the discharge tube. The monochloride was assumed by Rosenberg and Wartik (179) to be the result of B_2Cl_4 decomposition:

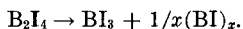


Rosenberg and Wartik (179) obtained the corresponding monobromide from an electric discharge through BBr_3 .



On the basis of the chloride reaction, Diener and Pflugmacher (57) suggested the formation of B_2Br_4 from BBr_3 in an electric discharge where Hg was used as a reducing agent.

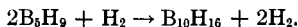
Schumb *et al.* (190) found that BI_3 , when sublimed under a reduced pressure of 1–3 mm Hg through a silent discharge tube powered by a 5 Mc/sec transmitter, gives B_2I_4 . This compound is pale yellow in color and disproportionates at room temperature:



The nature of $(\text{BI})_x$ is unknown.

2. Boron Hydrides

The decomposition of diborane in a silent discharge in the presence of an inert gas was described by Kotlensky and Schaeffer (128). Diborane passed slowly and at reduced pressure through an ozonizer-type discharge yields a mixture of boron hydrides. A yield of 40% B_4H_{10} , 20% B_5H_{11} , small amounts of B_6H_{10} , and a previously unidentified B_9H_{16} was reported. Gibbins and Shapiro (81) reported that their mass spectral studies of the discharge products indicated the presence of a hexaborane having a minimum of 12 hydrogen atoms, as the mass spectrum differed distinctly from B_5H_{10} . Decaborane-16 was also formed in an electric discharge between copper electrodes through a stream of hydrogen and pentaborane-9. Grimes *et al.* (86) explained the formation of decaborane by loss of one molecule of hydrogen between two molecules of pentaborane, and then the formation of boron-boron bonds between the remaining units according to



3. Metal Borides

TiB_2 was formed when a mixture of TiO_2 , H_3BO_3 , and C was exposed to an electric arc (113). The powder charge was arranged so that the evolved CO protected the reaction zone from atmospheric oxygen. Kahlsua (113) described an arc system applicable to the formation of heavy metal borides from their oxides.

Leonard (5) reported the formation of two new manganese borides in an electric arc.

4. Other Boron Compounds in Electric Discharges

A mixture of boron trichloride and carbon monoxide, when subjected to the action of an ozonizer-type discharge, produced an apparently polymeric solid possessing properties not commonly associated with boron compounds. The discharge, as well as the properties of the product, are described by Wartik and Rosenberg (235). The polymer deposit was a transparent light-yellow film on the walls of the discharge tube and had a cedarlike odor. The authors suggested the formula $\text{BCl}_3 \cdot 2\text{CO}$. A similar film was obtained by repeating the experiment, using BF_3 in a mixture with CO. Other discharge-induced reactions of boron halides with nonmetallic oxides are discussed by Rosenberg (178).

Pure carbides and nitrides of boron, along with other elements of Groups IV–VI such as Si and Ti, have been produced by mixing a volatile boron compound with a source of carbon or nitrogen and passing a high-frequency electric discharge through the mixture. Suckett (209) described an apparatus for mixing, electrical treatment, and disposal of the by-products of the reaction between BCl_3 and propane. A fine hard black product, B_4C , with some free carbon impurity was obtained. The pure nitride was similarly produced by replacing the hydrocarbon by hydrogen and nitrogen. Williams *et al.* (239) reported the formation of unidentified compounds in an electric discharge through pentaborane and acetylene. The carbon-boron compounds from this reaction were referred to as carboranes.

A high purity boron was obtained by passing a mixture of BCl_3 and hydrogen (optimum ratio 1:5) through an electric discharge. Markovskii *et al.* (147) carried out the process in the pressure range 30–200 mm Hg, and reported a boron purity of 99.9%.

B. SILICON AND ITS COMPOUNDS

1. Silicon-Nitrogen Compounds

Tris(trichlorosilyl)amine $(\text{SiCl}_3)_3\text{N}$ was formed by passing an equimolar mixture of SiCl_4 and nitrogen at reduced pressure (0.2–0.8 mm Hg) through a glow discharge, similar to the one shown in Fig. 14. Pflugmacher and Dahmen (169) reported that vacuum distillation of the reaction product yielded a crystalline solid which was collected at 1–20°C, along with a colorless oil collected in the boiling range 170–250°C and a yellow-brown resinous residue. Fractional distillation of the crystalline product gave $(\text{SiCl}_3)_3\text{N}$ and $(\text{Si}_2\text{NCl}_5)_n$. On ice-water cooling of $(\text{SiCl}_3)_3\text{N}$ vapor, lardlike crystals (m.p. 44–48°) were obtained. It changed, probably to a monoclinic form (m.p. 78°), on condensation at room temperature. At temperatures

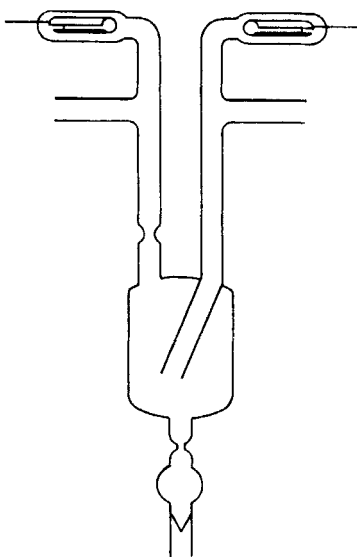


FIG. 14. Pflugmacher and Dahmen discharge tube (169).

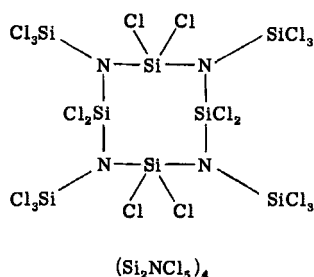
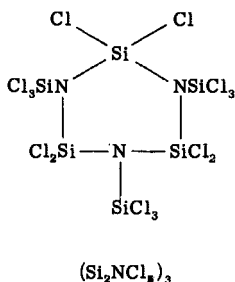
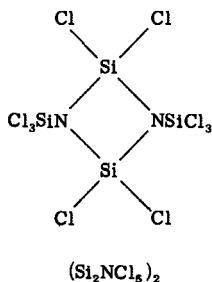
higher than its boiling point in vacuum (135°) it decomposed to SiCl_4 , Si, and a white solid of lower silicon and chlorine content. The authors (169) suggested a cyclic chain-like structure for the discharge products, according to a mechanism which involved the initial formation of $(\text{SiCl}_3)_3\text{N}$. Subsequently,



$(\text{Si}_2\text{NCl}_5)_2$ is probably the only product collected in the temperature range 170 – 250°C , but at higher temperatures,



The proposed structural formulas are:



2. Organosilicon Compounds

Organosilicon compounds, useful in the preparation of polymers, were reported by Akerlof (2-4) to be obtained in a continuous process when mixtures of hydrocarbons or their halogenated derivatives and SiCl_4 react in the vapor phase in the presence of an electric discharge. A dry mixture of SiCl_4 and CH_4 in a mole ratio 5:1 was passed through an electrodeless discharge operated at 14.5 kv, 120 ma, and 800 cycles/sec, as shown in Fig. 15, and gave organosilanes, which were liquids over large temperature

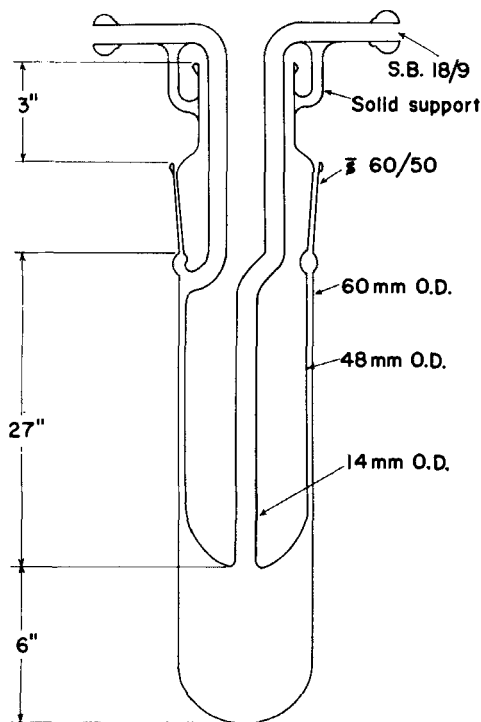
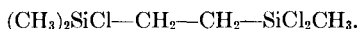


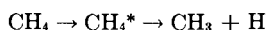
FIG. 15. Electrolyte-conduction discharge tube (3).

ranges with boiling points in the neighborhood of 400°C . The reaction product was assumed to contain CH_3SiCl_3 and a smaller amount of $(\text{CH}_3)_2\text{SiCl}_2$.

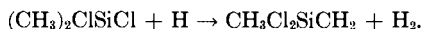
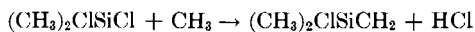
The reaction between $(\text{CH}_3)_2\text{SiCl}_2$ and CH_4 , using the same type of electrodeless discharge, was also studied. Fractional distillation of the reaction mixture gave a high boiling residue with a Cl:Si ratio of 3:2. Akerlof suggested a possible structure:



Assuming that the Wiener-Burton reaction (238)



initiates the mechanism, the following subsequent reactions may take place:



Recombination of the two new radicals yields the product proposed above. Other longer-chain compounds would appear likely to be found.

Andreev (10) obtained a mixture of octamethyl trisiloxane (b. 152°) and the isomers of $\text{C}_{11}\text{H}_{32}\text{O}_3\text{Si}_4$ (b. 190–195°), $\text{C}_{12}\text{H}_{34}\text{O}_3\text{Si}_4$ (b. 102–107°), $\text{C}_{13}\text{H}_{38}\text{O}_4\text{Si}_5$ (b. 145–155°) from a mixture of $(\text{Me}_3\text{Si})_2\text{O}$ with N_2 in a silent discharge operated at high voltage, ~23 kv. Acetylene was formed only at a lower voltage, ~8 kv, where a radical mechanism was proposed, based on Si—Me bond rupture. The use of an ozonizer-type discharge (Fig. 16) in

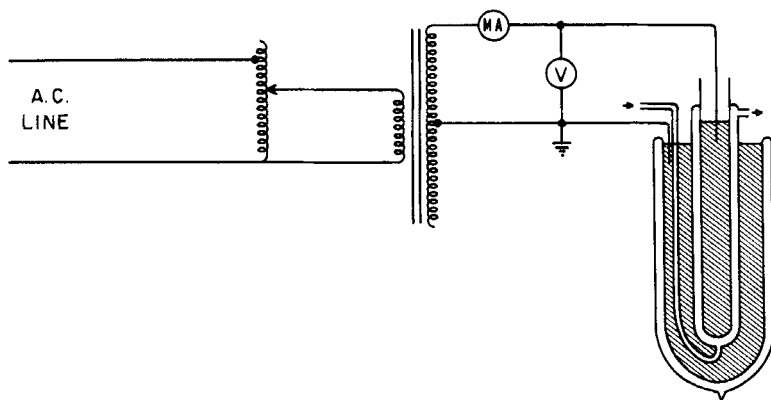


FIG. 16. Typical Siemen's ozonizer (106).

a stream of refluxing vapor of MeSiCl_3 and H_2 gave C_2H_2 , $\text{MeSiCl}_2\text{CH}_2\text{SiCl}_3$ (b. 182–185°), and $\text{MeSiCl}_2\text{CH}_2\text{SiCl}_3$ (b. 199–203°) (8, 9). The presence of chains of alternating C and Si atoms in the mixture is suggested.

Urry (224) reported the preparation of Si—C chain compounds similar to Andreev's from alkyl silanes in a Hg discharge. He proposed, as Andreev did, a free radical mechanism involving CH_3 , SiCl_3 , and H free radicals. Perchloropolysilanes were also prepared by Urry from electric discharges through Si_2Cl_6 under various conditions. The main polymeric products

seemed to be $\text{Si}_{10}\text{Cl}_{18}$ and $\text{Si}_6\text{Cl}_{14}$. The latter was polymorphic with at least two crystalline forms and one amorphous form.

Kautsky and Kautsky (117) described a process by which mists of solid metal particles having a suitable grain size with liquid organic or inorganic compounds, or solutions, were subjected to a spark discharge. The process permitted maintenance of extreme conditions where the spark had a temperature of several thousand degrees and the surrounding liquid was quite cool. The reactions between silicon particles suspended in halohydrocarbons, e.g., $\text{C}_2\text{H}_4\text{Cl}_2$, $\text{C}_2\text{H}_5\text{Cl}$, $\text{C}_2\text{H}_4\text{Br}_2$, CHCl_3 , or mixtures of pentane with ethyl ether and SiCl_4 , gave partially chlorinated silanes, e.g., SiHCl_3 . The products of an a.c. arc through Si dispersed in acetone were of a colloidal nature. Centrifugation of the dispersed phase (132) gave three fractions, which on drying yielded brown powder, black flakes, and a silica-like gel. In addition to free silicon all contained Si, O, C, and H in the form of an inorganic Si—O compound and an unsaturated hydrocarbon. Condensation of dimethyldichlorosilane in a silent discharge was also reported by Andreev (11).

3. Silicon Halides

Polymeric polysilicon chlorides of the general formula $\text{Si}_n\text{Cl}_{2n+2}$ were prepared with a submerged arc in a slurry of $\text{SiCl}_4 + \text{Si}$. Kautsky and Kautsky (116) reported the formation of $\text{Si}_6\text{Cl}_{14}$.

Silicon tetrafluoride was reduced with hydrogen by passage through a rotating electric arc. Cook *et al.* (46) reported the formation of SiHF_3 as a primary product, as well as SiH_2F_2 , SiH_3F , and higher silanes. An excess of H_2 was maintained to minimize formation of higher silanes. Rapid quenching and removal of by-product HF were desirable for good yields.

An electric discharge through SiCl_4 between Si electrodes gave high purity silicon by thermal decomposition of the halide. The temperature developed in the arc described (electric field 50,000 volts) was of the order of 10,000–60,000°K. (183).

4. High Purity Silicon

High purity metals have been produced in electric discharges through gaseous compounds of the metal. A high purity silicon was obtained with an a.c. arc (1 Mc/sec induction-excited discharge) through SiCl_4 at reduced pressure in the presence of H_2 (gas) as a reducing agent (41). The same arc has been operated through SiH_4 (40), and the process is reported to be applicable for elements of the 4th, 5th, and 6th groups of the Periodic Table, especially Si, Ge, As, Sb, Se, Te, Pb, and Bi.

C. SULFUR AND ITS COMPOUNDS

1. Sulfur-Oxygen Compounds

The products formed in electric discharges through sulfur and sulfur dioxide have been described by several workers (62, 111, 149, 155, 170, 228, 229, 231). Martin demonstrated the presence of SO in an electric discharge through SO_2 . Evans *et al.* (62) reported that the product of a high voltage discharge through a mixture of SO_2 and sulfur vapor maintained at a pressure of 4–3.24 mm Hg was a mixture of S_2O_2 and SO. The mixture was claimed not to undergo an appreciable dimerization after removal from the discharge tube when held at room temperature for about 45 minutes. Meschi and Myers (155) used an electric discharge tube due to Jones (111) (see Fig. 17) in their studies of this reaction. Sulfur vapor was maintained in the discharge tube by external heating, using a resistance wire, and the

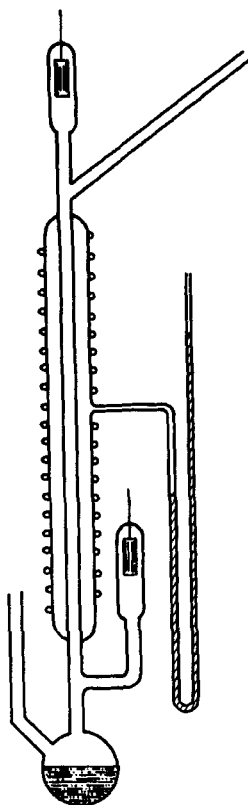
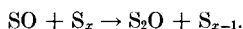


FIG. 17. Discharge tube for preparation of SO_2 and S_2O (111).

products were a mixture of SO_2 and S_2O . There was no evidence for S_2O_2 but SO could have been present in slight amount. The absorption spectrum in the ultraviolet region reported by Jones (111) as a probable spectrum of S_2O_2 was attributed by Meschi and Myers (155) to S_2O in the discharge products. They proposed a reaction mechanism:

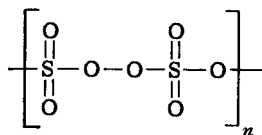


The absorption spectra showed SO_2 absorption systems in the region near 2100 \AA , but not near 3000 \AA where SO_2 was masked by the suggested spectra of S_2O . SO was considered to be the primary discharge product, and then underwent the reaction:



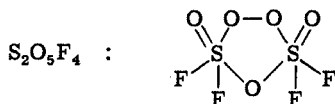
Oxygen atoms were assumed to be abundant, and could be captured by sulfur molecules in a way similar to the capture of oxygen atoms by molecular oxygen in the formation of ozone. Although S_2O is thermodynamically unstable at room temperature, it possibly becomes stable at elevated temperatures. An investigation of the thermodynamic stability of S_2O could throw light on the stability of SO in a sulfur-rich system at about 1000°C , as reported by Pierre and Chapman (170).

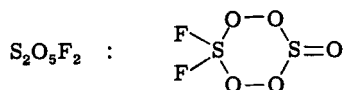
Wannagat *et al.* (228, 229, 231) showed that $\text{SO}_2\text{-O}_2$ mixtures, reacted in a static ozonizer-type tube, form solid unstable polysulfur peroxides $(\text{SO}_{3-3.9})_x$. These compounds are believed to have structures similar to the structure of SO_3 with linking oxide groups randomly replaced with peroxide groups:



2. Sulfur Oxyfluorides

An electric discharge passed through a static mixture of thionyl fluoride and oxygen in the ratio 1:1 produced a mixture of oxyfluorides, which condensed to liquid at -50°C . The mixture of products consisted of monoperoxytetrafluorodisulfur(VI) oxide $\text{S}_2\text{O}_5\text{F}_4$ and monoperoxydifluorodisulfur(VI) oxide $\text{S}_2\text{O}_5\text{F}_2$ (230). Wannagat *et al.* (230) suggested the structures:

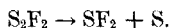




Microwave excitation of SF_4 in the presence of an oxidizing agent such as a nitrite, nitrate, or a metal oxide and NO_2 as a catalyst gave products containing SF_6 , SOF_4 , and SOF_2 (199). Smith and Engelhardt (199) assumed complete decomposition of SF_4 into atomic sulfur and fluorine. Under equilibrium conditions these species recombine to form SF_6 , the primary product of the reaction. A by-product of the microwave excitation of SF_4 in the presence of NO_2 is a volatile reactive solid of undetermined structure, believed to be $\text{N}_2\text{O}_5\text{SF}_5$.

3. Sulfur Fluorides

In common with other compounds, SF_6 is decomposed under a corona discharge and more rapidly in a spark discharge to form lower-valent fluorides of sulfur and the fluorides of the electrode metal. Depending on the discharge conditions, one may get one or more of the lower-valent fluorides of sulfur. Edelson *et al.* (59) reported the formation of SF_2 as a major product from a high current arc in SF_6 . The authors postulated the formation of S_2F_2 as the primary product since it is the only product of discharge decomposition under the mildest conditions. SF_2 is, then, the result of thermal decomposition of S_2F_2 :

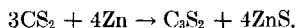


Other gaseous products such as SOF_2 were probably formed by the attack of SF_2 or F atoms on the silica in the reactor.

4. Organosulfur Compounds

Sulfur-containing amino acids were formed in an electric discharge in a reductive atmosphere. Hsi Kun Lu *et al.* (104), using a modification of the electric discharge described by Miller (157), introduced a gas mixture of H_2 , CH_4 , NH_3 , and H_2S in the ratios 1:2:2:1 at about 1 atmosphere total pressure into the discharge tube. After a week of continuous operation, a few amino acids containing sulfur were identified in the product. Cystine, cysteine, and methionine were identified by paper chromatography.

C_3S_2 has been prepared by striking an electric arc between Zn electrodes in CS_2 liquid (203):



On the other hand, CS_2 results from electrothermal heating of S and C. Seidel and Wilke (193) described a reactor into which superheated liquid sulfur was introduced through a hollow cathode by siphon action.

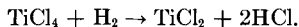
5. Pure Sulfur

Extraction of sulfur from its ores has also been possible by passing powdered sulfur ores through an electric arc at reduced pressure (180).

D. TITANIUM COMPOUNDS

Volatile metal chlorides may, in general, be converted to the corresponding metals in an electric discharge reaction with a reducing agent. The production of high purity titanium by this method is a common industrial practice. Akerlof (1) designed an apparatus in which the inner surfaces of the reactor were blanketed with hydrogen. The reaction zone had walls of a gas-permeable heat-resistant insulating material having a low expansion coefficient, such as porcelain or sintered Al_2O_3 . A continuous flow of hydrogen was passed through these walls. The method has been suitable for recovery of Ti from TiCl_4 .

Gutmann and Nowatny (94) reduced TiCl_4 with hydrogen in the presence of a Na electrode. The Na participated more strongly with respect to the reverse reaction of HCl than did H_2 . The process consisted of partial reduction of TiCl_4 by hydrogen to give TiCl_2 :



Further reduction to the metal was more efficient on dissolution at 800° in molten NaCl. In absence of the Na electrode, TiCl_2 was the main product. Kwasnik (131) utilized a brush discharge for the preparation of TiCl_2 according to the above reaction. Hydrogen at about 10% more than the stoichiometric value was used. Ishizuka (105) described an apparatus in which Ti of 99.6% purity was prepared by reduction of TiCl_4 in a hydrogen atmosphere. The primary product of an electric discharge at 2400 volts and 126 ma contained 90% Ti, besides lower chlorides of Ti. The high purity metal was recovered by heating at a high temperature in vacuum.

Dolgoplov *et al.* (58) reported the recovery of Ti from its oxides or chlorides by subjecting them to a high-frequency electric discharge at normal pressure in an atmosphere of the reactive gases, supplied in a continuous stream. Further melting of the powdered product in the same apparatus and interaction with the discharge gave the high purity metal.

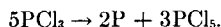
Reduction of TiCl_4 to lower-valent halides of titanium has been accomplished in other types of electric discharges. Bown *et al.* (26) described an electric arc method for reduction of TiCl_4 . Head (99) formed TiCl_3 in solution with a molten alkali halide. An arc was struck between electrodes on the surface of the molten salt. A feed of LiCl and KCl at 550° into an enclosed chamber of an arc between Ti electrodes through TiCl_4 vapor has also been used to form TiCl_3 and lower halides (215). In another arrange-

ment Mg electrodes act as the reducing agent (217). An electrolytic bath containing a moving electrode which comes periodically into contact with a fixed electrode has been described for the process.

An electric arc struck between TiC electrodes in a flask charged with TiCl_4 and purged with Ar gave a violet deposit of TiCl_3 . The method has been applicable for preparation of the lower halides of U, Nb, Ta, Mo, and W (103). Lower halides were also obtained by using Ti electrodes of adjustable separation (213) or Mg electrodes (216).

E. PHOSPHORUS COMPOUNDS

The reduction of PCl_3 in an electric discharge with Hg electrodes was reported by Finch (66). Circulation of PCl_3 vapor through an electric discharge powered by a 2000-volt 15-ma transformer gave a red and yellow wall scale, dark gray scale on the Hg electrodes, and small quantities of a volatile liquid freezing at $34\text{--}35^\circ$ to a white solid. At room temperature it decomposed to PCl_3 and a yellow nonvolatile solid known to be P_2Cl_4 . A microwave discharge through PCl_3 did not yield P_2Cl_4 without passing the discharge products over bronze wool before quenching (214). Tittle reported the formation of PCl_5 in absence of the bronze wool according to:



Attempts to produce P_2F_4 from the liquid product by fluorination were unsuccessful. On the other hand, N_2F_4 was formed in an electric discharge through NF_3 (110, 73).

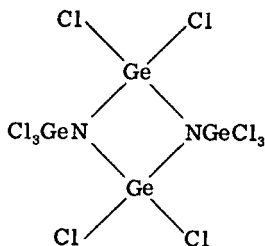
The subjection of hydrogen, in a mixture with PCl_3 at -10° , PBr_3 at 40° , or POCl_3 at room temperature, to an electrodeless discharge gave a small yield of red phosphorous, slight amount of white phosphorus, and unidentified liquid products. The same reaction in a discharge between copper electrodes gave a deposit of Cu_3P (92).

The reaction of 1:1 mixture of PF_3 and O_2 in an electric discharge at -60 to -75° gave a white solid which decomposed on heating to -38° to give POF_3 and PF_5 (232). Further increase of the temperature gave these two products, along with $\text{P}_2\text{O}_3\text{F}_4$, in the range $-25\text{--}0^\circ$. Heating to 20° gave POF_3 , $\text{P}_2\text{O}_3\text{F}_4$, and a solid residue assumed to have the formula $(\text{PO}_2\text{F})_n$. $\text{P}_2\text{O}_3\text{F}_4$ was observed to be a colorless mobile hygroscopic liquid which melted at -0.1° and boiled at 72° . Its hydrolysis indicated that it was the fluoride of a diphosphoric acid and the anhydride of difluorophosphoric acid, PO_2F . PO_2F , a white solid, was hygroscopic and decomposed at 500° to give P_2O_5 and $\text{P}_2\text{O}_3\text{F}_4$. X-ray patterns of PO_2F suggested that it was tetrameric and the anhydride of monofluorophosphoric acid.

F. METAL HALIDES

The existence of low-valent aluminum halides has been confirmed (191) by the production of $(AlI)_n$ in an electrodeless discharge at reduced pressure and a temperature above 50° . A solid deposit was collected on the walls of a dry ice trap, and, after extraction with anhydrous benzene and drying under vacuum, gave a buff-colored solid. Chemical analysis of the solid and X-ray diffraction data suggest that it was a mixture of metallic aluminum and $(AlI)_n$, although crystalline subhalides of aluminum have not been prepared in high purity.

Digermanium hexachloride was prepared by Shriver and Jolly (197) in a microwave discharge through $GeCl_4$. Ge_2Cl_6 was collected at -18° , while unreacted $GeCl_4$ and the liberated Cl_2 were collected at -196° . Tittle (214) formed an oily product from an electric discharge through $GeCl_4$ and nitrogen. He assumed the initial product to be tris(trichlorogermyl)amine, the analogue of the silicon compound, and suggested the structural formula:



for the oil.

Other examples of the reduction of volatile chlorides in an electric discharge include the decomposition of the chlorides of V^{+2} , Sn^{+4} , Sb^{+5} , As^{+3} in a hydrogen atmosphere (93).

Anhydrous ZrF_4 has been prepared in high yields by reaction of NH_4HF_2 with pure ZrC , ZrN , or impure $ZrCN$ derived by carbon arc reduction of natural $ZrSiO_4$ (166). Recombination between positive ions of cesium and negative ions of iodine has been observed in the afterglow of a discharge through cesium and iodine vapors. The reaction is assumed to occur by electron attachment (242). Metal chlorides have also been prepared from their respective oxides by a spark discharge in a fluidized bed containing carbon and the metal oxide while Cl_2 was passed through the bed (18).

G. REACTIONS OF HALOCARBONS

The effect of a silent discharge on a mixture of benzene vapor and chlorine was studied by Nakaoka *et al.* (165). An ozonizer-type tube,

operating at a range of 0–18 volts, was used in the synthesis of benzene hexachloride.

Chlorination of ethanol in a silent discharge was studied by Malhotra and Trivedi (141). Chlorine at a flow rate of 6 ml/sec mixed with ethyl alcohol was passed through an ozonizer at 3–8-kv potential. The less volatile portion of the product, containing chloral, CHCl_2CHO , and $\text{Cl}_2\text{CHCH}(\text{OEt})_2$ with small amounts of $\text{Cl}_3\text{COH}(\text{OH})\text{OEt}$, was returned to the alcohol feed. The condensed fraction contained paraldehyde and smaller amounts of the above products. The formation of $\text{Cl}_2\text{CHCH}(\text{OEt})_2$ seemed to be favored by higher applied potentials. Further investigation of the products was carried out by Malhotra (142) to study the possible role of CCl_3CHO and C_2Cl in the formation, and plausible schemes for the reactions were devised.

The effects of a.c. and d.c. glow discharges were studied for mixtures of C_4H_{10} and Br_2 under static conditions by Badareu and Popovici (15). An electric discharge between Pt and Pd disks as electrodes was passed through C_4H_{10} and Br_2 vapors at reduced pressures of about 4 and 2 mm, respectively. Both solid and liquid products were obtained. The solid products formed a reddish brown mixture and were identified as a polymer, $(\text{CH})_n$, of the cuprene type, an unknown crystalline substance, and cinnamic acid. The only discharge product containing bromine was a polymer of bromostyrene. The small yield of brominated product formed under the experimental conditions is attributed to the preferred reaction between Br_2 and atomic hydrogen in the discharge zone.

The preparation of a wide variety of halocarbons is now feasible by means of electric arc reactions between metal fluorides and carbon in an inert atmosphere. Wolfe *et al.* (240) obtained CF_4 as the main product of the reaction of a d.c. arc between graphite electrodes immersed in a charcoal- CaF_2 mixture. Other alkaline earth fluorides have been used. The gaseous products obtained from a similar arc in an equimolar mixture of anhydrous CaCl_2 and anhydrous CaF_2 comprised CF_3Cl , CF_2Cl_2 , CFCl_3 , and traces of higher fluorochlorocarbons. Cleaver *et al.* (43) prepared chlorofluoromethanes and bromofluoromethanes by passing either Br_2 or Cl_2 and CCl_4 or COF_2 through a carbon arc. A fluorocarbon mixture containing CF_4 , CF_2H_2 , CFH_3 , and $\text{C}_2\text{F}_5\text{H}$ was prepared in an arc discharge between graphite electrodes immersed in anhydrous liquid HF at 19° (241). Other reactions involving the transformation of a mixed halocarbon in a carbon arc were reported by Farlow and Muettterties (64). 1,2-Dichloro-1,1,2,2-tetrafluoroethane was passed through a carbon arc at a reduced pressure of 0.04–0.1 atm, 25 volts d.c., and 18 amps. The gaseous products were tetrafluoroethylene (20%), tetrafluoromethane (5%), monochlorotri-

fluoromethane (30%), dichlorodifluoromethane (20%), and 20% unchanged reactant.

H. REACTIONS OF OXYGEN WITH HALOGENS

The direct addition of fluorine and oxygen was first reported by Ruff and Menzel (181, 182). O_2F_2 was formed on the walls of a discharge tube immersed in liquid air. The orange-colored solid melted at 113°K to a cherry-red liquid. Distillation under reduced pressure at less than 173° gave a brown gas which decomposed into the elements at room temperature. Ayoma and Sakuraba (14) and Kirshenbaum *et al.* (119) studied the reactions of oxygen-fluorine mixtures in a discharge tube immersed in liquid air at 90°K. Ozone difluoride, O_3F_2 , was shown to be the major product. Kirshenbaum and Grosse (118) identified O_2F_2 and O_3F_2 in the warmed product from a yellow-orange solid (freezing pt. 115°K). O_3F_2 , a blood-red liquid, froze at 83°K and decomposed above 116°K to give O_2F_2 and O_2 :



O_4F_2 was reported by Grosse *et al.* (89) as the product obtained by passing an electric discharge through the gaseous mixture $O_2:F_2$ 2:1 at 77°K and a reduced pressure of 5–15 mm. The electric discharge was operated at 840–128 volts and 4.5–4.8 amps. A reddish brown deposit collected on the discharge tube walls between the electrodes. Sometimes it formed clusters of long needlelike crystals. O_4F_2 melted at about 90°K and decomposed at higher temperatures (110°K) into O_3F_2 and O_2 :

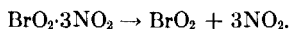


The composition of O_4F_2 was established by both synthesis and analysis (87). Its stability is accounted for on the basis of approximately equivalent strength of the bonds (-O-O-:62.1 kcal, -O-F-:50 kcal). Preparation of O_5F_2 and O_6F_2 with 5 or 6 oxygens in the ring seems possible under milder conditions (89).

Dioxides and trioxides of chlorine were prepared in an electric discharge by Cotton (48). High frequency discharges in the range 10–10,000 cycles and 2.68–187 Mc/sec under critical conditions of luminosity, heat, and light, with nickel electrodes, were reported to give a yield of 16.3% ClO_3 . The discharge tube and details of the power, flow rate, and temperature have been described (47, 48).

Bromine has been converted almost quantitatively into BrO_2 by the action of atomic oxygen on Br_2 at 83°K (187). Trinitrobromine dioxide $BrO_2 \cdot 3NO_2$ was produced from a d.c. glow discharge through a mixture of oxygen, nitrogen, and bromine (168). Also BrO_2 , N_2O_3 , and Br_2 were re-

ported as by-products condensed on the reactor walls at liquid air temperature. $\text{BrO}_2 \cdot 3\text{NO}_2$ decomposed at about 233°K according to:



Replacement of Br_2 by iodine gave only I_2O_5 (192). On the other hand, Cl_2 gave NOClO_4 , but not $\text{ClO}_2 \cdot 3\text{NO}_2$.

I. ATOMIC REACTIONS

Chemical reactions in arcs depend on the activation of some gaseous reactant, either a single species (atomic or molecular), which contacts another reactant at a lower temperature, or perhaps the reactants can be premixed and then passed into the discharge tube-reactor.

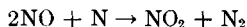
1. Nitrogen Reactions

Nitrogen, when excited in an electric discharge, exhibits greatly increased chemical activity and a yellow glow which persists after the excitation is removed. Spectroscopic investigations of the afterglow have shown that the "active nitrogen" contains atomic and molecular nitrogen in excited states. However, the essential component of active nitrogen is atomic nitrogen (107). Numerous investigations and comprehensive reviews of the physical and chemical behavior of active nitrogen have appeared in the literature (63, 108, 160).

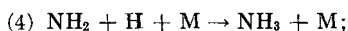
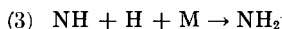
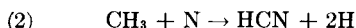
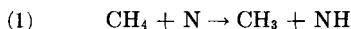
Chemical reactions involving active nitrogen with H_2 , O_2 , and CH_4 have interested numerous investigators. The investigations have sometimes been carried out on the quenched products at liquid helium temperature (4.2°K), where free radicals can be trapped.

The formation of NH_3 from the reaction of nitrogen and hydrogen in an electric discharge at atmospheric pressure was described by Suzuki *et al.* (211, 212). In another investigation, by Steward (201), small amounts of hydrazoic acid were obtained, along with ammonia, in an electric discharge through a mixture of hydrogen and nitrogen.

Reactions of nitrogen and oxygen in electric discharges yield various nitrogen oxides, depending on the system variables. The direct reaction between N_2 and O_2 is an endothermic one. Clyne and Thrush (44) reported the formation of NO from active nitrogen produced in an electric discharge and flowed through a tube in an electric furnace. Oxygen was introduced into the hot zone of the tube through four sealed-in mixing jets, 30 cm apart. The effluent gas indicated the formation of NO. In a different type of electric discharge and under different conditions, Henry (100, 101) reported NO_2 formation. Strutt (208) reported the formation of N_2O_3 in the quenched product from an electric discharge reaction, according to the mechanism:

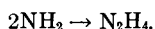


The formation of HCN by decomposition of CH_3OH in the presence of N_2 , N_2 and H_2 , N_2 and NH_3 gave an example of further possible reactions of active nitrogen (161). Cyanogen, $(\text{CN})_2$, was also decomposed in an electric discharge in the presence of N_2 and CH_4 to give HCN and MeCN (95). The reactions of methane, ethane, and acetylene with active nitrogen in an electric discharge were investigated by Zabolotny and Gesser (243). Predominant products of the reaction with C_2H_6 and C_2H_2 were HCN and NH_3 . The reactivity of nitrogen was increased when argon was added to nitrogen in the discharge. Mechanisms for the different reactions were presented, where the NH radical is a primary precursor. In the absence of argon the predominant first-step reactions may be:



in the presence of argon, reactions (1) and (3) compete and reaction (1) is favored at decreased flow rates of nitrogen. Active nitrogen produced in an electrodeless discharge, when passed over a rod of carbon at 800° in presence of H_2 , in slight amounts, formed HCN and NH_3 . The mechanism postulated by Zinman (244) is that active nitrogen became chemisorbed on carbon and perturbed adjacent C-C bonds. Atomic hydrogen then reacted with the chemisorbed CN to form HCN.

The activation of NH_3 and HN_3 in electric discharges offers another source of active nitrogen, and may give hydrazine, N_2H_4 . Jogarao and Sastri (106) used a Siemens ozonizer. Skorokhodov *et al.* (198) proposed a reaction mechanism similar to that of Wiener and Burton (238). The formation of N_2H_4 from NH_3 - HN_3 mixture in an electric discharge was reported by Wannagat and Kohnen (233), consistent with the view that HN_3 is first decomposed to N and NH which either yields N and H or gives NH_3 . The NH formed, on the other hand, reacts with NH_3 to give H_2NNH (N_2H_4). The kinetics of the reaction of NH_3 and HN_3 and N_2H_4 formation in an electric discharge were explored extensively by Rath sack (173) and Gager and Rice (77). More recent work by Hanes and Bair (96) included spectroscopic and kinetic evidence that NH_2 was the primary product in NH_3 discharges. The mechanism for N_2H_4 formation, then, would be:



The formation of silylamine from N_2 and $SiCl_4$ was discussed previously. The rapid quenching of an arc in a discharge vessel is necessary for nitriding metals without damage. An arc between Cd electrodes in a solution of 90% Ar and 10% N_2 at liquid argon temperature produced cadmium nitride, an explosive material at room temperature (70–72°F). The idea was to vaporize the metal so that it can react with the active nitrogen in the arc zone. Knuppel *et al.* (124) discussed the fundamentals, construction, and operation of an arc arrangement used for steel nitridation. Glow nitriding gives higher hardness penetration due to the high concentration of atomic or active nitrogen.

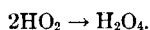
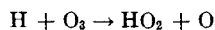
2. Oxygen Reactions

In addition to electric discharge reactions of oxygen with halogens, sulfur, and nitrogen, discussed previously, there are reactions leading to other compounds of long-time interest. For example ozone, O_3 , has been formed in a discharge through oxygen while the discharge tube was immersed in liquid nitrogen, as reported by Briner and Ricca (32). The formation of O_3 is suggested by Schiff (188), on the basis of mass spectrometric arguments, to take place during or after condensation. The effect of impurities in the discharge reactor on the dissociation of oxygen was studied by Kaufman and Kelso (115). A 20% dissociation was attributed to nitrogenous or hydrogenous impurities. Helium, argon, and carbon dioxide were reported to have no effect. The efficiency of hydrogen or nitrogen suggests chainlike sequences of very fast ion-electron reactions. Schemes for ozone production from O_2 in the discharge have been extensively reviewed by a number of investigators (20, 65, 139, 210). One view considers the possibility of low energy paths through O^- ions and at least one excited state of molecular oxygen. Thermal decomposition in the electric discharge becomes increasingly important when heat is not dissipated.

Atomic oxygen from an electric discharge reacts with H_2S at liquid air temperature to give H_2SO_4 (186, 187). In the presence of NH_3 , atomic oxygen gives HNO and NH_3O as products (79, 98).

3. Hydrogen Reactions

The reactions of atomic hydrogen in an electric discharge with O_2 are of interest and rather controversial. H_2O_2 was reported as the product of the quenched reaction in liquid nitrogen of atomic hydrogen and oxygen from an electric discharge (78). Atomic hydrogen, when quenched into liquid ozone at 77°K, reacts to give a superoxide:



according to Kobozev *et al.* (126, 127), but evidence for the existence of HO_2 as an intermediate species was indirect. Arguments, supplemented by esr (electron spin resonance) and X-ray diffraction studies, were reviewed by McGee (152). While HO_2 as a precursor in the reactions leading to H_2O_4 was favored by Livingston *et al.* (136), Giguere and Chin (82) postulated the occlusion of O_2 into H_2O_2 as the major product of the O_2 - H_2 reaction in the discharge, rather than H_2O_4 . Benson (21) has questioned the stability of the H_2O_4 molecule on the basis of bond energy arguments.

Atomic hydrogen produced on a hot tungsten filament in the center of a flask immersed in liquid nitrogen (77°K) can add to various olefins frozen on the walls of the flask. Klein and Sheer (121, 122) reported reactions of atomic hydrogen with propylene, butene-1, isobutene, 3-methylbutene-1, and 2-methylbutene-1 at a reduced pressure of about 30 microns. Analysis of the reaction products, after being warmed to room temperature, indicated that *n*-butane, butene-2, and 3,4-dimethylhexane were formed from atomic hydrogen reactions with butene-1. The mechanism of the reaction is based on formation of *sec*-butyl free radicals which dimerize either in the solid at 77° or during the warm-up to give 3,4-dimethylhexane. The propylene reaction with atomic deuterium established the preparation of propane according to:



More details of the reactions of atomic hydrogen with organic compounds have been given by Steacie (200). Activation of hydrogen in a high-frequency corona discharge was utilized by Coffman (45) in reactions with coal by hydrogenative scission to give a spectrum of compounds ranging from soft resinous materials to gaseous hydrocarbons. A peculiarity of the discharge was that a solid dielectric barrier between the electrodes prevented the transition to an arc discharge. The carbon coal was suspended in a hydrocarbon oil saturated with hydrogen at atmospheric pressure. Although the products were not completely identified, likely products were assumed to include phenols, benzene, xylenes, and naphthalene. Aromatics were possibly formed in the discharge at about 200°C and gaseous hydrocarbons at about 350°C.

The reaction of water with carbon in a microwave-excited discharge was investigated by Walker *et al.* (226). Under the influence of the discharge, water dissociated, and atomic hydrogen and oxygen as well as ions and electrons formed the plasma. The reaction with coal yielded CH_4 , C_2H_2 , CO, and hydrocarbon solids. Methane and C_2H_2 were identified downstream of the discharge zone. Complete reaction of carbon and oxygen at long distances downstream was reported to give CO as a main product.

The reaction of hydrogen molecules, formed by recombination of atomic hydrogen, and CO yielded CH_4 and C_2H_2 and solid hydrocarbons when the mixture was passed through a second discharge.

The formation of CH_4 in a high frequency discharge through a mixture of H_2 and CO_2 was thoroughly investigated by Epple and Apt (61). Effects of the mixture composition, frequency, discharge tube parameters, and power were discussed. The high frequency discharge in this specific case was unique since no other hydrocarbon products were formed as in d.c. discharges. The formation of CO as a precursor was assumed for the reaction mechanism.

Isotope labeling by tritium in an electric arc was reported by Sato *et al.* (184, 185). Stearic acid, used as a biochemical tracer, has been labeled with tritium by means of an electric discharge through a mixture of hydrogen and tritium in the presence of the acid. The electric discharge method has been favored over other methods of tritium labeling, because it yielded higher specific activities and was less destructive than the reactor method. The mechanism proposed involves the primary processes of ionization, excitation, and dissociation of the tritium. Another compound labeled by this same method was α -hydroximinopropionic acid.

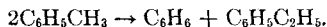
Thermally unstable hydrides have been produced from atomic hydrogen, formed when either hydrogen or hydrocarbons interact with a high current arc of at least 0.1 kw/cc, and elements like B, P, Al, Be, and Si. Silicon hydrides have been prepared from ferrosilicon and atomic hydrogen. Cooling the reaction system often enhanced the formation of the hydrides; water, hydrogen, and even benzene have been used for quenching media (42).

J. REACTIONS OF ORGANIC COMPOUNDS

The utilization of electric discharges for decomposition and/or transformation of organic compounds, alone or in the presence of other reactants, constitutes one of the major industrial activities in the application of electric discharges in chemical processes. The voluminous literature and the large number of industrial patents on hydrocarbon cracking and acetylene synthesis cannot be completely covered in this chapter.

The behavior of several aromatic compounds in a glow discharge at low temperatures and pressures was described by Boelhouwer and Waterman (25). An electric discharge tube fitted with two aluminum electrodes at 30–40-cm separation, a potential difference of 1500–3000 volts, and a current of 20–50 ma at 50 cycles/sec were used. The formation of biphenyl from benzene, bibenzyl from toluene, phenylbutane from ethyl benzene, 2,3-diphenylbutane from isopropylbenzene, 2,2-dimethylbibenzyl from *o*-xylene, and 4,4-dimethylbibenzyl from *p*-xylene were reported. Streit-

wieser and Ward (205) investigated the reactions of toluene in the presence of helium in a microwave discharge. The reaction products were mainly benzene and the C_8 hydrocarbons ethylbenzene, styrene, and phenylacetylene. The suggested mechanism was represented by:



Styrene and phenylacetylene were assumed to be further products from excited ethylbenzene. The reaction of *o*-xylene in a helium carrier formed benzene, toluene, ethylbenzene, *p*- and *m*-xylene, and 1-methyl-2-ethylbenzene. Other organic compounds reacted were cycloheptatriene and bicycloheptadiene. They showed cracking patterns similar to that of toluene. These investigators compared the conversion of a number of aromatic and aliphatic compounds under similar conditions, and reported a conversion of 5–60% for the former and 1–3% for the latter. Their conclusion was that the main method of energy transfer was by electron capture; they excluded photolysis. The electron capture mechanism was consistent with the greater reactivity of compounds having extensive π -electron networks.

Miller (157–159) in a series of experiments subjected a mixture of CH_4 , NH_3 , H_2O , and H_2 (which he referred to as the constituents possibly making up the atmosphere of the earth in its early stages) to spark and silent discharges for about a week. Formation of CO , CO_2 , and N_2 was confirmed. Other products, including polymers, were also formed. The separated fractions were characterized as acidic, basic, and ampholytic. Several amino acids such as glycine, DL-alanine, β -alanine, and others were identified. Most of the acid fraction was made up of DL-lactic acid, acetic acid, and propionic acid. Direct products of the discharge included HCN and aldehydes. The relation of the investigations to the formation of the earth and the origin of life is discussed. Miller argued the possible synthesis of these products if the earth had such a reducing atmosphere in the presence of ultraviolet light and electric discharges. The mechanisms of the reactions which led to these products through the primary formation of HCN and aldehydes are discussed.

K. METAL OXIDES

The oxides BeO and M_2O_3 , either in mixtures or in the form of small rods, have been fused in a d.c. carbon arc to give ternary solid solutions. $BeO \cdot Cr_2O_3$ and $BeO \cdot Al_2O_3$ are examples where a continuous series of solid solutions was obtained in a discharge reaction. Compound formation has been reported (236) between BeO and B_2O_3 , Ga_2O_3 , Y_2O_3 , and La_2O_3 , but no reactions of BeO were observed with Sc_2O_3 , In_2O_3 , or Fe_2O_3 .

Refractory oxides, such as Fe_3O_4 , NiO , CaO , Cr_2O_3 , CoCr_2O_4 , and MgCr_2O_4 , have been easily melted in arcs between an electrode of the refractory oxide and carbon electrode, since they all show increasing conductivity with increasing temperature. In certain cases it is necessary to preheat the oxide in a tubular furnace at $700\text{--}800^\circ$. The method is not applicable to oxides of very low electrical conductivity, such as Al_2O_3 and MgO (36). Arc-melted oxide refractories for the glass and steel industries are available commercially (123).

Fischer and Ilievici (67-69) reported a series of submerged arc experiments in which the electrode material had chemically combined with liquid air, O_2 , N_2 , or argon. Using metal electrodes in liquid argon containing some O_2 and N_2 impurities, they obtained solid products including the metal, the oxide, and the nitride. Sn, Zn, and Mn gave such products, but Ti, Pb, Sb, and Bi gave only small amounts of their nitrides.

L. RARE GAS REACTIONS

The early impression, based on a few experiments plus semitheoretical views about the stability of filled octet configurations, convinced scientists over the past 50 years that the "rare gases" were extremely unreactive. This led to the alternate name of "inert gases," and relatively few attempts were made to bring about chemical reactions of these gases prior to 1962. In spite of the presumed unfavorable electronic structure of these atoms and the general conviction that they were inert, certain instances of compound formation have been reported for many years. However, the products prepared and the conditions necessary for their formation are unusual for those not familiar with the behavior of matter under high temperature-high pressure conditions, and it is dangerous to state categorically that none of the older work on rare gas compounds is significant, although X-ray diffraction, optical and mass spectroscopy, and similar analytical tools were not used in the "proofs" of composition and/or structure.

Formation of rare gas compounds under excited conditions has been successful in the case of helium, xenon, and krypton. In helium a condition of chemical reactivity is provided by unpairing the $1s$ electrons and promotion to the $2s$ state. This process, which requires about 20 ev/gm mole (approximately 460 kcal), can be realized in electric discharges and by electron bombardment. It had been reasoned by Morrison (163) that He in its electronically excited state, 2^3S , should not be chemically different from hydrogen and hence a similar chemical behavior can be expected. Examples of bonds involving helium include species such as He_2^+ , $(\text{HeH})^+$, and $(\text{HeH}_2)^+$ which have been established from band spectra produced in discharge tubes.

The first attempt to combine helium with other compounds was reported by Berthelot (23), who claimed success with benzene and carbon disulfide. Manley (143-145) claimed the formation of a stable compound with mercury, HgHe_{10} , in a glow discharge. Electron bombardment of tungsten in an atmosphere of helium reportedly gave a tungsten helide WHe_2 (34). Evidence for the formation of helides of bismuth, thallium, indium, zinc, sodium, potassium, rubidium, platinum, palladium, iron, uranium, iodine, sulfur, and phosphorus has been presented by Broomer (34) and Krefft and Rompe (129). On the other hand, Thomson (221) found no reaction between helium and phosphorus in electrodeless discharges. Certain metals, when employed as electrodes in discharge tubes containing inert gases, appear to absorb essentially stoichiometric quantities of these gases and thereby have their densities decreased and their solubilities in acids altered. Compounds of approximate formulas such as Pt_3He , FeHe , PdHe , and BeHe are among the relatively stable compounds reported by Damianovich *et al.* (50-52).

Berthelot attempted the fixation of argon with a variety of organic compounds by subjecting the mixture to a silent discharge (22, 24). Positive evidence of fixation was claimed with benzene and CS_2 , but not with C_2H_2 , F_2 , C_2H_4 , and others. The view that argon entered into a chemical bond with these compounds was opposed by the argument that it is not unlikely to have argon ions acting as clustering centers, and that upon ion recombination the heavier gases escape with difficulty from the neutralized cluster (134). Complete recovery of argon from cuprene, for example, was effected by heating.

While the combination of fluorine with argon or with helium (22, 24) in an electric discharge was not accomplished by early investigators, the fluorides of xenon and krypton have recently been synthesized in electric discharges. Grosse *et al.* (91) synthesized krypton tetrafluoride in an electric discharge through krypton and fluorine. The discharge was maintained through a mixture of 1 volume of Kr and 2 volumes of F_2 at liquid air temperature and a reduced pressure of 10 mm Hg. These workers (91) also prepared XeF_4 and xenon oxyfluoride in the same manner (206): OF_2 was used as a source of oxygen and fluorine in the case of the oxyfluorides. Antropoff *et al.* (12, 13) investigated the reactions of Kr with Cl_2 , and Kr with Br_2 . They collected products, condensed at liquid air temperature, which were thought to be krypton halides, but unequivocal identification of the products was not accomplished.

It would appear that some very interesting and challenging "detective" work remains before the real "chemistry" of the rare gases can be fully recorded. Much of this work will involve electric arcs.

III. Chemical Reactions in Plasma Jet Reactors and High Intensity Arcs

A. GENERAL

The possibilities for chemical processes in a plasma jet have been of special interest since the advent of commercially available arc plasma-generating equipment several years ago. The high temperature decomposition of compounds to form the elements, the formation of endothermic compounds by either direct synthesis or decomposition, or the formation of free radicals to act as intermediates in subsequent reactions suggests the range of possible types of "plasma chemistry" and shows why plasma generators have definitely stimulated the study of high temperature reactions.

At the very high temperatures attainable in a plasma reactor (5000–20,000°K) the common species are electrons, ions, and neutrals with high kinetic energies. The new environment and special parameters characteristic of the plasma state make plasma chemistry different from conventional chemistry. Whereas ordinary chemical experience suggests that often simple substances become increasingly reactive and form compounds at higher temperatures, a temperature limit is reached at which this trend reverses and even strong interatomic bonds cease to form spontaneously. Atoms in highly excited states have some of their outer electrons in higher energy levels, thus altering the familiar physical properties and chemical behavior of the atom. Such excited atoms should react to give compounds not likely to be formed under conventional conditions.

Before predictions can be reliably made about reactions and the possibilities of chemical synthesis, many careful studies of well-defined systems will be required. Unfortunately, such analytical studies are seriously hampered by many obstacles. The experimental conditions in plasma reactors are difficult to define. Detailed knowledge of high temperature properties of many atoms, molecules, and most free radicals, and especially negative ions, is meager. In many cases thermodynamic and kinetic data have not been available. Currently research activities in the synthesis of compounds from their elements or from simpler compounds lie largely in the field of organic chemistry, especially where a reasonable amount of thermodynamic and kinetic data have been available from other studies. Among the systems of practical importance being investigated in plasma jet reactors are the acetylene synthesis, methane and nitrogen reactions, and NH_3 , H_2 , and N_2 reactions.

The products from plasma reactions are limited by the various complicated processes which take place in the reactor. As expected, one finds that the energy input, the temperature of the reaction mixture, the speed of

mixing between the plasma gas and the reactive substances, the residence time of the reactant in the hot stream, and the rate and point of quenching are among the critical variables that have to be considered. The importance of these variables is obvious from the fact that formation of products can take place only in three principal steps: (1) decomposition of the reactant molecules and/or activation of atoms and free radicals; (2) recombination between the interacting species to give certain products; (3) freezing out the chemical equilibrium system in the reactor by quenching.

At plasma jet temperatures all compounds have positive free energies of formation (204). Hence, an empirical method can be set up to detect whether a certain compound should be formed under certain operating conditions. The temperatures at which $\Delta F^\circ = 0$ give an indication of the ease of formation. Although plasma research activities reported in the literature are limited and preliminary and additional work is still needed to optimize the use of confined plasma jets to effect chemical synthesis, one can use the limited information for further exploration.

The approach to synthesis problems in plasma jet reactors deserves careful attention. The production of desirable end products must involve more than merely trapping the produced species. Two main points should be considered (150):

(1) The change in the path of the thermodynamic state of the system from plasma jet conditions to ambient conditions should be controlled. This is necessary so that the normal ambient conditions are kinetically suppressed in favor of recombination reactions leading to the desirable metastable products. As previously mentioned, this can be accomplished by letting the reactants expand through a nozzle, by quenching through contact with a cold surface, by injecting a cold inert medium, or by a combination of all.

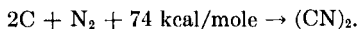
(2) The interaction between excited species produced in the plasma jet and an independently introduced reactive material is favored by spraying a reactive liquid or solid into the jet, dispersal of the jet gases through the reactants, fluidizing the solid with the jet gases, or transpiration cooling of an expansion nozzle with a reacting liquid. The choice of the technique depends on the specific case under consideration.

Marynowski *et al.* (150) reviewed the various aspects of current research in plasma jet synthesis, using a relatively simple system (H-C-N) for thermodynamic analysis as an illustrative example of a chemical system at plasma jet conditions. The importance of this specific system is perceivable because it involves the commercial processes for HCN, C_2H_2 , and $(CN)_2$ synthesis. The predictions made in these calculations were concerned with HCN from elemental N_2 and CH_4 and similar systems.

B. SYNTHESSES IN PLASMA JET GENERATORS

1. Cyanogen (C_2N_2)

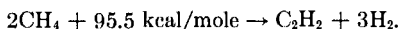
The preparation of cyanogen (C_2N_2) from its elements is an endothermic reaction:



Nitrogen has been used as the plasma gas (204) or else injected into the plasma jet of argon (88). Carbon was either vaporized from a graphite cathode or fed into the plasma downstream as a powder fluidized in nitrogen. Both methods gave conversions up to 15% based on carbon consumption. Unreacted carbon was condensed in the reactor while cyanogen gas was collected in traps cooled with dry ice. Fast quenching of the hot gas stream on a cold finger inserted into the plasma, a few inches from the nozzle exit, reduced the yield compared to that obtained without quenching. A temperature above 4000°C in the reactor was assumed because of the vaporization of the carbon. The residence time in the plasma jet stream was calculated to be of the order of 5–50 milliseconds.

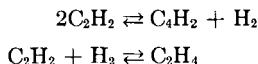
2. Acetylene (C_2H_2)

The preparation of acetylene (C_2H_2) in electric discharges has been of industrial interest, and the use of plasma jets for the study of this reaction was suggested by various workers (7, 132). Leutner and Stokes (132) produced acetylene by feeding methane into the jet of an argon plasma. The endothermic reaction is:



Runs at residence times of about 0.5 millisecond gave an acetylene yield of about 80%, but less than 10% of the original methane was unreacted with an average calculated plasma jet temperature of the order of 12,000°K.

A thorough analytical study of the decomposition of methane, assuming the formation of acetylene and also the following reactions:



was carried out by Anderson and Case (7). Their analytical treatment seemed to show good agreement with the experimental results for H_2 as a plasma gas. The yield of acetylene in this case was reduced by formation of diacetylene (5% of acetylene) and ethylene (5% of acetylene). The kinetic analysis indicated that a relatively high yield of acetylene (but at least 10% unreacted methane) could be produced at a final temperature

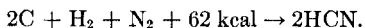
for the reaction mixture of the order of 1500–1800°K, with contact times in the range 0.2–5 milliseconds, and this has been confirmed by experiment. On the other hand, the yield for optimum cracking as indicated by the analysis was of the order of 80% acetylene, while the concentration of acetylene in the product gas was estimated as 16%. This agrees with the experimental results of 76% and 15%, respectively.

Although the analytical approach used by Anderson and Case is not general, it gives an indication of the valuable information one can get from such analytical studies based on thermodynamic and kinetic data.

The synthesis of acetylene directly from the elements was reported by Grosse *et al.* (88). Workers at the United States Bureau of Mines, Pittsburgh, Pennsylvania (37), reported the synthesis of C₂H₂ along with CH₄ from bituminous coal heated with a plasma torch, using argon as the plasma gas. The use of various reactive gases such as N₂, H₂, or Cl₂ was also proposed.

3. Other Nitrogen Compounds

a. *Hydrogen Cyanide (HCN)*. The synthesis of hydrogen cyanide in a plasma jet was investigated by Grosse *et al.* (88). The formation of gaseous HCN from the elements is also endothermic according to:



The synthesis was carried out by using compounds of carbon, hydrogen, and nitrogen, such as CH₄ and NH₃, as well as from the pure elements in different ratios.

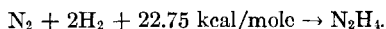
The data presented by these workers show that the highest yield of HCN was obtained when the elements were used as the starting materials. Hydrogen gas was fed into the plasma jet of nitrogen from a plasma generator with graphite as an electrode. A conversion of more than 50% to HCN, based on carbon, was reported. Acetylene was the only significant by-product. Replacement of hydrogen with ammonia gave similar results, since the NH₃ decomposed quantitatively into N₂ and H₂ in the plasma stream. Higher yields of C₂H₂ were obtained when CH₄ was used as a source of hydrogen and carbon. With NH₃ and CH₄ in an argon plasma, the conversion of the reactants into HCN and C₂H₂, based on carbon input, was 60–75%.

An important parameter in all of these experiments was the rate of quenching. For example, more C₂H₂ was recovered, in preference to HCN, at the faster quenching rates, as expected from thermodynamics since acetylene is a more endothermic compound than HCN. However, one must consider variations of the quenching rate with other experimental factors, such as the power input, the plasma gas flow, the feeding rates of the

reactive gases, and the specific quenching method used. Detailed investigations of this type have not been performed.

b. Nitrogen Fixation as NO and NO₂. The use of nitrogen as a plasma gas suggests the possibility of other fixation reactions besides formation of hydrogen cyanide or C₂N₂. One can form oxides of nitrogen under excellent operational conditions, since the plasma jet can provide the high temperatures and yet allow operation at high pressures of the order of 300–400 psia so that expansion cooling is possible (172). N₂ is used as the plasma gas, and O₂ is mixed with the plasma in a confined chamber adjacent to the device. A residence time in the hot zone of 1×10^{-3} second is allowed before passing the mixture through a deLaval nozzle to cool by expansion. So far little experimental work has been done, although Grosse *et al.* (88) formed small amounts of NO by feeding O₂ in the stoichiometric ratio into a nitrogen plasma. Additional experiments on other mixtures of oxygen and nitrogen did not improve the yield. On the other hand, NO and NO₂ have been prepared with air as the plasma gas in radiofrequency plasma jets at reduced pressure.

c. Nitrogen-Hydrogen Reactions. Hydrazine, a slightly endothermic compound, was obtained in small yield by direct reaction of hydrogen and nitrogen in the plasma jet according to:



The reaction failed to give NH₃, an exothermic compound (88).

d. Nitrides. Metal nitrides of titanium and magnesium were prepared in the plasma jet with little difficulty (204). Titanium powder fed at the rate of 1.72 gm/min into a nitrogen plasma gave lustrous crystals of titanium nitride (TiN) in a yield of about 30%. Magnesium nitride Mg₃N₂ was also prepared in a similar manner, with a higher yield of about 40%. A great deal of care was required in handling the Mg₃N₂ to minimize reaction with moisture from the air.

AlN has been predicted as a by-product in a nitrogen fixation reaction by Marynowski *et al.* (150), according to the following reaction:



NO could be converted into HNO₃ by quenching the gas stream with a spray of H₂O, and the nitride might be hydrolyzed to produce some NH₃ (although a protective oxide film would minimize the yield) or used as a refractory.

4. NiO_{1+x}

Various nickel compounds have been sprayed through an argon plasma jet diluted with O₂ to yield nickel fumes, a mixture of finely divided Ni

and Ni oxide (194). $\text{Ni}(\text{CO})_4$ maintained in an inert atmosphere or vacuum to prevent decomposition gave Ni fumes with surface areas of 36–91 m^2/gm , depending on the point of injection and location of the quenching surface on which the fume was collected. At low rates of plasma gas flow, NiO was favored in the product due to more efficient contact. Particle sizes of the nickel fume with area 150 m^2/gm were 30–300 Å. The stoichiometry of the oxide of excess oxygen content was found to be $\text{NiO}_{1.003}$.

5. Aluminum from Alumina

Preliminary investigations of reduction reactions in the plasma jet were made by Grosse *et al.* (88). They attempted to reduce aluminum oxide by passing it through a plasma jet. Because of the exothermic nature of this compound, a high rate of quenching is required so that recombination of the elements will not occur at a high rate. H_2 and methane were used as the alumina powder carrier as well as the source of the reducing action. In spite of fast quenching of the reaction in the plasma stream, only a very poor yield of aluminum was collected.

6. Synthesis of Hexachlorobenzene

Kanaan and Margrave synthesized hexachlorobenzene from CCl_4 (114). CCl_4 vapor carried by argon was introduced into a water-cooled quartz reactor confining a plasma jet. The plasma stream at the nozzle exit was at an estimated temperature of 6000°K. CCl_4 under the influence of the hot gas stream and intense radiation from the plasma jet suffered decomposition into transient species, which on cooling gave rise to a yellow-brown deposit on the reactor walls. Along with this deposit, chlorine gas was liberated as identified by its odor in the exhaust gas. The brown deposit was soluble in CCl_4 . Vacuum distillation and sublimation of the residue gave colorless needlelike crystals. Elemental analysis, X-ray powder pattern, infrared spectrum, and melting point (226–228°C) of this crystalline product confirmed its identity as hexachlorobenzene (C_6Cl_6). The formation of hexachlorobenzene from CCl_4 may be explained by a free radical mechanism, in which the parent compound is assumed to be stripped of its chlorine atoms, stepwise, and then the fragments (CCl , CCl_2) undergo dimerization and polymerization. There is also evidence for C_2Cl_4 formation in a radio-frequency plasma device.

C. CHEMICAL PROCESSES IN THE HIGH INTENSITY ARC

The unique property of the high intensity arc is the rapid and efficient vaporization of the electrode material, which makes it possible to process refractories and ores incorporated into a matrix with a reducing agent and used as a consumable electrode. An advantage of this technique is that

reactions can be performed without contacting any furnace or reactor walls. Reduction in an inert atmosphere or in a vacuum, halogenation, and oxidation are possible applications. At the high temperatures developed in the arc plasma, the reactions occur in the gas phase even with the most refractory materials, and an ideal configuration for quick quenching, to freeze an equilibrium which may be favorable at high temperatures, is provided in the tail flame of the arc. Most applications of this type of arc at present are for metallurgical processes on account of the high power requirements, but the potentiality of this tool in chemical synthesis should not be overlooked. A few examples of the reported work in this area are summarized here.

Fine fumes of silica (SiO_2) (30–40 $\text{m}\mu$ in diameter) were formed from silica incorporated in a carbon anode (80% silica and 20% carbon). The ions in the vapor provide high efficiency centers for nucleation (225).

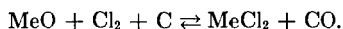
Separation of various constituents of an ore has been possible, where the volatilities of the various constituents were different. Phosphorus and selenium have been distilled from their ores by vaporization and interposition of a dust filter in the arc effluent stream at a point where the temperature in the tail flame was below that of the condensation point for the more refractory constituent, but still high enough to maintain phosphorus or selenium in the vapor. The latter were then condensed at lower temperatures downstream (225).

Decomposition of complex oxides into simpler oxides by sublimation in the arc was reported by workers at the Vitro Laboratories (225). For example, metal silicates, MeSiO_3 , were decomposed in the arc open to air into the metal oxide and silica:



By rapid condensation the two oxides had not time to recombine and form the original ternary oxide. Decomposition of rhodonite to give MnO and SiO_2 was reported by Harris *et al.* (97).

If the arc is run in a reactive atmosphere, chlorine for example, a metal oxide may react to form the metal halide and CO ;



Vapor phase reduction of MgO with carbon in the tail flame of the intensity arc has been reported by Korman and Sheer (120). Thermodynamic calculations showed that the reduction should be complete at temperatures above 1800°C , and the lowest recorded temperature in the tail flame, about 2000°C , favors such a reaction. Removal of oxygen by carbon is also favored by the formation of the very stable CO at the high temperature in the tail. The main problem of carbothermic reduction is to

conduct the reaction at a sufficiently high temperature to allow reduction to proceed to a favorable equilibrium point, and then to inhibit or at least minimize back-reaction by providing appropriate conditions of cooling.

Acetylene was synthesized in a high intensity arc from carbon and H_2 and from methane; Baddour and Iwasyk (16) obtained a yield of 25.5% from the first reactants and a yield of 52% from methane. Conversion of CF_4 into C_2F_4 and other by-products, such as C_2F_6 and C_3F_8 , was also reported in a high intensity arc. The proposed mechanism involves formation of C_2F_2 as an intermediate, which reacts with free fluorine atoms to give C_2F_4 . A yield of 64% C_2F_4 was recently reported (17) from an arc powered by 25 kw, a reactant flow of 25 cc/sec, and reactor pressure of 0.5 atmosphere.

IV. Miscellaneous Applications of Electric Discharge Devices

The importance of plasma-generating devices in modern technology is not restricted to chemical reactions involving new methods of synthesizing known compounds or unique methods of synthesizing new chemicals, but extends to several other areas of research. For example, several processes that can be performed in an electric furnace, a solar furnace, or a thermite process can be better performed in the plasma jet, where inert gases are used and even higher temperatures and more efficient heat exchange are attained.

A. PURIFICATION OF METALS

In metallurgy several scarce materials can often be separated from their ores in fairly high purity by means of electric discharge devices, as discussed earlier. Use of a controlled atmosphere permits isolation of even chemically reactive substances. The high temperatures attained in certain plasma-generating devices allow melting of high melting-point refractories. Beall *et al.* (19), in a study of melting by the consumable electric arc, reported the melting of Zr. The method involves the compaction, sintering, and/or welding of an electrode of the material to be melted. This electrode serves as the electric conductor from which the arc is struck to additional metal contained in a water-cooled cup or vessel. Molybdenum was fused in both vacuum and argon atmospheres in a.c. and d.c. arcs operated at optimum currents of 1.1–1.3 kiloamperes at 20–35 volts. The metal ore was used as the consumable electrode (207). Melting of molybdenum in an arc furnace, without the problem of oxidation which arose when Mo was fused in a ceramic crucible, was described by Stroev *et al.* (207). Repeated fusion at reduced pressures was reported to yield the metal with an oxygen content of about 0.001%. A review of arc melting processes for refractory metals is given by Moss (164). A further metallurgical application is the

alloying of metals in the vapor phase by vaporizing the metals individually and allowing them to condense in appropriate order. Alloys of Ti and of Zr with other metals have been made by using the oxide or carbide of these metals with the carbide or oxide of the alloying agent. Powder of the appropriate composition was pressed into the shape of rods and used in electric furnaces as electrodes. Alloying ingredients specified were Mo, W, Ni, Cr, Al, and Mn (156).

B. COATINGS

Coatings of organic and inorganic materials, regardless of their melting point, on substrate materials of various shapes have been successfully applied by arc spraying techniques. For example, coatings applied with plasma jet generators have been used to improve thermal resistance and abrasion resistance and to prevent erosion of the coated piece. The coating material is melted in the jet of the plasma torch and deposited by spraying on the surface to be coated. Usually the coating substance is fed into the plasma stream as a powder, rod, or wire, and impacts in a molten state onto the part to be coated, to form a high-density, uniform, and well-bonded coating. The coating bond is mechanical rather than chemical, and the particle size, gas velocity, melting point and thermodynamic properties of the coating substance are among the variables to be considered for a good coating. In using a mixture of powders, simultaneously applied, the particle sizes should be chosen so that heat capacity per particle is as balanced as possible. Nearly any substance that does not decompose at the high temperature of the plasma jet can be applied. Thermal Dynamics, Inc. has claimed the formation of coatings of a wide variety of pure metallic refractories, chemically inert ceramics, and glass. For example, coatings of tungsten, tantalum, molybdenum, palladium, platinum, aluminum, copper, nickel, chromium, refractory oxides, carbides and borides of niobium, titanium, zirconium, hafnium, and others are mentioned (222b). Plasmadyne has claimed the possible application of coatings of low-melting organic materials like penton, nylon, Teflon, and most epoxies by plasma spraying on a base material without the requirement of a furnace curing cycle.

Coatings of materials usually considered stable and resistant to chemical reactions were found to undergo unexpected changes when a plasma jet was used. Davis (56) reported that a coating of BeO applied with a nitrogen plasma contained 15% BeN and a complex Be-O-N compound. Carbides of refractory metals required certain depositing conditions, and analysis revealed less free carbon than in the sprayed powder. Coatings of thickness 0.001–0.375 inch were obtained. Use of surfacing alloys in powder form furnishes a means of altering the composition of alloy coatings to suit cer-

tain requirements without restriction to the form in which the material is available.

For fabricating simple shapes from the most refractory materials, one can spray powdered tungsten, molybdenum, hafnium oxides, hafnium carbide, etc. onto a mandrel of the desired configuration. Levinstein *et al.* (133) reported coatings of wall thickness of 0.01–0.06 inch as compared

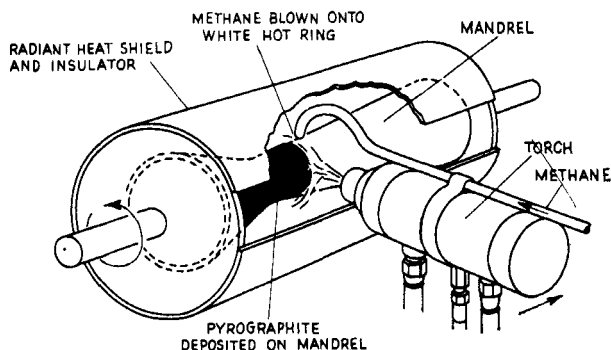


Fig. 18. Pyrographite coating by a plasma jet (218).

with 0.125 inch by other processes. A discussion of this application of plasma jet devices is presented by Walton (227). Pyrographite was deposited in this manner by passing heated methane or propane from a plasma reactor over a hot mandrel of the desired shape (222a). As the gas broke down the carbon was deposited on the hot mandrel surface and the hydrogen passed off, as illustrated in Fig. 18.

C. CRYSTAL GROWTH

The induction-coupled plasma torch has a number of desirable features for growing crystals. For example, the torch may be operated with inert, oxidizing, or reducing atmospheres. Sapphire crystals were grown by Reed (176) in an argon plasma. Peed was also able to grow single crystals of stabilized zirconia for the first time by means of this device. Rubies have been prepared in an electric arc, described by Kuan Hsuing Ch'en (130). An electric arc was produced between two horizontally placed graphite electrodes, 0.5 cm in diameter and 20 cm long. A third vertical electrode, 1 cm in diameter and 10 cm long with a central hole 2 mm in diameter, was in contact with one of the two horizontal electrodes. Al_2O_3 powder containing 2.5% Cr_2O_3 was dropped through the hole of the vertical electrode into the arc plasma, and translucent rubies of 1–1.5 carats were obtained.

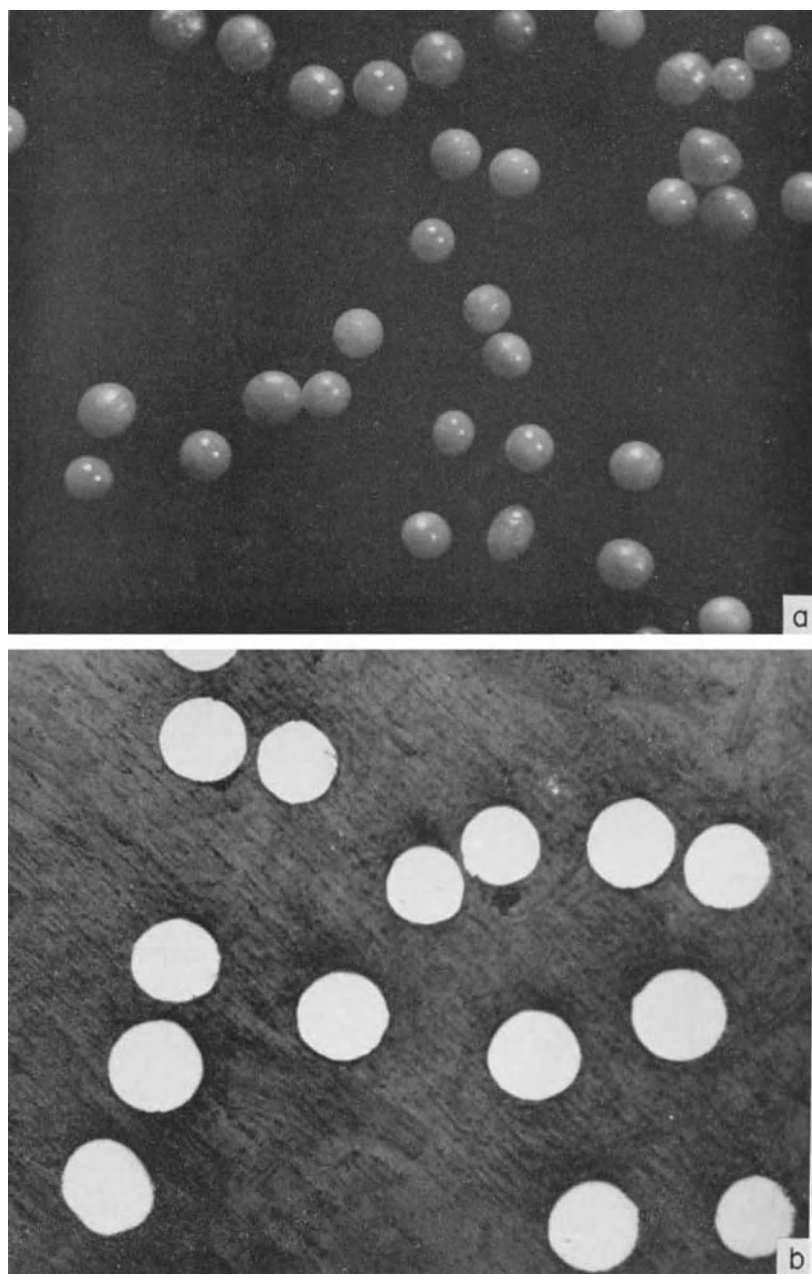


FIG. 19. Particles of zirconia (a) and tungsten (b) spheroidized by the plasma jet processes (219).

D. SPHEROIDIZING

Refractories have been spheroidized in the plasma jet into uniform spheres of various sizes. Spheres of refractories (m.p. 2100–3200°C) as small as 100–150 μ in diameter were reported to be formed in a plasma jet operating at temperatures of 16,500–2700°C and a jet velocity of 100–500 ft/sec (153). The different sizes and typical uniformity of some of these spheres are shown in Fig. 19.

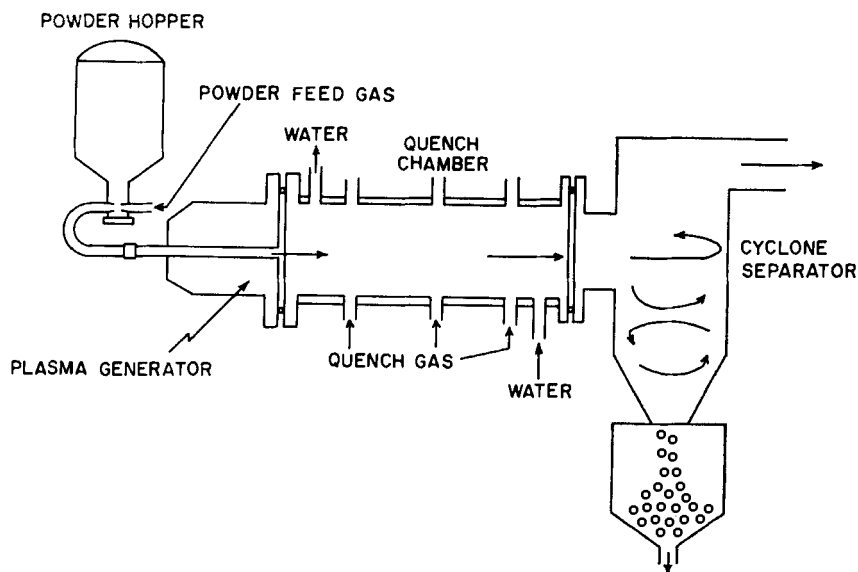


Fig. 20. Spheroidizing process by the plasma jet (153).

The equipment required for refractory spheroidization includes a powder feeder chopper, controlled by the rate of gas feed, and a quenching chamber consisting of a water-cooled reaction tube bolted to the plasma

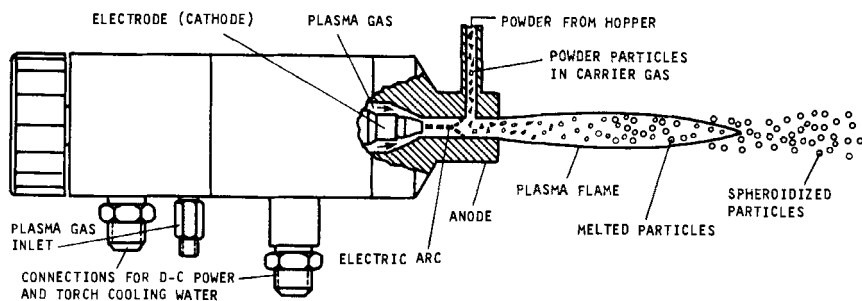


Fig. 21. Spheroidizing apparatus by the plasma jet process (219).

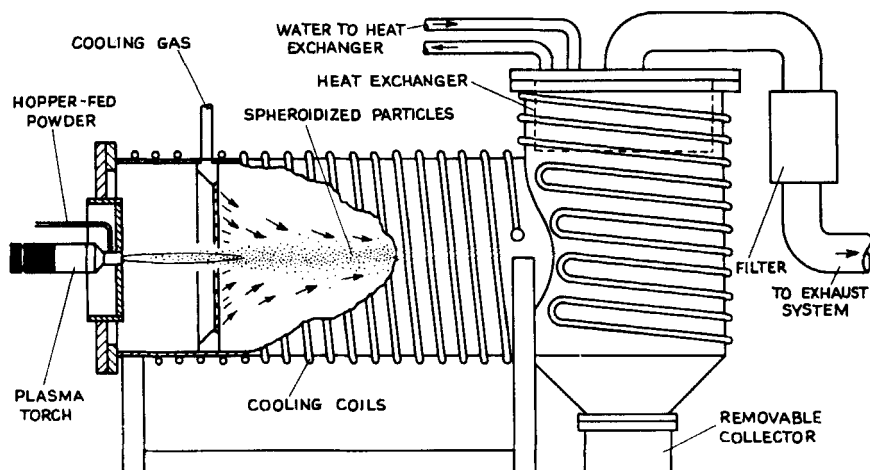


FIG. 22. Spheroidizing apparatus by the plasma jet process (219).

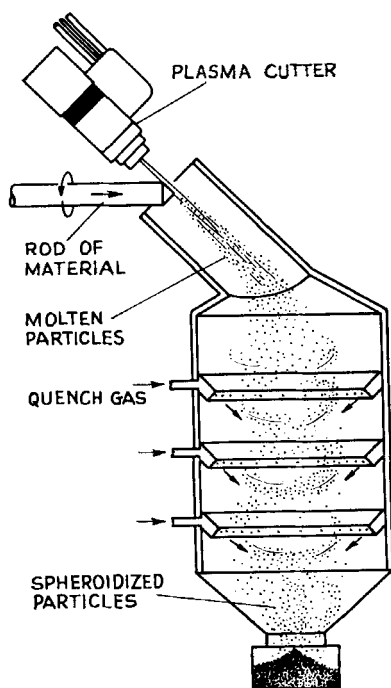


FIG. 23. Spheroidizing apparatus by the plasma jet process (220).

generator by means of flanges and joints. The quenching chamber should be gastight and provided with ports for observation and entry of the quenching fluid at different locations along the axis. The spheres formed may be collected and separated into various sizes with a cyclone separator. Figures 20–23 show arrangements for spheroidization marketed by Plasma-dyne (153) and by Thermal Dynamics, Inc. (219, 220).

E. METAL SUSPENSIONS

The preparation of suspensions of various metals in solutions has been considered as a method for arc utilization in process chemistry. An arc is usually formed by touching two wires of the metal under a liquid and then separating the electrodes slightly to provide the necessary potential drop for a stable arc. An ordinary 110-volt power supply of 10–15 amperes and a resistance of approximately 100 ohms in series form the simple electric circuit for this process. A potential difference of the order of 20–25 volts, depending on the metal of the electrodes, is expected. Quenching of the metal vapor in the liquid results in the formation of the suspension (49).

Extreme reaction conditions can possibly be maintained by subjecting to a spark discharge mists of solid particles (metals or nonmetals having suitable grain size and structure) with liquid or molten organic or inorganic compounds, in mixtures or solutions. The high temperature supplied by the discharge and rapid cooling by the surrounding liquid provide quenching in a minimum reaction time. Partially chlorinated silanes were reported to be formed from Si in halohydrocarbon liquids (117).

The preparation of cadmium niobate ($\text{Cd}_2\text{Nb}_2\text{O}_7$) is another example of spark synthesis in solutions. An anodic spark of Cd in a niobate solution, after distilling to saturation at 650°C, left crystals of $\text{Cd}_2\text{Nb}_2\text{O}_7$ in the solution (154).

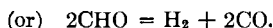
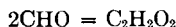
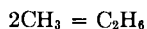
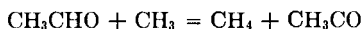
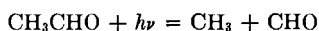
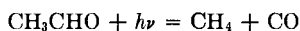
F. SPECTROCHEMICAL ANALYSIS

Electric discharge devices have long been used as spectroscopic sources, and there are many textbooks in this area. However, the recent development of the plasma jet requires special attention. The plasma jet has proved to be an energetic source of radiation, which may be utilized for excitation of various substances to high energy states. An interesting application was the excitation of solutions and use of the spectra obtained for accurate quantitative spectral analysis. The conventional plasma torch can be modified for such studies, and examples of these modifications have been reported. To illustrate, Co_2O_3 powder and graphite were fed into a cup-shaped electrode (125) in one case. A transfer-type arc with tungsten as an external yet integral cathodic electrode was operated in another case (167), where the sample was sprayed into the discharge zone. As the jet emerged from

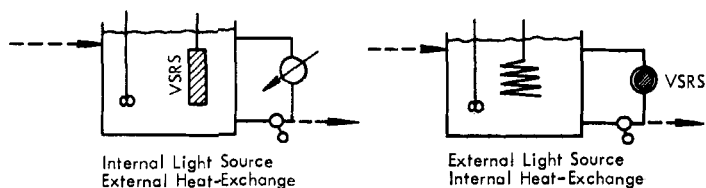
the cathode, it contacted the tungsten rod to which the electric path was transferred. The sample was sprayed into the jet from an atomizer. While helium was used as the plasma gas, argon was used in the atomizer assembly to carry the solution. Precise analyses of various metallic species in solution were obtained by a device described by Margoshes and Scriber (162). Their results for the analysis of Cr, Fe, and Ni in stainless steel proved to be more satisfactory than other conventional methods. A detailed description of the structure of the plasma generator is given in the original paper. (See Figure 6.)

G. PHOTOLYSIS STUDIES

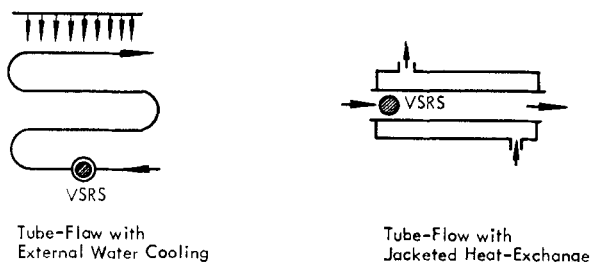
The use of electric discharges as radiation sources to induce photochemical reactions is not new, but most types of radiation sources have been limited either in intensity or in the spectral region of radiation. The mercury-arc lamp, Xe-arc lamp, and hydrogen lamp are familiar examples. The spark discharge and the plasma jet have recently been used as radiation sources for photochemical applications. Marcus *et al.* (148) reported the use of a spark discharge as a source of monochromatic radiation for photolysis. They described a spark discharge between magnesium electrodes in a low pressure tube. A 10-microfarad capacitor was discharged at 200,000 volts. The characteristic light of the spark emitted intense radiation at 2800 Å. Use of the spark in the photolysis of acetaldehyde was studied and the products (CO, H₂, CH₄, and C₂H₆) were identified. The suggested mechanism involved the formation of CH₃, which dimerized to give C₂H₆ at temperatures above 100°C:



The plasma jet was proposed by Damon and White (55) to be used to promote photochemical and photosensitized reactions, such as oxidation, reduction, polymerization, decomposition, or combination reactions. The controlled chlorination of CH₄, the oxidation of cyclohexane to nylon intermediates and of acetaldehyde to acetic acid, the reduction of propane to methane, ethane, and ethylene, and the polymerization of ethylene, propylene, etc. to polyolefins are a few examples. Figure 24 (55) shows schematically some suggested arrangements for using plasma reactors in photochemical reactions.



BATCH OR TANK-FLOW REACTORS



TUBULAR FLOW REACTORS

FIG. 24. Schematic illustrations of a few ways to adapt the plasma jet to photolysis reactors (55); VSRS = very strong radiation source (plasma jet).

V. Some Proposed Applications of Plasma Devices

Chemical processing in plasma jet reactors is still in its infancy. Few studies of organic and inorganic reactions have been made so far, but the unique potentiality of this device should not be ignored because of the limited work reported. The producers of plasma devices are eager to find and exploit chemical applications. For example, Damon and White (53, 54) have surveyed several potential plasma arc reactions and proposed chemical processes in plasma reactors of interest in inorganic and organic synthesis. The following are but a few of their proposed systems worthy of investigation.

Organic Reactions:

1. Acrylonitrile from C_2H_2 and HCN in one step.
2. Catalytic air oxidation of NH_3 and propylene.
3. Catalytic vapor phase oxidation of naphthalene and *o*-xylene to phthalic anhydride.

4. Air oxidation of benzene to give maleic anhydride. The plasma generator is proposed as a preheater for the reactant.

5. Direct oxidation of benzene in air to phenol and of cyclohexane to adipic acid.

6. The manufacture of C_2H_2 from CH_4 and H_2 preheated in a standard tube furnace to 1000 and 2000°F, respectively, before reaction in the plasma reactor.

Inorganic Reactions:

Reduction of phosphate rock $Ca_3(PO_4)_2$ using CH_4 is feasible in the range 2100–3400°K, if side reactions involving CaO are avoided. This can possibly be performed by feeding the finely powdered ore downstream into the jet. The phosphorus produced need not be quenched as long as it is in a reducing atmosphere.

It is apparent that a great variety of chemical reactions remains to be studied in electric discharges.

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THE CHEMISTRY OF ASTATINE

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I. Introduction

Astatine, as the heaviest member of the family of halogens, forms a number of compounds in which the element has different valencies and which do not readily interchange. This means that a fairly large amount of chemical information will eventually become available. However, astatine is one of the most difficult elements to study from a chemical point of view, and our knowledge of its compounds is rather incomplete compared to what we know about other elements. For this there are several reasons.

No stable isotopes of astatine are known and it is evident that none can be expected. Earlier reports on the occurrence* of stable isotopes of element 83 are certainly due either to unreliable experimental techniques or to erroneous interpretation of observations. Alleged discoveries of this kind have been reviewed (24).

The stability of astatine isotopes can be judged from the information

* Although the isotopes of astatine used for normal purposes are all artificial, it is not correct to say that astatine has no naturally occurring isotopes. Karlik and Bernert discovered At^{218} and At^{215} in side chains of the uranium and the actinium families (25, 26), and Hyde and Ghiorso discovered At^{219} in a similar position in the latter family. A discussion of this group of nuclides is given by Haissinsky (16). The half-lives of these nuclides are, however, so short as to be useless for purposes of chemical research.

available on the masses of nuclei in this region. The recent compilation by Everling *et al.* (14) indicates that no isotope of astatine is β -stable with the possible exception of At^{215} , although even here it may well be that the β -stable isobar is Em^{215} and that At^{215} decays to this nuclide by β^- emission. Apart from disintegrations by β emission or by electron capture, all astatine isotopes are α -active. As a matter of fact in the case of the heavier isotopes, the half-life of the α decay is so much shorter than that of the β decay that the latter has not been observed in most cases.

Although it could be suggested that some astatine isotopes might have a half-life sufficiently long to make possible their survival in nature from the time of nucleogenesis of the material in the solar system, all isotopes which might be suspected to have a reasonably long half-life have already been synthesized and observed. This means that for survival of primordial astatine the occurrence of nuclear isomers would be required. Isomers do as a matter of fact exist in the case of At^{208} , but it seems most unlikely that any isomer would have a half-life comparable to 10^9 years. The products of α emission by astatine isotopes have a next-to-magic number of protons, which causes the α -decay energy to be exceptionally high and the α half-life to be correspondingly short. This means that the chances of finding any long-lived "natural" astatine seem from our present state of knowledge to be negligibly small.

Research on the properties of astatine is, moreover, complicated by the fact that the preparation of its isotopes is more difficult than with most elements, as they cannot be prepared by neutron irradiation. This means that a nuclear reactor cannot be used and that an accelerator is required. For ordinary purposes a helium ion accelerator is used and all chemical work on astatine has until now been based on cyclotron irradiations.

A further difficulty is due to the fact that a fairly satisfactory carrier element (comparable to cesium as a carrier for francium) is not available. Although the closest chemical relative, iodine, is often used for the purpose, it does not always fulfill this role in a satisfactory way. Ions or molecules of astatine compounds often do not fit the lattice of the corresponding iodine compound with sufficient accuracy, which means that the astatine may easily be pushed out of the solid phase in the process of recrystallization. Another complication is due to the fact that astatine compounds are often more strongly adsorbed than the corresponding iodine compounds, which may again upset the functioning of iodine as a carrier for astatine.

A final complication in astatine research is the short half-life of even the most suitable isotopes—about 8 hours, making it difficult to work with this element in laboratories which do not themselves produce its isotopes. For this reason it is not surprising that the larger part of our present knowledge concerning astatine and its chemical properties is due to the activities

of only a small number of laboratories. In this connection we may specially mention the work from Berkeley (2, 4, 12, 22). Biological work on astatine has been done mainly in Berkeley and in Brookhaven. References to this work will be given later.

Several excellent reviews have been published recently on the properties and behavior of astatine (1, 3, 7).

II. Isotopes: Production and Measurement

A. BASIC INFORMATION

A very large number of astatine isotopes are now known (Table I). Their half-lives and decay energies, both for α emission and for electron capture, are of great interest in the study of the influence of magic numbers on nuclear structure, as both magic numbers $Z = 82$ and $N = 126$ make their influence felt in these data. However, it is not reasonable to discuss the nuclear properties of astatine isotopes for this purpose without including the corresponding data concerning other elements in this region.

The isotopes of importance in the chemical study of astatine are At^{211} and At^{210} . Both are prepared by He^{++} -irradiation of bismuth. The cross-sections for these reactions are given in Fig. 1. It is evident that the minimum α energy, which can be used for astatine production, is 20 Mev, but that one cannot conveniently use energies below about 25 Mev.

For many purposes the isotope At^{211} (half-life 7.2 hours) is preferred, mainly because it can be measured by α counting. For every disintegrating nucleus one α particle is emitted, but the energy of the α particles is by no means the same in all cases. As is seen in Fig. 2, about 40% of the α particles have an energy of 5.86 Mev and 60% of 7.44 Mev. The extremely short half-life of Po^{211} (about 1 second) causes the observed α decay to follow exactly the half-life of At^{211} . For the purpose of ordinary α counting the energy is of no importance. If desired, At^{211} can also be determined by X-ray counting, as 60% of the decays give rise to an X-ray in Po^{211} . However, if the astatine is prepared by irradiating bismuth with He^{++} of higher energies, i.e., above about 32 Mev, the quantity of At^{210} prepared will be quite comparable to that of At^{211} and the half-life observed will no longer correspond to the exact value of the latter isotope. In many cases this will not cause a serious inconvenience; even so some laboratories prefer to use He^{++} ions with an energy of only 29 Mev, which gives pure At^{211} (2, 21).

In At^{210} (half-life 8.3 hours) the α emission is negligible, i.e., less than 0.2%. The nuclide can be measured either by its X-rays or by its γ -rays. Every decay process produces a 1.18-Mev γ -ray and about 18% also produces γ -rays in the region 1.44–1.49 Mev. For chemical purposes it does not as a rule matter very much if the astatine activity observed is due

TABLE I
DECAY AND HALF-LIVES OF ASTATINE ISOTOPES^a

Isotope	Half-life	Decay
At ²¹⁹	0.9 min	97% α 3% β
At ²¹⁸	1.3 sec	99.9% α 0.1% β^-
At ²¹⁷	0.018 sec	α
At ²¹⁶	0.3×10^{-3} sec	α
At ²¹⁵	0.1×10^{-3} sec	α
At ²¹⁴	short	α
At ²¹³	<2 sec	α
At ²¹²	0.22 sec	α
At ²¹¹	7.2 hr	40.9% α 59.1% EC
At ²¹⁰	8.3 hr	99.9% EC 0.1% α
At ²⁰⁹	5.5 hr	95% EC 5% α
At ²⁰⁸	1.6 hr	99% EC 0.5% α
At ²⁰⁸	6.2 hr	EC
At ²⁰⁷	1.8 hr	α EC
At ²⁰⁶	30 min	EC α
At ²⁰⁵	26 min	α EC
At ²⁰⁴	9.3 min	EC α
At ²⁰³	7.4 min	α EC
At ²⁰²	3.0 min	α EC
At ²⁰¹	1.5 min	α
At ²⁰⁰	0.9 min	α

^a It should be kept in mind that all astatine isotopes, with the exception of At²¹³, produce other radioactive nuclides by their decay. In many cases the radiation of the daughter nuclide is observed together with that of the astatine mother, thus occasionally giving rise to complicated decay curves. In astatine isotopes electron capture always produces K-radiation.

partly to At²¹⁰ and partly to At²¹¹. An average half-life of about 8 hours will be measured. Interpolation of different measurements and comparison of the activity of different samples will be easy and the precision will be quite satisfactory.

Irradiation of bismuth with He⁺⁺ ions may also produce lighter astatine

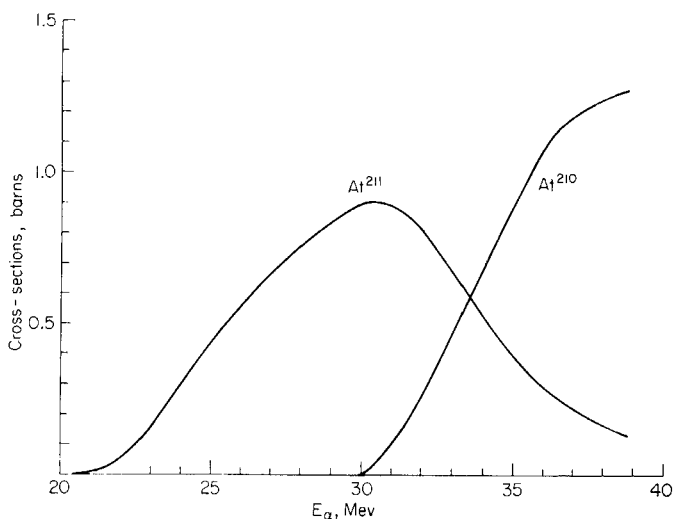


FIG. 1. Cross-sections (in barns) for the formation of the most important astatine isotopes by the reactions $Bi^{209}(\alpha, 2n)At^{211}$ and $Bi^{209}(\alpha, 3n)At^{210}$ (27).

isotopes. Such isotopes are useless as tracers for chemical research, but they may seriously upset the observation of the activities of At^{210} and At^{211} .

At^{209} (half-life 5.5 hours) is formed with a fairly large cross-section by α particles of 60 Mev (8). Presumably its formation will be quite important even at lower energies. (The curve drawn by Barton, Ghiorso and Perlman

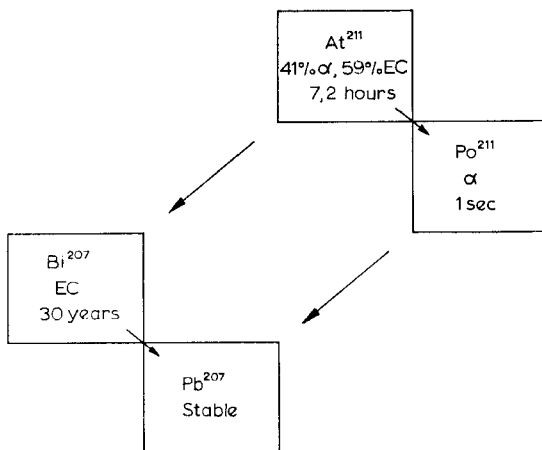


FIG. 2. Decay scheme of At^{211} . For each nucleus of At^{211} , which decays, one α particle will be emitted during the measurement, either by At^{211} or by Po^{211} . The X-rays due to electron capture in At^{211} can also be observed, but those due to capture in Bi^{207} will be lost because of the long half-life of this nuclide. The α -particles from At^{211} have an energy of 5.86 Mev, those from Po^{211} of 7.44 Mev.

through their observed points is hardly convincing, and the actual cross-sections may well be higher than an extrapolation from their curve to lower energies would lead one to expect.) Since only 5% of the decay of this isotope is α emission, At^{209} will hardly disturb measurements of At^{211} made by α counting. (Using α -measurements Barton, Ghiorso, and Perlman could not observe At^{209} in samples of astatine prepared with He^{++} ions having energies of less than 55 Mev.) On the other hand, the presence of At^{209} may well upset measurements of At^{210} and At^{211} by X-ray counting. At^{209} also shows a strong γ -ray emission, but the energies (mainly 0.195 Mev, 0.544 Mev, and 0.780 Mev) are quite different from those of At^{210} . Thus if the γ counting is done with a crystal with good resolution, At^{210} may easily be counted without interference from At^{209} , but if no energy discrimination is made, distinction between At^{210} and At^{209} may be very difficult.

A large number of lighter astatine isotopes are also produced by He^{++} -irradiation of bismuth, but most of them have half-lives of less than 2 hours. This means that in the course of ordinary chemical experiments they will practically disappear and are not likely to upset the measurement of At^{211} and of At^{210} . There is, however, one exception in that At^{208} has two isomers, one of which has a half-life of 6.2 hours. Little is known about it except that it does not seem to emit α particles. It will certainly produce X-rays and its possible occurrence should be taken into consideration if astatine is determined by X-ray counting.

Instruments used for astatine determination are the normal ones. As sufficient activity is usually available, their sensitivity need not be very high nor do backgrounds have to be very low.

Proportional counters and ionization chambers were used for α counting in early investigations, but at present scintillation counters are usually more convenient. It should be kept in mind that in α counting of astatine there is always the danger of the presence of Po^{210} . On the one hand this nuclide is formed by the decay of At^{210} , but the activity produced in this way will usually be fairly small compared to the α activity of At^{211} . A much more serious danger is contamination of the He^{++} beam with D^+ ions, which produce Po directly. It is, of course, possible to separate the polonium from the astatine during the chemical preparation of the latter, but it is always desirable to make sure that this separation has been successful. This is, of course, easily done by following the decay of the α activity of At^{211} over a number of half-lives and preferably by another α measurement after the astatine has disappeared completely.

The α activity of astatine samples may be measured either on an infinitely thin sample or on an infinitely thick one. The former method is more accurate as far as the α counting is concerned, but the preparation

is as a rule more risky. The preparation of thick samples is generally quite simple, but their assay, if done with high degree of efficiency (approximately 2π counter), may produce errors as high as 10%.

Counting of X-rays and of γ -rays is conveniently done by well-type crystal counters. By discrimination these counters make it possible to count γ -rays without X-rays, thus excluding At^{211} , or to count individual γ -rays to distinguish between At^{210} and At^{209} . However, if one wishes to use inexpensive counting equipment, it is generally acceptable to count a mixture of X-rays and γ -rays by means of a GM counter. The counting efficiency of these instruments is low, but the geometry can be made to approximate 4π . (The counters of Philips, Eindhoven, of the type No. 18508 are very satisfactory for this purpose.) If astatine is determined by X-ray counting or γ -ray counting, it should be kept in mind that the decay of At^{209} produces some Bi^{205} , which emits both X-rays and γ -rays with a half-life of 15 days. As a rule, however, this activity will be too low to cause complications.

Autoradiography of astatine has been used successfully in biological work. The activity measured is, of course, the α emission of At^{211} .

B. EXPERIMENTAL METHODS

For the production of astatine, bismuth is irradiated either as the metal or as the oxide. The bismuth metal is normally fused onto a metal plate, preferably of gold (30) or silver (21). Bismuth oxide can easily be pressed into holes drilled in a metal slab (5), from which it can be separated after an irradiation by mechanical means. If a high power press is available, the oxide may be pressed into a little boat scooped out of the metal plate. For a synchrocyclotron, which has a very narrow beam, a boat 30 mm long, 1 mm wide, and 1 mm deep is satisfactory. Evidently this boat must be as near as possible to the edge of the metal plate to avoid losing part of the beam. Whatever target construction is used, care should be taken to combine target shape and beam current in such a way that the temperature of the bismuth or the bismuth oxide does not become too high. Overheating may easily cause losses of astatine by evaporation.

Separation of astatine from irradiated bismuth or bismuth oxide is normally done either by distillation or by extraction.

Distillation is done from molten bismuth. It is either performed in a gas which may be stationary air (8) or a stream of inert gas (30), or it may be carried out in a vacuum (22, 27). The astatine is normally caught on a cold finger. The glass surface may be used to collect the astatine, but it may also be equipped with a platinum disk for the purpose. The astatine is dissolved by immersing the finger or the disk in a suitable solution. If a fairly high temperature is required for the distillation, the astatine will be contaminated with polonium and possibly even with gravimetric quantities

of bismuth. Under these conditions the astatine tends to form radiocolloids (17, 30), which may very seriously interfere with many experiments. (Such disturbances were especially noted with alkaline solutions; in acid solutions this complication will probably be less noticeable.) For these reasons a redistillation of the astatine may sometimes be advisable (2, 4).

The advantage of these distillation methods is that they provide an astatine solution which does not contain weighable quantities of dissolved material. On the other hand, the yields obtained are generally low and irreproducible. This is hardly surprising, since the astatine will probably be present during the distillation in a chemically unstable condition, possibly as astatine atoms. This means that it will easily be lost by adsorption or by chemical reactions on walls or other materials present and that it will be difficult to recover from such parts. Fairly complete recovery (85%) has been reported for the distillation *in vacuo* at 310° from molten bismuth onto a silver foil (27), but it seems doubtful whether such quantitative behavior can be relied on to be reproduced in other experimental arrangements. A good adsorption of astatine by silver would be expected from chemical considerations.

Wet methods for the isolation of astatine can be used either for the preparation of carrier-free solutions or for solutions in an excess of iodine.

Extraction from hydrochloric solution into isopropyl ether seems to be satisfactory (8, 29). It has the advantage that after the addition of a suitable quantity of tributylphosphate (TBP), polonium and bismuth can be extracted back into an aqueous phase containing nitric acid and hydrochloric acid.

Astatine iodide in a solution containing an excess of iodine is easily prepared by dissolving irradiated bismuth oxide in aqueous HClO_4 (containing I_2) and precipitating the bismuth with phosphate (5). For many purposes this liquid can be used as an aqueous solution of AtI . However, it still contains a certain amount of polonium, which in some cases may cause difficulty. A good purification is obtained if the I_2 containing AtI is extracted into CCl_4 , from which it may be extracted back into a reducing aqueous phase. If the CCl_4 extraction is used, the phosphate precipitation may be omitted, but no special tests have been made to ensure that the purity in this case is as good as it is in the separation of BiPO_4 . If an organic solution of AtI is required, the back-extraction is omitted. Chloroform may be used instead of CCl_4 (6).

The preparation of astatine for counting is largely dependent on the composition of the solution. If only volatile materials are present in appreciable quantities and if one is dealing with aqueous solutions, the liquid may be evaporated to dryness on silver or platinum. In this case α counting

is indicated. It is advisable to make the solution acidic (3 *M* HCl) before evaporation (2, 4). It might perhaps also be advisable to make sure that the astatine is in the reduced form, e.g., by dissolving some SO₂ gas in the liquid. Quantitative deposition of astatine on evaporation is difficult to obtain from organic systems. It is also possible to precipitate astatine from aqueous solutions onto a silver foil in a way similar to that used for polonium. (It seems uncertain whether such a method would work in the presence of carrier amounts of iodine.) Precipitation on a silver foil is suitable for the collection of astatine from oxidized biological material, if the destruction has been done with a mixture of perchloric and nitric acids. After the oxidation is finished, the nitric acid is distilled off and the perchloric acid diluted to 3 *M*. A silver foil of convenient size is put into the beaker and the solution is stirred for 30 minutes (15).

An alternative method is to coprecipitate the astatine with other materials. Tellurium precipitation carries astatine in a satisfactory way, if the element is obtained by reducing tellurous acid with SO₂ in the presence of HCl. There is no objection to the presence of perchloric acid, which makes the method suitable for the analysis of biological samples (15). (No information is available to indicate whether this precipitation is reliable if the system contains iodine.)

In the presence of iodine, astatine is best isolated by the precipitation of an iodide from a reducing solution. Silver iodide would seem an attractive choice, but measured activities sometimes tend to be low with this method. This is probably due to losses of astatine from the AgI lattice by recrystallization. It has been suggested that the mixture of AgI and Ag obtained by adding AgNO₃ and an excess of sulfite might hold the astatine more efficiently (5), but even with this technique occasional losses occur. Precipitation with PdI₂ from a solution containing sulfite and an excess of nitric acid (6) is more reliable. This is probably due to the fact that palladium iodide recrystallizes much more slowly than silver iodide, because of the presence of a bivalent ion in the crystal. (Palladium iodide is difficult to filter. It is advisable to centrifuge the liquid containing the precipitate, wash the iodide by centrifugation, and use an organic liquid, like ethanol, either to transfer the liquid to a filter or to dry it in the centrifuge tube.)

Absolute determinations of the activity of astatine can easily be done by α counting. For this purpose liquid scintillation counting has been used (9), but probably scintillation counting with a well-defined geometry (10, 31) would be equally satisfactory. This technique requires only a rough vacuum and presumably carrier-free astatine would not evaporate from a silver (or possibly a platinum) backing, though this point would have to be checked. Another possibility would be to rely on X-ray counting, but this

would be feasible only if the astatine did not contain At^{210} . A mixture of At^{210} and At^{211} might be standardized by a combination of X-ray counting and γ -ray counting with a NaI crystal calibrated for both. However, it is evident that α standardization will be far more accurate than other methods.

When thick samples (preferably, of course, samples of infinite thickness) are counted, an absolute calibration can be obtained by precipitating astatine samples, calibrated (in a carrier-free state) beforehand, with a known quantity of PdI_2 . However, the counting of the α activity of thick samples is not nearly so reproducible as that of very thin samples.

Although we have mentioned several methods for the quantitative isolation of astatine, no one acquainted with the chemistry of this element will rely on any of these methods without keeping in mind the possibility of its proving to be untrustworthy on occasion. Probably this danger is greatest in those methods which depend on precipitation, but even transferring and dispensing solutions of astatine may possibly cause occasional losses due to adsorption (22).

III. Chemical Properties of Astatine

Although study of the chemical properties of astatine began more than 30 years ago (12), much of the behavior of this element is still in doubt. As with other tracers, its chemistry has been studied mainly by extraction and by coprecipitation and neither method provides results easy to interpret. It is evident that the chemical similarity between astatine and iodine does not go very far and in many cases the astatine tracer does not follow its iodine carrier in the way one would expect. The situation is complicated by the fact that the chemical properties of the series of halogens do not present a pattern which is easily recognized; in many respects bromine does not interpolate well between chlorine and iodine.

The chemistry of astatine is discussed as a rule under different headings, each one indicating a separate valency state; we shall follow the same scheme in this report.

The general trend in the periodic system suggests that astatine should be more "metallic" than other halogens. This means that it will take up a positive charge more easily than iodine and a negative charge less easily. It will be seen that this is actually the case.

In this connection it may be worth mentioning as an example that strong coprecipitation of astatine has been observed with SnS and with HgS from hydrochloric acid solution and also with several hydroxides (12, 22). These experiments are, however, difficult to interpret owing to lack of knowledge of the valency of the astatine.

A. At^-

The astatide ion presents the best known chemical state of astatine and its similarity to the iodide ion is very striking. Even so astatide is not retained very well by some iodide precipitates like AgI , though initially it coprecipitates quite efficiently.

Astatide ion is normally prepared by reduction of some chemical state of astatine (usually and preferably AtI or At^0) with SO_2 . The resulting solution coprecipitates entirely—at least initially—with iodide, and no astatine is extracted by CCl_4 (2, 4, 22). Reduction to astatide is also possible by means of ferrocyanide or by arsenite in acid solution. However, in these cases reduction seems to be somewhat incomplete. [Almost all of the activity coprecipitates with I^- ; only a small but observable fraction—of the order of one or a few percent—is still extracted by CCl_4 (2, 4).]

Measurements have been made of the mobility of astatide ions (23). The diffusion of a mixture of I^{131} and At^- ions was determined through the wall of Visking sausage-casing bags in solutions containing I^- and SO_3^{2-} . The ratio of the diffusion coefficient was found to be:

$$D_{\text{I}^-}/D_{\text{At}^-} = 1.41.$$

If the ratio of the mobilities in the plastic is equal to the ratio in pure water, this result is of the highest interest; it clearly demonstrates the maximum in the mobility of the halide ions as a function of the atomic number, as shown in Fig. 3.

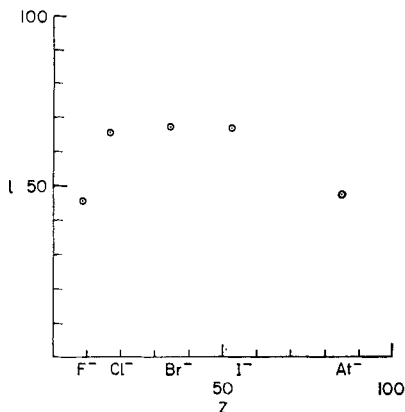


FIG. 3. Equivalent conductivity of halogen ions in water at 18°C. Equivalent conductivities (Λ) in $\text{cm}^2\Omega^{-1}$ for a solution containing 1 gm ion/ cm^3 . Values for F^- , Cl^- , Br^- , and I^- from (28); the value for At^- was calculated as $1(\text{I}^-)/1.41$.

The negative charge on astatide ions was demonstrated by means of migration experiments (22).

B. At^0 AND AtI

Elementary astatine, unless diluted with a carrier amount of iodine, shows a most irreproducible behavior. This is by no means astonishing, as similar observations have been made on carrier-free radioactive iodine (24). It has occasionally been suggested that pure astatine in aqueous solutions should consist of At_2 , but this seems rather doubtful in view of the very low concentration of the element. It is generally assumed that astatine in solution reacts with a number of impurities. This means that a "pure" solution of astatine has a composition which is unknown and irreproducible. It is hardly surprising that attempts to observe the chemical behavior of At^0 have not given satisfactory results. Appelman observed distribution ratios of 1-10 of At^0 between organic liquids, such as benzene or CCl_4 , and water.

The assumption that carrier-free At^0 reacts with a number of impurities is supported by the observation that this activity can only partially be back-extracted from an organic solution into an aqueous phase. Another alarming fact is that a large but very irreproducible percentage of At^0 is absorbed onto glass wool from I_2 -free aqueous solutions. Part of this activity can again be leached off the glass wool, but part always gets lost in experiments of this kind (2).

However, if a large excess of iodine is present, the behavior of astatine becomes much more reasonable. In this case the zero-valent element is present entirely as AtI molecules and a large excess of I_2 molecules protects the astatine against adsorption. Under these circumstances Appelman was able to obtain a fairly accurate and reliable value for the distribution ratio between CCl_4 and water:

$$[\text{AtI}]_{\text{CCl}_4}/[\text{AtI}]_{\text{H}_2\text{O}} = 5.5.$$

Extraction experiments of this kind have been used, together with coprecipitation tests, to study the formation of the zero oxidation state of At.

AtI is easily obtained by reduction of more oxidized forms of astatine with Fe^{++} ions, or with VO^{++} ions, in the presence of iodine. It is, however, essential that the reaction be carried out in the dark (2, 4). The same reduction with Fe^{++} ions may be used to produce At^0 , at least under favorable circumstances. Dilute nitric acid easily oxidizes At^- to At^0 (22). At^- is changed to AtI by the action of I_2 (4) (which evidently requires that no I^- or only very little be present, as otherwise AtI_2^- will be formed. This is discussed in Section III,G.)

The coprecipitation of AtI with I₂ from chloroform solutions has also been studied (6). The uptake of AtI by iodine crystals was found to follow the logarithmic distribution law of Doerner and Hoskins (38) with an initial distribution coefficient:

$$\lambda = \frac{\log\{(\text{AtI in solution})/(\text{AtI in solution} + \text{solid})\}}{\log\{(\text{I}_2 \text{ in solution})/(\text{I}_2 \text{ in solution} + \text{solid})\}} = 4.$$

C. At⁺

In a solid or in an organic solvent iodine can easily be obtained as a monovalent positive ion, especially if it is stabilized by complex formation, e.g., with two molecules of pyridine. It is to be expected that the formation of such positive ions will be as easy or easier in the case of astatine. Both iodinedipyridineperchlorate—I(C₅H₅N)₂ClO₄—and the corresponding nitrate are easily prepared. It is not surprising that the ratio of astatine to iodine is higher in the perchlorate and in the nitrate than in the I₂ used for the synthesis (33).

D. At(X)

In aqueous solutions there also seems to exist an intermediate oxidation state between At⁰ and AtO₃⁻. Presumably this is either AtO⁻ or AtO₂⁻, but no convincing evidence is available on this subject. In the case of iodine the ion IO⁻ seems to occur, although it has not been isolated. On the other hand, the existence of IO₂⁻ does not seem to have been established (34). The analogy here, however, between astatine and iodine does not seem to be very good, since this state of astatine seems to be much more stable than either of the two iodine states mentioned.

At(X) can be produced from astatine in a higher oxidation state by reduction with chloride. It can also be obtained from At⁰ by oxidation with VO₂⁺ or with Fe₃⁺. Both oxidations are photochemical processes and both can take place in the absence or in the presence of excess iodine.

Conclusions concerning the occurrence of At(X) are based in general on negative evidence. Astatine in aqueous solution, which does not coprecipitate with insoluble iodides or iodates and which does not extract into CCl₄, is considered to be At(X).

E. AtO₃⁻

Astata ions seem to be fairly stable and are easily recognized by their coprecipitation with insoluble iodates. Appelman (2) has used coprecipitation with both Pb(IO₃)₂ and Ba(IO₃)₂.^{*} Several means exist for oxidizing

^{*} A very curious fact has been pointed out by Appelman (2). In many oxidizing systems astatine coprecipitates well with Pb(IO₃)₂, but a large part of this activity may be washed off this precipitate by means of acetone.

astatine quantitatively—or almost so—to astatate. Persulfate, ceric ion, or periodate all seem to be satisfactory. An acid solution of elementary chlorine or chromate oxidizes part of the astatine to astatate, but as a rule the oxidation does not seem to be quite complete (2).

The negative charge on astatate ions was demonstrated by means of migration experiments (22).

F. AtO_4^-

Appelman considers that perastatate has not been prepared and probably does not exist. He treated astatine with very strong oxidants, and by using a much higher concentration of iodate than of periodate was able to obtain a precipitate of $\text{Ba}(\text{IO}_3)_2$ containing very little periodate. From similar solutions he could precipitate periodate as KIO_4 (2). The activity in the periodate precipitate was negligible compared to that of the iodate. (The actual observations indicated that less than 10% of the total activity precipitated with KIO_4 . If one takes into consideration the contamination, which is always observed in astatine chemistry, one will not consider such a small percentage coprecipitation as proof of the formation of perastatate.)

G. At IN POLYHALIDES

The fact that iodine forms a large number of polyhalides suggests a similar behavior on the part of astatine. The formation of such compounds has been studied by means of solvent distribution experiments by Neumann (29) and Appelman (2). The basic assumption is that charged complexes are extracted into polar organic solvents like isopropyl ether, but not into apolar liquids like CCl_4 or C_6H_6 . (The extraction is done from acid solutions and it is not suggested that the polyhalide is present in the organic phase in an ionized state.) Strong evidence was obtained for a chloroastatide, but it was not possible to decide whether this ion should be formulated as AtCl_2^- or AtCl_4^- (29). Appelman has determined distribution coefficients between water and CCl_4 in systems containing different halogens, and from this has derived a number of equilibrium constants for the formation of various complexes of At, I, Br, and Cl. It is interesting to note that astatine is always complexed a little more strongly than iodine in the corresponding position, the differences in the equilibrium constant amounting to a factor of 2.5–8 (2). Another general rule is that halogen molecules consisting of two identical atoms are extracted more strongly into CCl_4 than molecules containing two different halogen atoms, due to the fact that the former type of molecule is entirely apolar, whereas the latter type represents a dipole. The distribution coefficient for iodine between CCl_4 and water is 86 and for AtI is 5.5.

An alternative way to investigate polyhalides is by obtaining them in a solid. CsI_3 containing CsAtI_2 is easily prepared from an aqueous solution of CsI , which is first used to extract I_2 containing AtI from chloroform and to which a suitable quantity of solid I_2 is added afterwards. Heating and cooling produces CsI_3 containing astatine.

A general rule in the chemistry of polyhalides says that in the decomposition of a polyhalide the lightest halide remains behind to form the monohalide (35). Evidently this rule has been observed with pure polyhalides, whereas in the case of astatine we are dealing with a mixed lattice containing a tracer quantity of AtI_2^- in a carrier of I_3^- . Even so it is gratifying to observe that the same rule holds in this case and that during the decomposition of CsAtI_2 in CsI_3 the AtI follows the iodine vapor (11).

H. At IN ORGANIC COMPOUNDS

The difficulties encountered in the work on inorganic astatine are even more upsetting in the study of its organic chemistry. Irregular extraction and coprecipitation combined with the instability of many astatine compounds often make the interpretation of observations quite uncertain. If, for instance, iodoform is synthesized from iodine containing AtI (36), the first precipitate of CHI_3 shows a very appreciable At activity, which disappears rapidly in the course of a series of recrystallizations (32). It is hardly possible to say for certain whether this means that the lattice did not contain CHAtI_2 at all, or whether this compound was formed initially but decomposed very easily. However, the first explanation seems to be the more reasonable. This situation probably explains the rather conflicting remarks repeatedly made about the synthesis of organic compounds of astatine. Thus one laboratory reported the preparation of phenyl astatide (21), whereas the preparation of this compound was not successful in another institute (18). In some cases attempts to synthesize organic astatine compounds give negative results (32), e.g., in the case of *p*-iodoaniline (37). In other cases successful synthesis has been reported, e.g., for *p*-astatobenzoic acid and *p*-astatobenzenesulfonic acid. The latter compound provides a means for incorporating astatine into different proteins (20, 21). This can also be done by means of a diazo coupling of benzidine to protein (21).

A general consideration of the chemical properties of astatine suggests that the best chance for the incorporation of astatine into organic molecules exists in those cases where the astatine atom carries a partial positive charge, both in the final product and in any intermediate stage through which it passes during the reaction. Workers interested in the synthesis of organic astatine compounds may find it useful to give this point serious attention.

I. BIOCHEMICAL COMPOUNDS OF At

Astatine in the living organism is taken up rapidly by the thyroid gland, due to its similarity to iodine. It is not clear whether the astatine is carried by the blood as At^- or as At^0 . For some time its chemical condition in the thyroid gland was also in doubt, but, recently it has been shown that a large fraction of the astatine in the thyroid follows the protein fraction as it is precipitated by trichloroacetic acid or by concentrated ammonium sulfate (19). This suggests that astatine can take up positions in the thyroid protein similar to those normally occupied by iodine.

IV. Biological Behavior

The fate of astatine in living organisms is very similar to that of iodine, as is to be expected. Much work has been done on the absorption and distribution of the element; it has been observed that if astatine is administered as a radiocolloid, it tends to accumulate in the liver (17, 30), a tendency common to most radiocolloids. If administered as a true solution, astatine is concentrated strongly in the thyroid. A large number of publications on this subject are listed in a recent paper by Hamilton *et al.* (13). The distribution of astatine can be observed very easily in autoradiograms, in which At^{211} is recognized by its α tracks (23). The uptake of astatine by the thyroid gland is reduced by the administration of thiocyanide, a behavior quite analogous to that of iodine. However, the influence of propylthiouracil enhances the uptake of astatine, but reduces that of iodine (19).

Because of its α emission, most of the decay energy of At^{211} is strictly localized in the region where the element is concentrated, i.e., the thyroid. For this reason astatine has been suggested as a "thyroidectomizing" agent (19).

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THE CHEMISTRY OF SILICON-NITROGEN COMPOUNDS

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I. Introduction

Silicon and nitrogen, because of their positions in the periodic system, can combine in a variety of ways. Thus it can be shown that, in principle, four nitrogen atoms may be bound to one of silicon, or three silicon atoms to one of nitrogen, and that a fourfold silyl-substituted ammonium ion is possible. Addition compounds should exist in which one, two, or even four tertiary amine molecules are linked to a silicon halide molecule by using the vacant $3d$ orbitals of silicon and the free pair of electrons on the nitrogen atom of the tertiary amine. Furthermore, compounds of higher molecular weight with —SiN— units in chains or as members of rings must be possible, and compounds with oxidation states other than +4 for silicon or -3 for nitrogen should also be obtainable.

It is astonishing that these abundant possibilities have been so little used in preparative and synthetic chemistry until recently, in spite of the fact the first SiN compounds were prepared 150 years ago. Only in the last 20 years since organohalosilanes, the most important starting materials

ring compounds. Thus, for example, the trisilylamine sometimes has wrongly been called trisilazane. In cases of doubt it is advisable to base the nomenclature on hydrocarbon chains and to designate the replacement of CH_2 with SiH_2 by the prefix sila and that with —NH— by aza.

SiN = silylamine	NSi = aminosilane
SiNSi = bis(silyl)amine	NSiN = bis(amino)silane
Si_3N = tris(silyl)amine	N_4Si = tetrakis(amino)silane
Si_nN	N_nSi
$\text{Si}(\text{NSi})_n$ = polysilazane,	($n = 1$) disilazane
	($n = 2$) trisilazane, etc.
$(\text{—NSi—})_n$ = cyclosilazane,	($n = 3$) cyclotrisilazane
	($n = 4$) cyclotetrasilazane
$\text{me}_3\text{SiNHCH}_2\text{COOH}$ = trimethylsilylaminoacetic acid	
	or
	= 3-aza-4-sila-4,4-dimethylvaleric acid
$\text{me}_2\text{Si—Nph—Nph}$	= 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-
phN—Nph—SiMe_2	1,4-disila-2,3,5,6-tetrazacyclohexane

II. Preparation and Properties of the Si—N Bond

Only in the rarest cases are redox reactions used in the preparation of Si—N bonds. The general method almost always involves substitution or condensation reactions involving reactants with the appropriate oxidation state of Si or N already established. Thus elementary silicon reacts with N_2 or NH_3 only at temperatures above 1200° , when Si_3N_4 results (11, 51), and the interaction of elementary nitrogen and silicon tetrachloride is possible only in a glow discharge. A complex mixture of reaction products results (38, 105).

The most common way of establishing a bond between Si and N is by the reaction of >SiCl with an >NH group. The generally accepted view of the mechanism is that the following steps are involved:

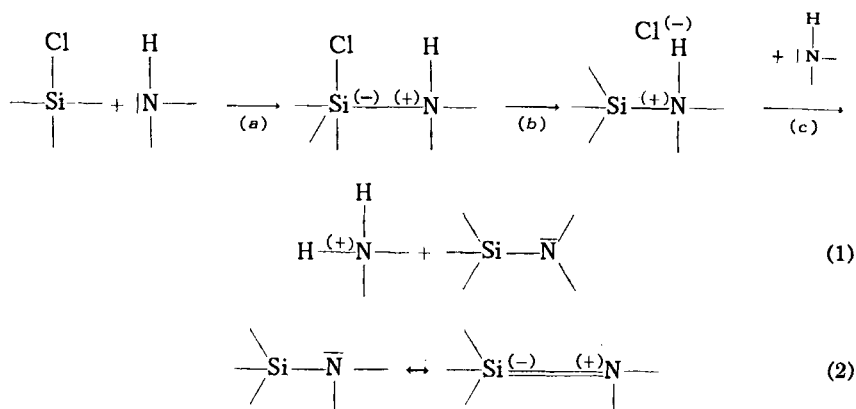
(1) Addition of the amino group to the chlorosilane by interaction of a free electron pair of N with a vacant $3d$ orbital of Si. Nitrogen then has an ammonium structure with Si in a 5-coordinated state and has a formal negative charge (Reaction 1a).

(2) Cleavage of the Cl, initially bonded covalently, as a chloride ion (Reaction 1b); a silyl-substituted ammonium salt is left.

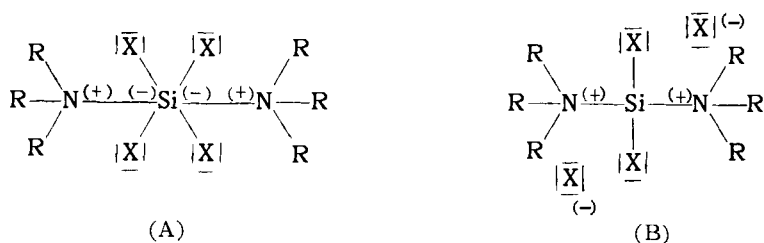
(3) The strongly basic amine taken initially removes a proton from this silyl-substituted ammonium salt (Reaction 1c).

(4) The Si—N compound formed establishes a mesomeric equilibrium and forms a $d_\pi\text{—}p_\pi$ double bond between the Si and N atoms (Reaction 2).

Primary and secondary amines react rapidly via Reactions 1a and 1b. Tertiary amines interact only with silanes such as RSiCl_3 or SiCl_4 , which are extensively halogenated; reaction is restricted, however, to the primary



addition. A second NR_3 molecule is often added. The addition of four NR_3 molecules is known with certainty only in the case of SiI_4py_4 (py = pyridine) (99, 140, 167). With ureas or acid amides, addition ratios as high as 1:6 and 1:10 are observed (50, 123, 140). Although more than 50 publications have appeared which deal with addition compounds between silicon halides and amines, it has not yet been possible to prove conclusively whether the structure of these addition compounds is of type A, with coordinate links in a monomolecular structure, or of type B, with ionized halide

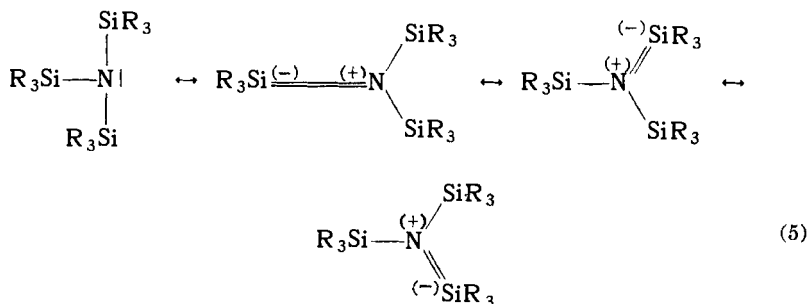
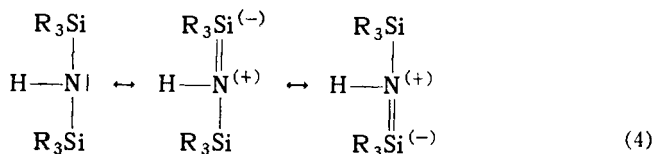
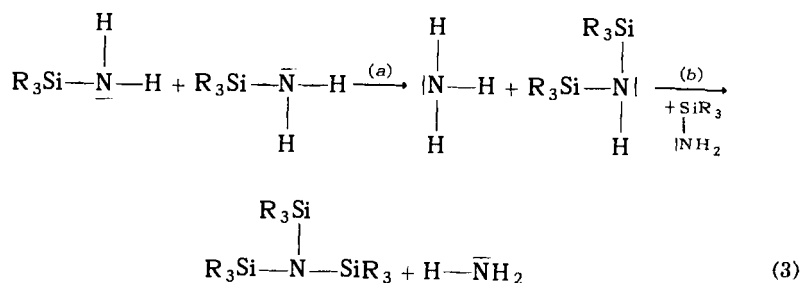


(7, 8, 62, 100, 121, 122). Since the addition compounds are extremely sensitive to moisture and tertiary amines are very difficult to obtain in an anhydrous state, the majority of publications on this class of compound may well contain incorrect observations: even the presence of small quantities of water in solvents suffices to precipitate mixtures of silicic acids and ammonium halides, which in most cases cannot be distinguished analytically from the addition compounds being sought. It would be a rewarding task to bring some light to this confused section of silicon-nitrogen chemistry by the use of unexceptionable experimental procedures and modern methods of elucidating structure.

In many cases, such as that of the carbonic acid amides RCONH_2 , the

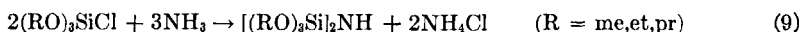
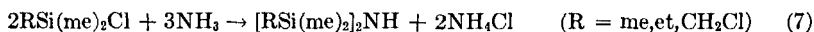
amine base is too weak to bring about step 1c in the reaction scheme. In such cases the addition of tertiary amines to remove protons has been found to be a very useful way of promoting silylation (15, 18, 31, 113).

If the reactions are carried out with secondary amines, R_2NH , Reaction 1 is terminated at the 1c stage. The same is true in most cases for primary amines. With ammonia as the starting material, subsequent multiple condensation reactions take place, leading to two- or even threefold silyl substitution of the ammonia.

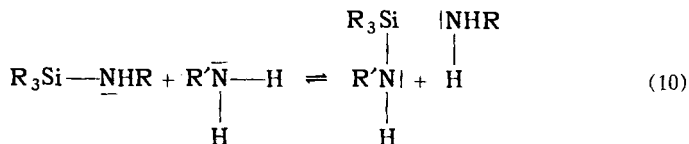


The extent of these subsequent condensation reactions depends on how far the electron pair of the N atoms in the limiting mesomeric forms shown in Reaction 2 or 4 is available for further addition reactions or is blocked by $d_\pi-p_\pi$ bonding. It is also dependent on steric factors due to the R substituents on the silicon atom. Thus the chlorosilane $RSiH_2Cl$ reacts with ammonia successively to form the tris(silyl)amines; $RSi(me)_2Cl$ below

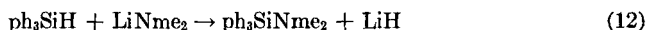
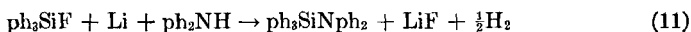
50° goes to bis(silyl)amines and $\text{RSi(et)}_2\text{Cl}$ only to silylamines (if R is not H). With the alkoxychlorosilanes $(\text{RO})_3\text{SiCl}$, condensation to the bis(silyl)-amines occurs more readily than with alkylchlorosilanes.



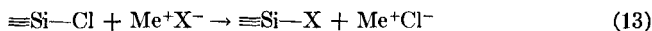
Condensation by Reaction 3a to a doubly silyl-substituted amine may often be brought about by increasing the temperature or, better, by using an acid catalyst such as NH_4Br or $(\text{NH}_4)_2\text{SO}_4$, though even under the most drastic reaction conditions the formation of the threefold silyl-substituted amine is not observed. Exchange reactions of amines in Si-N compounds proceed in the same way: the readily volatile amine RNH_2 is distilled off from the equilibrium mixture and thus dislodged from the silyl group (87, 90):



The behavior of $\equiv\text{Si}-\text{Br}$ or $\equiv\text{Si}-\text{I}$ groups is like that of $\equiv\text{Si}-\text{Cl}$ groups, though they have hardly been used at all in preparative work. On the other hand, $\equiv\text{Si}-\text{F}$ or $\equiv\text{Si}-\text{H}$ are often found to react only with metallated amines (25, 49). Hydrogen has a higher electronegativity than Si (2.1 as against 1.8) and therefore behaves like a halogen when bonded to silicon.



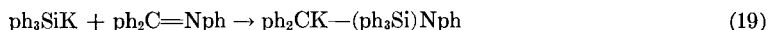
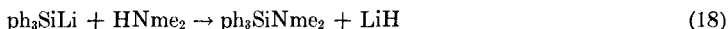
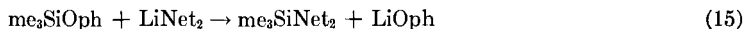
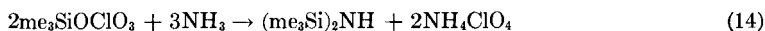
Attachment of a pseudohalogen through nitrogen to a silicon atom may be effected by splitting off a metal halide:



where $\text{Me} = \text{Li, Na, K, NH}_4, \text{Ag, Pb}$; $\text{X} = -\text{NCO}, -\text{NCS}, -\text{NNN}, -\text{NCN}-, -\text{NC} (?)$.

Other reactions, as for example the transformation of $\equiv\text{Si}-\text{O}-$ to $\equiv\text{Si}-\text{N}=$, are of much less importance. "Silyl esters" of inorganic acids react readily with ammonia (134, 145). The $\text{Si}-\text{O}-\text{C}_6\text{H}_5$ bond is cleaved by $\text{NaN}(\text{SiR}_3)_2$, LiNR_2 , or NaNH_2 (164) while, under more drastic condi-

tions, $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ is cleaved by NaNH_2 (63). Nucleophilic cleavage of $\equiv\text{Si}-\text{C}\equiv$ by NaNH_2 may also sometimes occur (55). Alkali silyl compounds can condense with amines, with elimination of alkali hydride (182), or may be added across the double bond in $-\text{N}=\text{N}-$ or $\text{C}=\text{N}-$ (181):

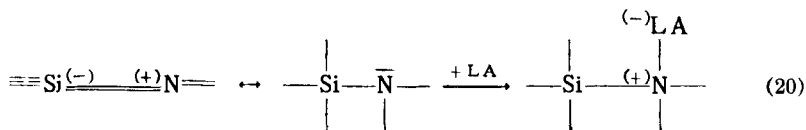


Formation of a $d_\pi-p_\pi$ bond (30) is especially characteristic of the Si-N bond. In the bond between N and Si the combined effect of atomic radii, electronegativity difference, bond polarity, and tendency to donate electrons is clearly an optimum compared with the bond between silicon and all other elements, leading to extensive overlapping of the p orbitals of the free electron pair of N with the unoccupied d orbitals of Si. The tetrahedral configuration of the Si atom is scarcely changed in this process, for electron diffraction and X-ray studies on SiN compounds show only minor deviations from the tetrahedral angle ($110 \pm 5^\circ$). The nitrogen bond angle, on the other hand, undergoes considerable widening compared with that for the sp^3 and sp^2 configurations; it is in the range $130-135^\circ$ in me_3SiNHme , $(\text{me}_3\text{Si})_2\text{NH}$, and $[-(\text{me}_3\text{Si})\text{N}-\text{Si}(\text{me})_2-]_2$ (75, 109, 174). It amounts to $119.6 \pm 1^\circ$ in the planar NSi_3 unit of tris(silyl)amine, $\text{N}(\text{SiH}_3)_3$ (56), and presumably also in other isolated NSi_3 structures (52). The three angles for the N atom in $[-(\text{me}_3\text{Si})\text{N}-\text{Si}(\text{me})_2-]_2$ have been found to be 91.7° , 135.4° , and 132.8° for a planar arrangement of the Si_3N unit (174). In H_3SiNCS and H_3SiNCO the SiNC angle is 180° (35, 36, 64). For the variable results of N angle determinations in the cyclosilazanes, see Section VI. The results so far obtained are so few and confusing that definite conclusions can hardly be drawn.

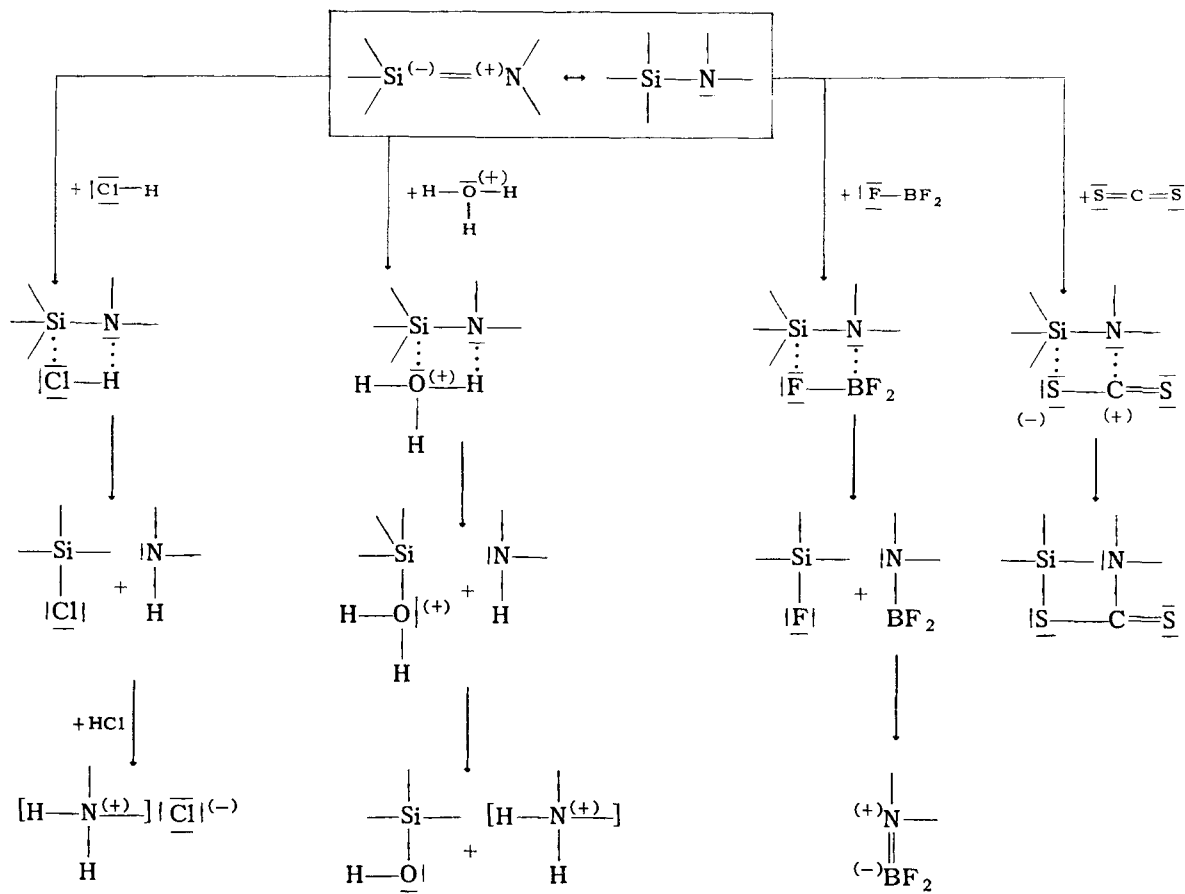
The position regarding bond distances is clearer. Compared with the calculated ($p-p$) single bond in $\text{Si}-\bar{\text{N}}$ calculated from the sum of the covalent radii (variously assessed as 1.87 or 1.80 Å) and a ($p_\pi-p_\pi$) double bond in $\equiv\text{Si}=\text{N}-$ (1.62 Å), an interatomic distance of 1.73 ± 0.01 Å has been found for a series of SiN compounds such as me_3SiNHme , $\text{N}(\text{SiH}_3)_3$, H_3SiNCS , and $[-(\text{me}_3\text{Si})\text{N}-\text{Si}(\text{me})_2-]_2$. This indicates a structure $\equiv\text{Si}^{(-)}=\text{N}^{(+)}\equiv$. From spectroscopic data the force constant of the SiN bond is seen to be substantially increased. It lies in the region of 4.0 mdynes/Å, compared with 3.26 mdynes/Å for a single SiN bond, and shows that the shortening of the distance does not arise from the contribu-

tion of polar structures (34, 75, 76, 78). The calculated bond order of 1.26 for $\text{N}(\text{SiH}_3)_3$ and of 1.18 for $(\text{me}_3\text{Si})_2\text{NH}$ shows that the free electron pair on nitrogen is not fully absorbed in the d orbitals of Si. For the mesomeric equilibria shown in Reactions 4 and 5 the canonical forms with a SiN single bond have considerable weight. With complete transfer of the electron pair from nitrogen, bond orders of 1.33 or 1.50 would occur (75, 76). The Si—N dissociation energy derived from spectroscopic data is 77 kcal/mole for $(\text{me}_3\text{Si})_2\text{NH}$ and 82 kcal/mole for $\text{N}(\text{SiH}_3)_3$; the Si—N bond energy from calorimetric measurements is 83.3 kcal/mole for $\text{me}_3\text{SiNet}_2$ (26, 75, 76). Formation of $d_\pi-p_\pi$ bonds also accounts for the relatively low dipole moments of SiN compounds (28, 116). In the infrared and Raman spectra of SiN compounds, among which structures containing SiN^-Si^+ , $\text{Si}^-\text{N}^+\text{Si}^+$, and $(-\text{SiN}-)_n$ units have been most studied, the characteristic antisymmetrical Si—N(Si) stretching frequency lies in the region 900–1000 cm^{-1} , and the symmetrical stretching frequency for the same group is at 400–600 cm^{-1} . Increasing use has recently been made of NMR spectra in determining the constitution of SiN compounds (37, 86, 108).

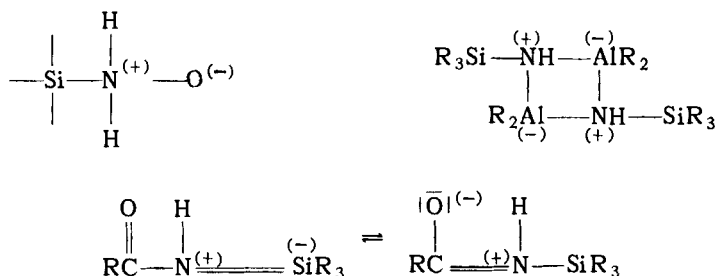
The strongly developed $d_\pi-p_\pi$ double bond component of the SiN bond is reflected in the chemical behavior of these compounds. The silicon atom is protected to a major extent against nucleophilic attack. Thus the majority of SiN compounds are insensitive to hydrolysis, provided a pH value of 8 is not exceeded. Tris(silyl)amines may be heated for long periods with concentrated alkali without decomposition; they sublime unchanged into the condenser (52, 147, 156a). SiN compounds react more readily with Lewis acids (LA), which withdraw the electron pair of the N atom from the $d_\pi-p_\pi$ bond with the Si atom:



Elements of the third main group of the periodic system are particularly suitable for this purpose. By varying the substituents one is able to influence the stability of the newly formed addition compounds and also to examine the base strength of the SiN compounds. The compounds used include B_2H_6 , BR_3 , BF_3 , Al_2Cl_6 , $\text{Al}(\text{me})_3$, $\text{Ga}(\text{me})_3$. One typical example of the sequence of basicities, taken from a large number of investigations, is: $\text{me}_3\text{N} > \text{me}_2\text{N}(\text{SiH}_3) > \text{meN}(\text{SiH}_3)_2 > \text{N}(\text{SiH}_3)_3 < \text{O}(\text{SiH}_3)_2 < \text{FSiH}_3$ (95). Addition products of Lewis acids and SiN compounds often dissociate below room temperature and are also sensitive to moisture since the Si atoms are no longer protected. Pronounced sensitivity of an SiN compound to mois-



ture is always indicative of a silylammonium structure, in which the $d_{\pi}-p_{\pi}$ bond has disappeared or is very weak (119, 153, 154).

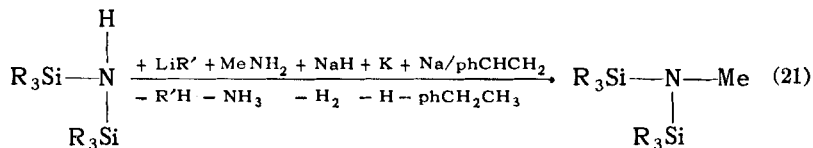


Alkyl and silyl halides prove in general to be too weak as Lewis acids to convert SiN compounds into substituted ammonium derivatives such as $[(\text{H}_3\text{Si})_4\text{N}]^+\text{X}^-$ or $[(\text{H}_3\text{Si})_3\text{Nme}]^+\text{X}^-$ (136).

If a four-center mechanism with combined electrophilic and nucleophilic attack on the SiN bond is involved, cleavage of the bond will occur very readily, as for example in its reaction with aqueous acids, hydrogen chloride in benzene, or nonmetallic halides (e.g., see 20). These reactions have been used not only in detecting SiN bonds but also very extensively in preparative synthesis.

III. Silyl-Substituted Alkali Metal Amides

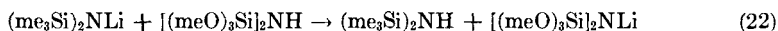
Alkali bis(silyl)amides were discovered only very recently, but they have become most interesting groups of inorganic reagents because of their convenient physical properties and surprising versatility. They are produced by metallation of bis(silyl)amines (120, 146, 149, 156, 164a), but not by silylation of alkali amides (170a). Suitable metallating agents are the organic alkali metal compounds, alkali amides, and alkali hydrides. Even the alkali metals themselves will serve, though only in special cases and then preferably in solution in liquid ammonia or in suspension in styrene or a naphthalene-tetrahydrofuran mixture (52, 107, 163):



(where $\text{R}' = \text{pr, bu, ph}$; $\text{Me} = \text{Na, K}$).

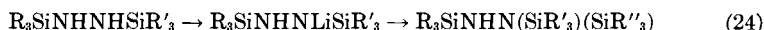
Metallation with NaNH_2 in benzene suspensions is particularly simple and quantitative. In the case of bis(alkoxysilyl)amines $[(\text{RO})_2\text{Si}]_2\text{NH}$, which have become readily available (23), the organolithium compounds

are not suitable as reagents as they cleave the Si—O bonds. Controlled metallation in the homogeneous phase may be brought about in this case by double decomposition, as for example (156a):



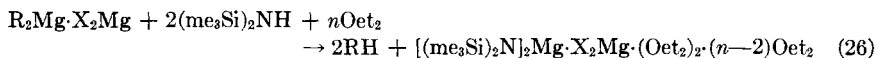
The same is true for metallation of cyclosilazanes such as $(-\text{R}_2\text{Si}-\text{NH}-)_3$, where the separate NH groups are metallated stepwise. Metallation of the last NH group occurs as a rule only under more drastic conditions (43, 163, 169).

The analogous metallation of NH_2 or NH groups with subsequent silylation has led to a number of Si—N compounds not accessible by other routes (147, 148, 150).



Alkali bis(silyl)amides have previously been formulated as intermediates in complicated reactions, without having been isolated, e.g., in the reaction of et_3SiH with KNH_2 (74), of $\text{me}_3\text{SiCH}_2\text{ph}$ with KNH_2 (54), or of $(\text{me}_3\text{Si})_2\text{NH}$ with Na and me_3SiCl in styrene (52).

Metallation of bis(silyl)amines is possible not only with alkali metals but also by way of magnesium and aluminum derivatives. Particularly well-formed crystals are obtained with the Grignard reagent in the following reaction (155):



(where R = me, et, pr; X = Cl, Br, I; $n = 2$ for Cl and Br, $= 4$ for I). Lithium aluminum hydride yields hexakis(trimethylsilyl)aluminum triamide, which melts at about 230°C and in which the PMR spectrum shows all the 54 H atoms to be equivalent (107).

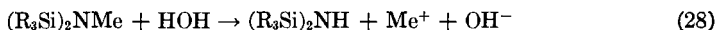


The alkali bis(silyl)amides prepared up to the present are shown in Table I; all are solids except $(\text{me}_3\text{Si})(\text{et}_3\text{Si})\text{NLi}$. They may be recrystallized (or where their solubility characteristics are unsuitable, dissolved and reprecipitated) from hydrocarbons in well-formed but relatively soft colorless crystals. They have definite melting points and may be distilled in vacuum without decomposition, though there is a marked tendency to sublime at a little above the melting point. As a rule they are stable in air, though some turn yellow or brown under the influence of oxygen, particularly when in solution. It is best therefore to carry out the preparations and

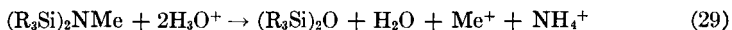
TABLE I
ALKALI BIS(SILYL)AMIDES AND THEIR ADDUCTS

Group I				Group II				
$ \begin{array}{c} R_3'Si \quad Me \\ \diagdown \quad / \\ N \\ / \\ R_3Si \end{array} $				$ \begin{array}{c} R_3'Si \quad \overset{(-)}{Me} \\ \diagdown \quad / \\ N \\ / \\ R_3Si \end{array} \quad \overset{(+)}{Don} $				
				(Don = donor molecule)				
No.	Me	R ₃ Si	R' ₃ Si	Donor	B.P.	Torr	M.P.	Reference
Group I								
1	Li	me ₃ Si			115°	1	70–72°	(146, 149)
2	Li	me ₃ Si	et ₃ Si		162–164°	2	—	(149)
3	Na	me ₃ Si			204°	2	183°	(149, 168)
4	Na	me ₃ Si ₂					58–62°	(157)
5	Na	(meO) ₃ Si					182–184°	(156)
6	Na	(etO) ₃ Si					104°	(156a)
7	Na	(^t prO) ₃ Si					204–206°	(156a)
8	Na	me ₂ (etO)Si					97°	(162a)
9	Na	me(meO) ₂ Si					171–172°	(162a)
10	Na	vi(meO) ₂ Si					184°	(162a)
11	Na	me(^t prO)viSi					70°	(162a)
12	K	(meO) ₃ Si					202°	(120)
Group II								
1	Li	me ₃ Si		1 Oet ₂			95–110° (decomp)	(149)
2	Li	me ₃ Si		0.75 OC ₄ H ₉ O			200° (decomp)	(149)
3	Li	ph ₃ Si		1 Oet ₂			380° (decomp)	(149)
4	Na	me ₃ Si		1 Oet ₂			72–74°	(149)
5	Na	me ₃ Si		1 OC ₄ H ₉			70–85° (decomp)	(149)
6	Na	me ₃ Si		0.5 OC ₄ H ₉ O			Charring	(149)
7	Na	me ₃ Si		1 py			150–160° (decomp)	(149)
8	K	me ₃ Si		2 OC ₄ H ₉ O			Charring	(149)

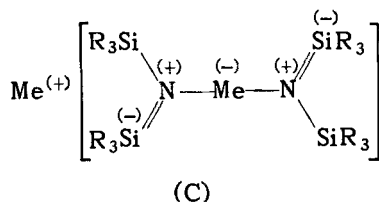
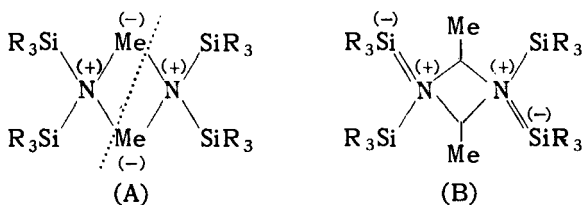
to work up the compounds in an inert atmosphere. The lithium derivatives decompose explosively when heated in a stream of oxygen or treated with concentrated nitric acid. All alkali silylamides burn with a somewhat smoky flame of the characteristic color of the alkali metal and with some of the luminosity due to SiO_2 . Sodium bis(trimethylsilyl)amide, which represents an optimum as regards both stability and reactivity, may be stored in a well-sealed flask and, with rapid manipulation, may be removed with a spatula. Hydrolysis by atmospheric moisture is slow. In solution this occurs on adding water in a rapid first stage:



This is followed by slow conversion of the disilazane to the disiloxane. Acids bring about immediate decomposition to the ammonium ion (149):



Alkali bis(silyl)amides dissolve readily, sometimes extremely readily, in nonpolar organic solvents such as benzene, toluene, and xylene, e.g., 140 gm $(\text{me}_3\text{Si})_2\text{NLi}$ in 100 gm xylene at 30° . In these solutions they are present with few exceptions as dimers and show no conductivity. The ^7Li NMR spectrum shows only a single signal. Autocomplexes (C), such as are formed by the dimeric organolithium compounds are thus clearly excluded; the remaining structural possibilities are a bridge complex (A) and a three-center bond complex (B):



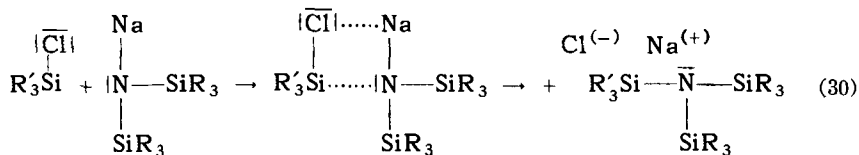
In reactions the dimeric complexes split off. The monomeric units show unusually strongly developed nucleophilic properties and support structure (A). On the other hand, spectroscopic data and the influence of substituents

(R) on the Si atom lead to the conclusion that the free electrons of N are more strongly drawn into the SiN bond than in the case of bis(silyl)amines. A full elucidation of the structures of these compounds (bond angles, bond distances, force constants, and electron distribution) would be valuable in view of their many reactions.

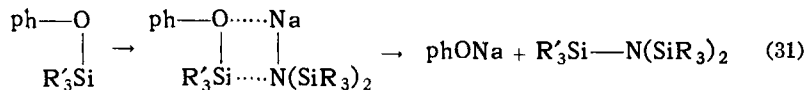
The alkali bis(silyl)amides are not only strongly nucleophilic but, because of the coordinative unsaturation of the alkali atoms which in this case apparently show a strong tendency towards covalency with a maximum coordination number of 2, are also electrophilic reagents. They readily add electron-pair donors such as diethyl ether, tetrahydrofuran, dioxane, and pyridine with, as a rule, one donor molecule per alkali metal atom. When this occurs the dimeric structure is broken down.

Alkali bis(silyl)amides exhibit a wealth of possible reactions which are certainly not fully explored at present. In explaining them it is simplest to represent the compounds by the monomeric formulas and to consider them as reacting by a four-center mechanism, when their nucleophilic and electrophilic properties are both operative and appear to induce analogous polar structures in the reaction partners.

Among the nonmetallic halides and all other halides which are not salt-like in structure, the reactions with halosilanes are the most clearly defined; as a rule it suffices to heat under reflux in a high-boiling hydrocarbon as solvent. Yields are high. Whereas previously amines substituted by three silyl groups were accessible only when RSiH_2 units were available, over sixty tris(silyl)amines of the most varied types have now been made from alkali bis(silyl)amides by Reaction 30:



Examples are given in Table II. Silyl phenolates ($\text{R}_3\text{Si}-\text{Oph}$) react analogously, whereas "silyl alcoholates" ($\text{R}_3\text{Si}-\text{Oalk}$) remain unattacked:



The halides of other elements react similarly in so far as they possess free *p* or *d* orbitals: otherwise the reaction is more complicated (as with CCl_4 or CHCl_3). However, R_3SiCl is often split off in addition to NaCl . If a di- or trichloride is used, reaction can go in two ways for the same mole-

TABLE II
 THE KNOWN TRIS(SILYL)AMINES^{a,b}

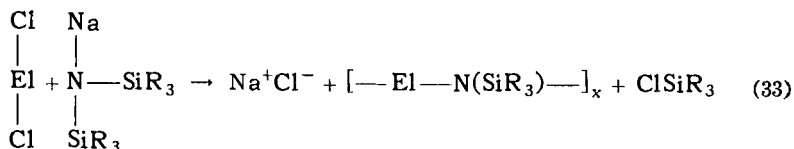
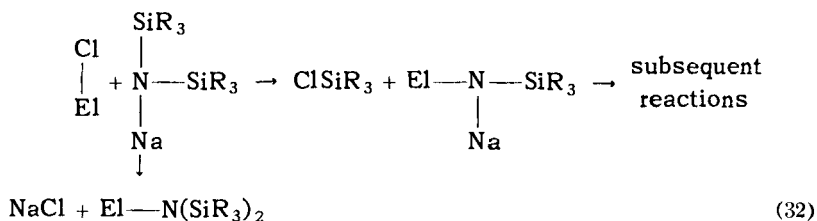
Type	Substituent ^c
N(SiR ₃) ₃	R = H, Cl, me, Ome, Oet, O ⁱ pr
N(SiR ₂ R') ₃	R = H; = Ome; = me R' = me, SiH ₃ ; = me, vi; = Oet
N(SiRR'R'') ₃	R = me; R' = vi; R'' = O ⁱ pr
N(SiR ₃)(SiR' ₃)(SiR'' ₃)	R = me; R' = et; R'' = pr
(me ₃ Si) ₂ N-SiR ₃	R = H, F, Cl, Br, I, me, pr, Ome
(me ₃ Si) ₂ N-SiRCl ₂	R = me, vi, pr, ch, ph
(me ₃ Si) ₂ N-SiRX ₂	R = me, ph; = vi X = OH, Ome, NH ₂ ; = Ome
(me ₃ Si) ₂ N-Si(me) ₂ X	X = Si(me) ₃ , NH ₂ , Net ₂ , N[Si(me) ₃] ₂ , OH, Ome, Cl
(me ₃ Si) ₂ N-SiRR'Cl	R = ph; R' = me, ph, NH ₂
[(RO) ₃ Si] ₂ N-SiR'Cl ₂	R = me; = et; = ⁱ pr R' = pr, vi, Cl; = Cl; = me, vi, Cl
(R ₂ R'Si) ₂ N-SiR'' ₃	R = Ome; R' = vi; R'' = me, Ome, Cl = et; = Ome, Cl
(R ₂ R'Si) ₂ N-SiR'' ₂ R'''	R = Ome; R' = me, vi; R'' = Cl; R''' = me, vi = me; = Oet; = me; = Cl, Net ₂
(RR'R'') ₂ N-SiRR'R'''	R = me; R' = vi; R'' = O ⁱ pr; R''' = Cl, O ⁱ pr

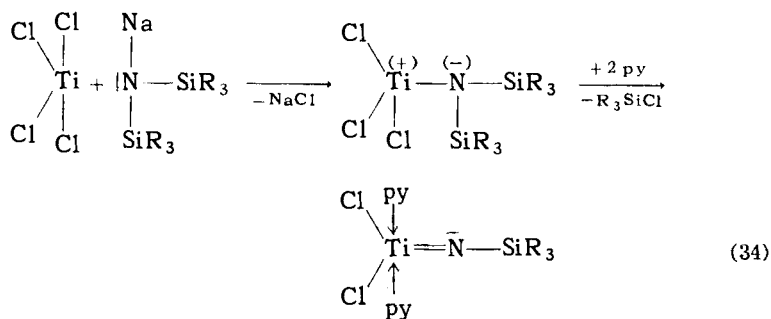
^a References: 34a, 52, 102, 105, 136, 146, 147, 149, 151, 156, 156a, 157, 160, 162, 162a, 164, 165, 171.

^b Spring, 1963.

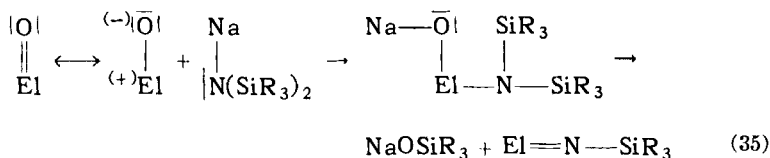
^c Abbreviations: me = CH₃; et = C₂H₅; pr = CH₂CH₂CH₃; ⁱpr = CH(CH₃)₂; ch = C₆H₁₁ (cyclohexyl); vi = CHCH₂; ph = C₆H₅; py = NC₅H₅ (pyridine); dp = N₂C₁₀H₈ (α,α'-dipyridyl); alk = alkyl; ar = aryl; Me = univalent metal.

cule, leading to a polymeric structure or to formation of a double bond (Reactions 33 and 34):

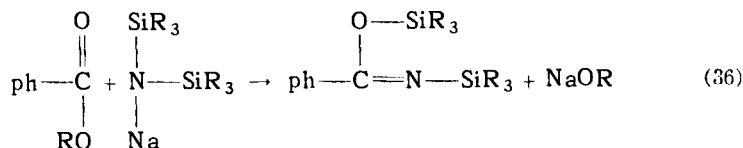




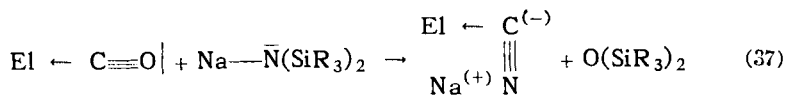
Doubly bonded oxygen is exchanged for silylamino groups:



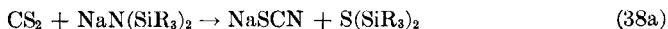
Ketones such as benzophenone, fluorenone, and benzoquinone may be transformed in this way into the analogous *N*-silyl-ketimines. From CO₂ or COCl₂, bis(silyl)carbodiimide results, while SO₂ or SOCl₂ yield the analogous diimide of quadrivalent sulfur. Benzoic esters, on the other hand, are transformed into *N,O*-bis(silyl)benzimidic acids:



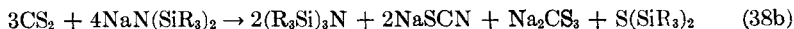
Carbonyls are converted to the corresponding cyanides with loss of disiloxane:



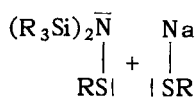
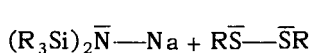
Carbon disulfide reacts essentially according to the equation:



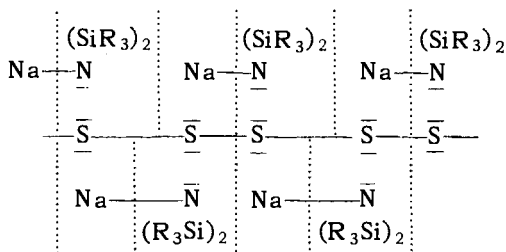
In addition, the following reaction takes place:



Sulfur chains are cleaved:



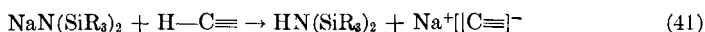
(39)



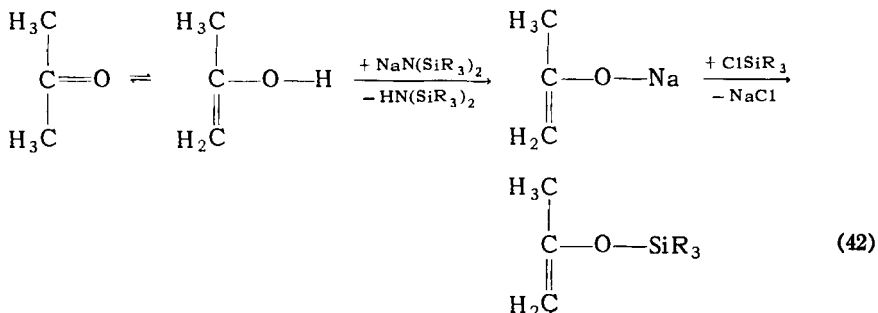
(40)

The S_8 ring with $\text{NaN}(\text{SiR}_3)_2$ in excess gives $(\text{R}_3\text{Si})_2\text{N}-\text{S}-\text{Na}$, while with a deficit of the reagent derivatives such as $(\text{R}_3\text{Si})_2\text{N}-\text{SSS}-\text{Na}$ are formed.

The metallating properties of sodium bis(trimethylsilyl)amide are particularly strongly developed in exchanges with "active" hydrogen atoms bonded to carbon:



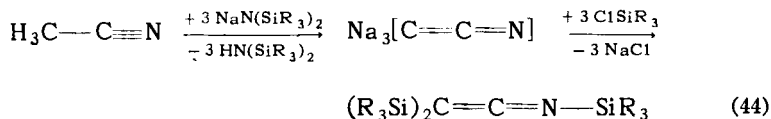
Enolic structures in tautomeric equilibrium with ketones are easily fixed:



Sterically hindered Claisen or Stobbe condensations take place in good yield when using $\text{NaN}(\text{SiR}_3)_2$:



Acetonitrile is thrice metallated:



In Wittig reactions, $\text{NaN}(\text{SiR}_3)_2$ may also be used with advantage:

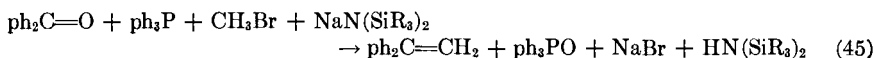
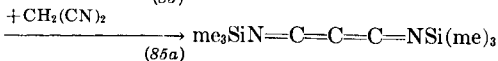
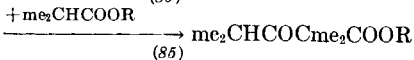
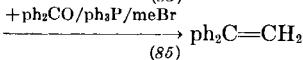
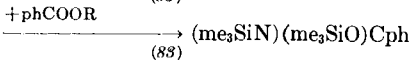
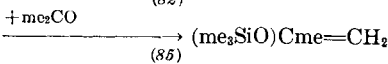
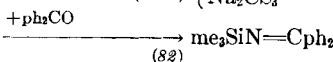
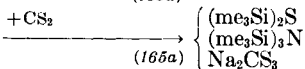
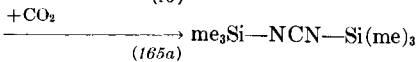
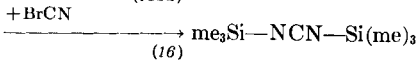
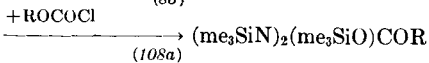
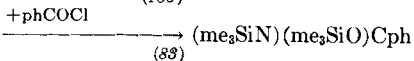
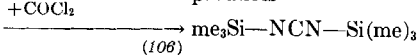
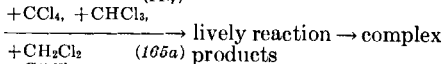
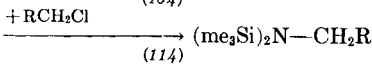
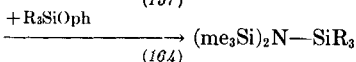
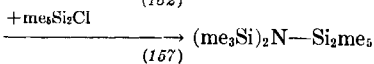
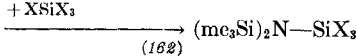
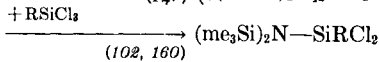
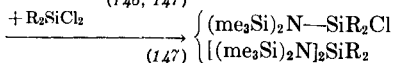
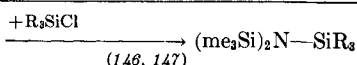
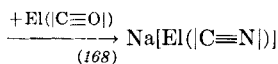
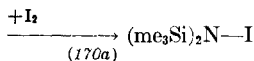
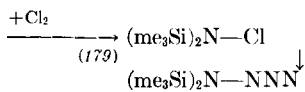
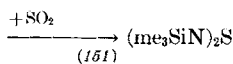
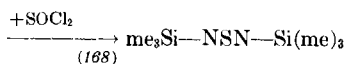
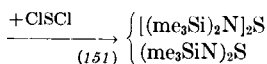
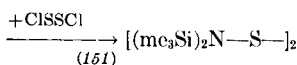
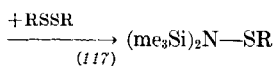
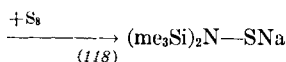
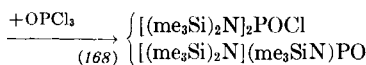
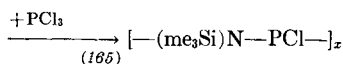
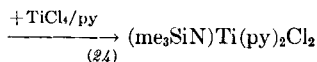
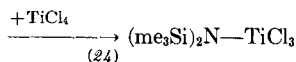
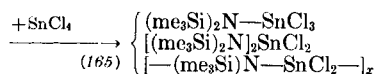
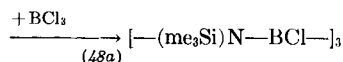
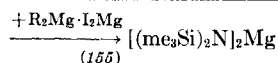


TABLE III
REVIEW OF THE REACTIONS OF SODIUM BIS(TRIMETHYLSILYL)AMIDE

$(\text{me}_3\text{Si})_2\text{NNa}$



A summary of the most important reactions carried out to the present with sodium bis(trimethylsilyl)amide is given in Table III.

IV. Silicon-Nitrogen Compounds with Nitrogen in a Higher Oxidation State Than —3

The versatility of nitrogen in its compounds depends in large measure on the existence of a range of oxidation states between —3 and +5. In its combination with silicon, systems are known in which N has an oxidation state of —2, as in the derivatives of hydrazine, H_2NNH_2 ; of —1, as in derivatives of hydroxylamine, H_2NOH , or diimine, $\text{HN}=\text{NH}$ (diazene); and —1/3, as in derivatives of hydrazoic acid, HN_3 :

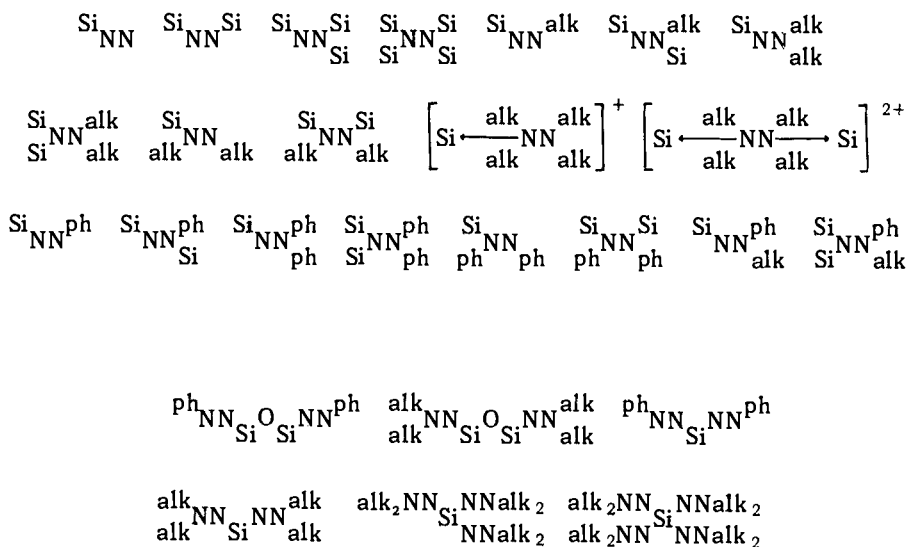


On the other hand, compounds where N has an oxidation state of +1 or +3, as in $\geq\text{Si}-\text{N}=\text{O}$ or $\geq\text{Si}-\text{NO}_2$, have not yet been prepared.

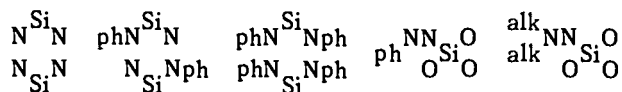
A. SILICON-HYDRAZINE COMPOUNDS

1. Survey

The preparative objectives of replacing H atoms in H_2NNH_2 by Si atoms and the halogen atoms in $\text{Si}(\text{hal})_4$ by hydrazino groups have been largely realized. The following structural units have so far been synthesized with H, alk ($=\text{C}_n\text{H}_{2n+1}$; $n=1-3$), or ph ($=\text{C}_6\text{H}_5$) attached to Si and H on the N atoms (in all cases where alk or ph is not so shown).



continued



Synthesis of the following missing members of this systematic series should only be a matter of time:

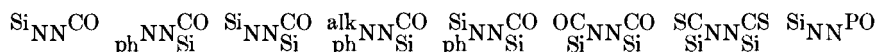


For the following it seems likely that new preparative methods will have to be found:



So far only one representative Si derivative has been discovered (4) for the hydrazinium(1+) and (2+) ions, $[\text{N}_2\text{H}_5]^+$ and $[\text{N}_2\text{H}_6]^{2+}$; silicon halides seem to show little tendency to add to hydrazine.

A series of silyl derivatives of the acid hydrazides has been prepared, particularly from hydrazides of carbonic acid (153) and, in one case, also of phosphoric acid (9). The compounds with the structural units shown below [PO denotes $-\text{P}(=\text{O})$; CO denotes $-\text{C}(=\text{O})-$] are difficult to obtain in the pure state and are very sensitive to hydrolysis:

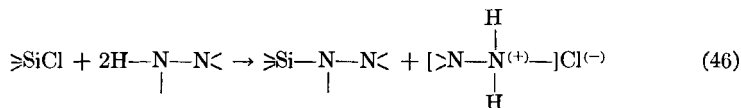


Silyl derivatives of organolithium hydrazides have been prepared many times but actually isolated only in the case of $\text{mesSi}^{\text{NN}}\text{Li}^{\text{ph}}$ (152). Normally they are converted, without isolation, into multiply substituted silyl hydrazines. In almost all known silicon-hydrazine compounds, the residual silicon valencies are saturated with hydrogen atoms or organic groups; in only a few cases is silicon simultaneously bonded to oxygen (101, 143, 166).

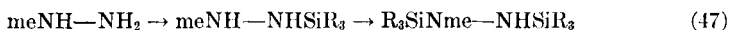
2. Preparation of Silyl Hydrazines

The methods used are essentially the same as for amines.

a. Reactions of Hydrazine with Halogenosilanes. In inert organic solvents or in the gas phase (19) these reactions occur exothermally, half of the hydrazine being fixed as hydrochloride:



In that way only *one* Si group can be bonded to one N atom of the hydrazine. Methyl groups on the same N atom do not interfere with the substitution, though a free NH_2 group will be substituted first (65, 144):



Phenyl groups, like silyl groups (except SiH_3), allow no further silyl substitution on the same N atom. Primary silyl hydrazines with $\text{R} = \text{me}$, et , or pr cannot be isolated as they immediately undergo further condensation to symmetrical bis(silyl)hydrazines with elimination of hydrazine (19, 141, 142):



For the readily isolated $\text{ph}_3\text{SiNHNH}_2$ this condensation occurs under more drastic conditions (142). The use of mixtures of chlorosilanes such as $\text{me}_3\text{SiCl}/\text{et}_3\text{SiCl}$ with hydrazine leads to a mixture of $\text{me}_3\text{SiNHNHSime}_3$, $\text{me}_3\text{SiNHNHSiet}_3$, and $\text{et}_3\text{SiNHNHSiet}_3$ in statistical proportions (142). Hydrazine is converted by H_3SiI directly into the fourfold silyl-substituted derivative $(\text{H}_3\text{Si})_2\text{NN}(\text{SiH}_3)_2$ (3). It has not so far been possible to prepare other fourfold silyl-substituted hydrazines, probably because of steric hindrance by the bulky alk_3Si groups. Dihalogenosilanes react with terminally substituted hydrazines to form compounds of Class IVb (101, 129, 143).



With hydrazine itself, six-membered rings, $[\text{—R}_2\text{SiNHNH}]_2$, are formed together with polymers in which the structural unit $\text{—R}_2\text{SiNHNH—}$ predominates (19, 101, 141). In condensations of silyl hydrazines according to the scheme: $2\text{>SiNN<} \rightarrow \text{>SiNNSi<} + \text{>NN<}$, the tendency for reaction to occur has been defined qualitatively as:

$\text{me}_3\text{SiNHNH}_2$ (strong) $>$ $\text{me}_3\text{SiNHNHme}$ (weak) $>$ $\text{me}_3\text{SiNHNme}_2$ (very small);

$\text{R}_2\text{Si}(\text{NH}_2)_2 < \text{R}_2\text{Si}(\text{NHNH}_2)_2 > \text{R}_3\text{SiNHNH}_2$; $\text{alk}_2\text{Si}(\text{NHNHR})_2 <$
 $\text{alk}_2\text{Si}(\text{NHNH}_2)_2 > \text{ar}_2\text{Si}(\text{NHNH}_2)_2$

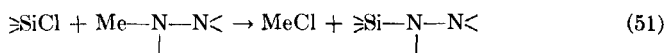
(101, 144).

b. Reaction of Hydrazines with Silylamines. This reaction occurs according to the equation:

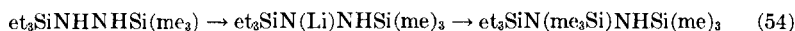
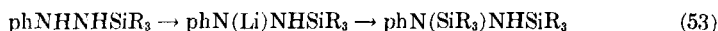


in satisfactory yield only in presence of small quantities of $(\text{NH}_4)_2\text{SO}_4$ as catalyst (40, 130). Since $(\text{me}_3\text{Si})_2\text{NH}$ must first be prepared from me_3SiCl , the reaction using method (b) is more expensive than when (a) is used. It can be employed, however, with advantage for valuable hydrazines, since the loss due to forming the hydrazine hydrochloride is eliminated. Silylation with $(\text{me}_3\text{Si})_2\text{NH}$ or me_3SiNHme has also been carried out with varying success for $(\text{phO})_2\text{PO}(\text{NHNH}_2)$ and $\text{NH}_2\text{CONHNH}_2$ (9, 153).

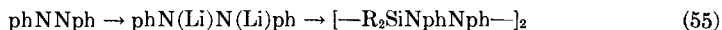
c. Reaction of Metallated Hydrazines with Halogenosilanes. The reaction according to the equation



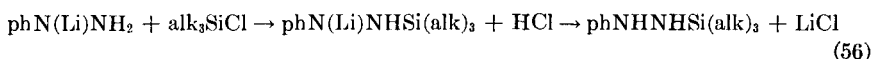
leads to silyl substitution also on such N atoms as already carry a silyl or phenyl group (146, 148, 152):



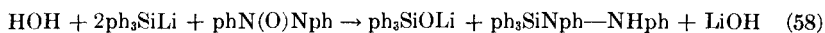
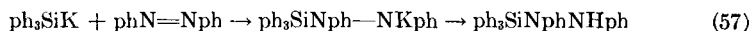
Metallation takes place for $\text{phNH}-\text{N}<$ more readily than for $\text{R}_3\text{SiNH}-\text{N}<$, and for $\text{et}_3\text{SiNH}-\text{N}<$ more readily than for $\text{mc}_3\text{SiNH}-\text{N}<$. Alkyl lithiums and aryl lithiums (prLi, buLi, phLi) are particularly suitable as metallating agents for hydrazine derivatives; NaNH_2 in benzene suspension, which is effective for metallating silyl-amines, causes cleavage of the N—N bond. Further silyl substitution may be brought about most readily by adding the solution of the metallated silyl hydrazine dropwise to the halosilane in question. Reaction of hydrazines doubly metallated in the N, N' positions, which may be prepared by e.g., addition of Li to azobenzene, with dihalosilanes R_2SiCl_2 gives mainly six-membered rings (47, 101):



Metallation of phenylhydrazine to $\text{phN}(\text{Li})\text{NH}_2$ and subsequent reaction with trialkylchlorosilanes leads, not to N -phenyl- N -trialkylsilyl hydrazine, but to N, N' isomers, presumably according to the equation:



d. Addition of Triorganosilyl Alkalis to Azobenzene or Azoxybenzene. The addition and subsequent careful hydrolysis take place according to the equations (48, 181):



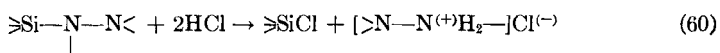
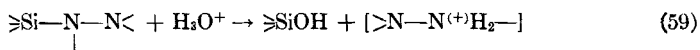
Reduction of azoxybenzene and addition of ph_3SiLi to the intermediate phNNph occur simultaneously, leading to the silyl hydrazines IVa/34 and IVa/35.

3. Properties of Silyl Hydrazines

The majority of the known silyl hydrazines are colorless mobile liquids, which sometimes smell like camphor or the silyl-free hydrazine. They may

be distilled readily in vacuum and are not sensitive to heat; explosive decompositions have never been observed. Silylation as a rule raises the boiling point very little [b.p./12mm of phNHNH_2 , 120° ; of $\text{phNHNHSi}(\text{me})_3$, 117° ; of $\text{phN}(\text{me}_3\text{Si})\text{—NHSi}(\text{me})_3$, 123°]; there is clearly a balance between the increase in the mass of the molecule and the decrease in the tendency to association due to the breaking of hydrogen bridges between —NH— units. Melting points of trialkylsilyl hydrazines are usually very low, below -100° . Triphenylsilyl hydrazines, on the other hand, are solid white substances at room temperature.

Most silyl hydrazines of Class IVa are readily soluble in the usual organic solvents and are not particularly sensitive to moisture. They are, however, readily cleaved solvolytically by acids or by hydrogen chloride in ether:



They inflame with concentrated HNO_3 and explode with fuming HNO_3 ; $(\text{H}_3\text{Si})_2\text{NN}(\text{SiH}_3)_2$ oxidizes explosively on exposure to air. All other silyl hydrazines burn with a luminous white smoky flame. Chloranil oxidizes $\text{me}_3\text{SiNHNHSi}(\text{me})_3$ in a vigorous reaction to N_2 and $\text{me}_3\text{SiSi}(\text{me})_3$ (19); $\text{et}_3\text{SiNHNHph}$ and $\text{pr}_3\text{SiNHNHph}$ are colored deep blue by exposure to atmospheric oxygen (144, 158).

Substances of types IVb and IVd are particularly sensitive to protolysis. Even traces of water transform the bis(hydrazino)silanes IVb/8 and IVb/9 into the hydrazinodisiloxanes IVc/1 and IVc/2. The polysildiazanes $(\text{—me}_2\text{Si—NHNH—})_x$ corresponding with the polysilazanes, which are viscous oils or glassy products of molecular weight ca. 3000 formed by reaction of me_2SiCl_2 with N_2H_4 , show chain cleavage due to hydrolysis and oxidation, even during careful preparation (101). A number of compounds of type IVd also cannot be obtained in a pure state.

Silyl hydrazines have reducing properties. When a Si—H bond is present, as in $\text{RSiH}(\text{NHNHR}_2)_2$ (IVb/1), they may have very strong reducing properties, e.g., they will convert Cu^{2+} to Cu in the cold, $[\text{Ag}(\text{NH}_3)_2]^+$ to Ag , and Hg^{2+} to Hg_2^{2+} and Hg . There is a parallel increase in reactivity with hydroxyl groups: IVa/11 is decomposed by alkalis to H_2 , $\text{H}_2\text{SiO}_4^{2-}$, and N_2H_4 , and IVb/1 reacts explosively with water or alcohols (3, 129).

Silyl hydrazines with H atoms still linked to N react with phenyl isocyanate and as a rule only one phNCO is added per N atom:

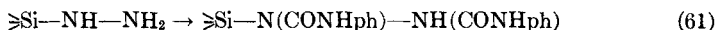


TABLE IV
SILICON-HYDRAZINE COMPOUNDS(IV)

<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> $\begin{array}{c} \text{R}^1 \quad \text{R}^3 \\ \quad \\ \text{[N} - \text{N]} \\ \quad \\ \text{R}^2 \quad \text{R}^4 \end{array}$ <p>IVa</p> </div> <div style="text-align: center;"> $\begin{array}{c} \text{R}^3 \quad \text{H} \quad \text{R}^1 \quad \text{H} \quad \text{R}^3 \\ \quad \quad \quad \quad \\ \text{[N} - \text{N} - \text{Si} - \text{N} - \text{N]} \\ \quad \quad \quad \quad \\ \text{R}^4 \quad \text{R}^2 \quad \text{R}^4 \end{array}$ <p>IVb</p> </div> <div style="text-align: center;"> $\left[\begin{array}{c} \text{R}^3 \quad \text{H} \quad \text{R}^1 \\ \quad \quad \\ \text{[N} - \text{N} - \text{Si} - \\ \quad \\ \text{R}^4 \quad \text{R}^2 \end{array} \right]_2 \text{O}$ <p>IVc</p> </div> <div style="text-align: center;"> $\begin{array}{c} \text{R}_2 \quad \text{R}_3 \quad \text{[O]} \quad \text{H} \\ \quad \quad \quad \\ \text{[N} - \text{N} - \text{C} - \text{N]} \\ \quad \quad \quad \\ \text{R}_1 \quad \quad \quad \text{R}_4 \end{array}$ <p>IVd</p> </div> </div>												
No.	R ¹	R ²	R ³	R ⁴	M.P.	B.P.	Torr	n _D	°C	D ₄	°C	Prep. Eqn. Reference
Group IVa												
1	H	H	H	ph ₃ Si	92°	—	—	—	—	—	—	(46) (141, 142)
2	me ₃ Si	H	H	me ₃ Si	—	153–154°	732	1.4177	26	—	—	(50) (19, 40)
					–137°	69–70°	40	1.4268	22	0.8165	21	(46) (141, 142)
3	et ₃ Si	H	H	me ₃ Si	–126°	122°	40	1.4422	17	0.8418	22	(46) (141, 142)
4	et ₃ Si	H	H	et ₃ Si	–123°	161–162°	40	1.4560	20	0.8595	23	(46) (19, 142)
5	pr ₃ Si	H	H	pr ₃ Si	–105°	189–190°	20	1.4562	24	0.8480	21	(46) (141, 142)
6	ph ₃ Si	H	H	ph ₃ Si	+140°	—	—	—	—	—	—	(48) (141, 142)
7	me ₃ Si	me ₃ Si	H	me ₃ Si	—	89°	13	1.4442	20	0.8460	24	(51) (146, 148)
8	et ₃ Si	me ₃ Si	H	me ₃ Si	—	126°	9	1.4612	20	0.8723	24	(51) (146, 148)
9	et ₃ Si	et ₃ Si	H	me ₃ Si	–91°	142–145°	3	1.4739	20	0.8950	22	(51) (148)
10	et ₃ Si	me ₃ Si	H	et ₃ Si	–87°	164°	3	1.4764	20	0.8918	21	(51) (146, 148)
11	H ₃ Si	H ₃ Si	H ₃ Si	H ₃ Si ^a	–24°	109.5°	760	—	—	0.83	20	(46) (3)
12	me ₃ Si	H	H	me	—	96–97°	760	—	—	—	—	(47) (144)
13	me ₃ Si	H	me	me ₃ Si	—	73–75°	40	1.3820	19	0.7708	19	(47) (141, 144)
14	me ₃ Si	H	me	me	—	100°	760	1.4018	22	0.7659	20	(46) (130, 144)
15	et ₃ Si	H	me	me	—	55–56°	8	1.4348	20	0.8202	20	(46) (128)
16	pr ₃ Si	H	me	me	—	87–89°	7	1.4405	20	0.8209	20	(46) (128)
17	(^t prO) ₃ Si	H	me	me	—	45–49°	1	1.3980	20	0.9003	20	(51) (166)

18	me ₃ Si	H	et	et		144–145°	760	1.4195	20	0.7948	20	(46)	(128)
19	et ₃ Si	H	et	et		85–87°	11	1.4441	20	0.8340	20	(46)	(128)
19a	et ₂ HSi	H	et	et		79–81°	20	1.4341	20	0.8194	20	(50)	(130)
20	pr ₃ Si	H	et	et		114–115°	10	1.4471	20	0.8301	20	(46)	(128)
21	me ₃ Si	me ₃ Si	me	me		67°	12	1.4390	20	0.8431	19	(51)	(146, 148)
22	me ₃ Si	me	me	H		61–63°	260	1.3818	20	—	—	(46)	(144)
23	me ₂ SiCl	me	me	me ₂ SiCl		43–46°	10 ⁻⁴	—	—	—	—	(46)	(19)
24	me ₃ Si	H	H	ph	21°	114°	10	1.5254	20	0.9574	26	(46) (50)	(144, 152)
												(56)	(19, 40)
25	me ₃ Si	H	H	<i>n</i> meC ₆ H ₄		118°	9	1.5174	20	0.9407	20	(56)	(152)
26	et ₃ Si	H	H	ph		129–130°	1	1.5210	20	—	—	(46) (56)	(144, 152)
27	pr ₃ Si	H	H	ph		145.5°	1	1.4918	20	—	—	(46) (56)	(144, 152)
28	ph ₃ Si	H	H	ph	82°	—	—	—	—	—	—	(46)	(144)
29	(^{<i>i</i>} prO) ₃ Si	H	H	ph	—	104°	1	1.4493	20	0.9692	20	(51)	(166)
30	me ₃ Si	H	ph	me ₃ Si	1°	123°	10	1.5060	20	0.9277	25	(51)	(152)
31	me ₃ Si	H	ph	ph	57–60°	135–138°	1	—	—	—	—	(51)	(148)
32	me ₃ Si	me ₃ Si	ph	ph	—	124–126°	2	1.5720	20	—	—	(51)	(148)
33	me ₃ Si	ph	H	ph	55°	138°	1	—	—	—	—	(51)	(146, 152)
34	ph ₃ Si	ph	H	ph	140–141°							(57) (58)	(48, 181)
35	meSi(ph) ₂	ph	H	ph	119–120°							(58)	(48)
36	ph ₃ Si	ph	ph ₃ Si	ph	265–266°							(57)	(181)
37	me ₃ Si	H	et	ph		113°	10	1.5152	20	0.9329	24	(62)	(148)
38	me ₃ Si	H	ph	phCH ₂	–33°	113°	0.5	1.5645	20	1.0032	20	(62)	(152)
39	me ₃ Si	H	ph	me ₃ C		95–97°	0.5	1.5108	20	—	—	(62)	(152)
40	me ₃ Si	me ₃ Si	et	ph		100°	2	1.5155	20	0.9356	26	(51)	(148)
<hr/>													
Group IVb													
1	H	me	me	me		45°	10	1.4348	20	0.8676	20	(49)	(129)
2	H	me	et	et		103°	19	1.4440	20	0.8636	20	(49)	(129)
3	H	et	me	me		75°	22	1.4392	20	0.8645	20	(49)	(129)
3a	H	et	et	et		103°	7	1.4481	20	0.8646	20	(50)	(130)

TABLE IV (Continued)

No.	R ¹	R ²	R ³	R ⁴	M.P.	B.P.	Torr	n _D	°C	D ₄	°C	Prep. Eqn.	Reference
3b	Cl	et	et	et		111°	4	1.4580	20	0.9611	20	(50)	(130)
4	me	me	me	me		62°	22	1.4298	20	0.8504	20	(49)	(129)
5	me	me	et	et		105°	14	1.4419	20	0.8594	20	(49)	(129)
6	et	et	me	me		85°	12	1.4415	20	0.8648	20	(49)	(129)
7	et	et	et	et		130°	14	1.4530	20	0.8673	20	(49)	(129)
8	ph	ph	me	me	42-43°	191-193°	10	—	—	—	—	(49)	(101, 143)
9	ph	ph	H	ph	105-115°	—	—	—	—	—	—	(49)	(101, 143)
10	meSi(NHNet ₂) ₃					130-131°	6	1.4529	20	0.8935	20	(50)	(130)
11	etSi(NHNet ₂) ₃					134-135°	5.5	1.4578	20	0.8961	20	(50)	(130)
12	Si(NHNet ₂) ₄					153-155°	5.5	1.4587	20	0.9009	20	(50)	(130)
Group IVc													
1	ph	ph	me	me	146-148°	—	—	—	—	—	—	—	(101, 143)
2	ph	ph	H	ph	157-158°	—	—	—	—	—	—	—	(101, 143)
Group IVd													
1	H	H	H	me ₃ Si	80-95°							(61)	(153)
2	me ₃ Si	H	H	me ₃ Si ^b	—							(50)	(153)
3	me ₃ Si	H	me ₃ Si	me ₃ Si	110°							(61)	(153)
4	H	ph	me ₃ Si	ph	ca. 37°							(61)	(153)
5	me ₃ Si	ph	me ₃ Si	ph	oil							(61)	(153)
6	et	ph	me ₃ Si	ph	ca. 5°							(61)	(153)
7	[phNH-CO-N(me ₃ Si)-] ₂				ca. 60°							(61)	(153)
8	[phNH-CS-N(me ₃ Si)-] ₂				214-216°							(61)	(153)
9	me ₃ Si-NHNH-PO(Oph) ₂				53-54°							(50)	(9)

^a Heat of vaporization 8.19 kcal/mole, Trouton's constant 21.4.^b Sublimes at 100-110°/1-2 Torr.

The resulting silyl semicarbazides and silyl-substituted hydrazinodicarbonic anilides of substances of type IVd hydrolyze readily. This allows a differentiation, for example, between the isomers $R_3SiNph-NH_2$ and $R_3SiNH-NHph$. The first will give $phNHNHCONHph$ by $phNCO$ addition and hydrolysis and the second $HN(CONHph)-Nph(CONHph)$. In this way it has been possible to elucidate the position of ph or R_3Si on N or N' in a series of bis(silyl) or phenylsilyl hydrazines (19, 153).

N-Lithium-*N*-phenyl-*N'*-trimethylsilyl hydrazine, $phNLi-NHSi(me)_3 \cdot Oet_2$, separates from ether in large colorless crystals which immediately turn blue in air and may inflame. Here and in all other cases where the $LiCl$ formed in the metallation reactions (Section IV,A,2,c) contains some undecomposed lithiumsilyl hydrazide, it is necessary to anticipate ignition during filtration or centrifugation if air is admitted. The lithiumsilyl hydrazides react not only with halosilanes but also with organic halides (152).



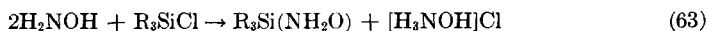
(where $R = et, me_3C, phCH_2$). Oxidation with Br_2 or I_2 leads to the deep blue silyldiazenes $R_3Si-N=N-R$ (158). The properties of SiN rings with $SiNN$ structural units are dealt with in Section VI.

Little is known of the physical properties and detailed structures of the silyl hydrazines apart from the usual determinations of melting point, boiling point, density, refractive index, and molecular refraction. Infrared and Raman measurements on $(H_3Si)_2NN(SiH_3)_2$ and $(D_3Si)_2NN(SiD_3)_2$ have shown a staggered D_{2d} configuration and not a planar framework Si_2NNSi_2 . The ν_{as} $SiN(Si)$ vibrational frequencies lie at $1026-1013\text{ cm}^{-1}$ and are unusually high (5).

In the Si hydrazine compounds the free electron pair on N is considerably involved in $p_\pi-d_\pi$ bonding, as in other SiN compounds. No quantitative study has yet been made of the basicity of these compounds or of reactions with strong Lewis acids.

B. SILICON-HYDROXYLAMINE COMPOUNDS

Hydroxylamine, H_2NOH , does *not* react with trialkylchlorosilanes in a manner analogous to hydrazine, N_2H_4 , in spite of the structural relationship. It might be expected that a monosilyl-substituted derivative $R_3Si(NHOH)$ would first be formed and that this would lose hydroxylamine and condense to bis(silyl)hydroxylamine, $R_3SiNHOSiR_3$, which after metallation could be transformed into a tris(silyl)hydroxylamine, $(R_3Si)_2NO(SiR_3)$. The exothermic reaction

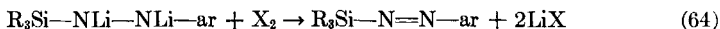


(where R = me, et, ph; and ether suspension is at 0°) stops, however, at the stage shown, even when the proportions of reactants are varied, giving a simple silyl-substituted hydroxylamine (154, 186). Infrared and NMR studies show that of the three possible isomeric structures (a) $\text{H}_2\text{N}-\text{O}-\text{SiR}_3$, (b) $\text{R}_3\text{Si}-\text{NH}-\text{OH}$, and (c) $\text{R}_3\text{Si}-\text{N}^{(+)}\text{H}_2-\text{O}^{(-)}$, (c) is the most probable (154).

The trialkylsilyl hydroxylamines are colorless liquids which are miscible with the usual organic solvents, can be stored in ampoules without decomposition, and do not decompose when heated to their boiling points. The case for structure (c) is supported by their sensitivity to hydrolysis (no stabilization of the SiN bond by the $p_\pi-d_\pi$ component) and by the reactions with phNCO (154), CH_2CO and $\text{CH}_2\text{CHCOOR}'$ (186). These lead to the corresponding doubly substituted hydroxylamine derivatives via the silylated derivatives $(\text{phNHCO})\text{N}(\text{SiR}_3)\text{O}(\text{CONHph})$, $(\text{CH}_3\text{CO})\text{N}(\text{SiR}_3)\text{O}(\text{COCH}_3)$, and $(\text{R}'\text{OCOCH}_2\text{CH}_2)\text{N}(\text{SiR}_3)\text{O}(\text{CH}_2\text{CH}_2\text{COOR}')$ after hydrolytic cleavage of the silyl group. Hydrogen chloride in benzene brings about cleavage to R_3SiCl and $[\text{H}_3\text{NOH}]\text{Cl}$. The hydrolyzates reduce $[\text{Ag}(\text{NH}_3)_2]^+$ and give a positive benzhydroxamic acid reaction.

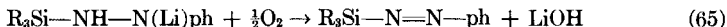
C. SILICON DIAZENES

Trialkylsilyl groups when bonded to an N atom behave like aromatic organic groups in many cases. In spite of many attempts, silicon compounds of the type $\text{R}_3\text{Si}-\text{N}=\text{N}-\text{SiR}_3$, analogous to the organic azo compounds $\text{ar}-\text{N}=\text{N}-\text{ar}$, have not yet been isolated. Even the mixed diazenes $\text{R}_3\text{Si}-\text{N}=\text{N}-\text{ar}$ are markedly unstable, although they are formed from the analogous hydrazines $\text{R}_3\text{Si}-\text{NH}-\text{NH}-\text{ar}$ on exposure to air and are recognized by a deep blue color on the surface (144). They may be obtained in yields up to 30% by the reaction below, after a complicated processing of the reaction mixture (158):

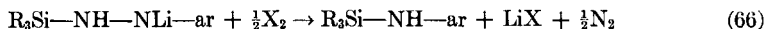


(where X = Br, I; R = me, et, pr; ar = ph, $p\text{-C}_6\text{H}_4(\text{CH}_3)$; at $< -30^\circ$ in ether).

A less useful reaction is:



The trialkylsilylaryl diazenes VI/1-4 cannot be obtained pure in spite of repeated distillation. They are always contaminated by 10-60% of trialkylsilylaryl amines formed in the secondary reaction



Studies of the ESR, NMR, ultraviolet, infrared, and Raman spectra lead to the conclusion that they are diazenes and not hydrazyl radicals,

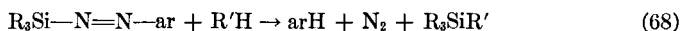
$R_3Si-NH-\dot{N}-ar$ (84). The deep blue compounds show strong absorption at 575–585 $m\mu$ and at 275 $m\mu$ in the ultraviolet. They are quite stable thermally and may be stored for years in sealed ampoules; there is only slight decomposition to N_2 and $arSiR_3$ on distillation. The most stable and easiest to prepare in a pure state is tripropylsilylphenyldiazene, VI/3.

The compounds are, however, uncommonly sensitive to the solvolytic reagents. Ether or benzene solutions of $me_3SiNNph$ are decolorized on standing for a few days. Solvolytic cleavage occurs as follows:



(where $R = me, pr$; $R' = OH, Ome, Cl, phCOO$).

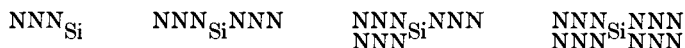
A secondary decomposition reaction is:



Hydrogenation with hydrogen over a palladium catalyst sometimes leads quantitatively to $R_3SiNHNHar$ ($R = pr, ar = ph$) with formation sometimes of up to 50% of $R_3SiNHar + \frac{1}{2}N_2$ ($R = me, ar = ph$) (159).

D. SILICON AZIDES

Since the earlier preparation (1954) of silicon tetraazide $Si(N_3)_4$ (175), this type of compound has been studied in more detail only recently after it had been established that most compounds of this group did not possess the extraordinarily explosive character of organic azides, but had a fairly high thermal stability. Derivatives with 1, 2, 3, and 4 azido groups on one Si atom are known; other substituents on Si are H, me, ph, and Cl:



Silyl azides may be prepared by the following methods:

a. *Cleavage of a Si-N Bond with Hydrazoic Acid.* Cleavage occurs according to the equation:



Dibutyl ether is a suitable solvent. The compounds $(H_3Si)_3N$, $(H_3Si)_2N$ et (36), and $(me_3Si)_2NH$ (17) have been decomposed in this way. Liberation of H_2 from SiH and HN_3 is not observed, not even with SiH_4 (175).

b. *Reaction of Halosilanes with Alkali Azides.* Reaction is according to the equation:



These reactions are favored by catalytic quantities of Al_2Cl_6 , $LiAlH_4$, or AlH_3 (175) and occur within 1–3 days in high yield at room temperature

TABLE V
SILICON-HYDROXYLAMINE COMPOUNDS(V), SILICON DIAZINES(VI), AND SILICON AZIDES(VII)

<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> $\begin{array}{c} \text{H} \\ \\ \text{R}_3\text{Si}-\text{N}^{(+)}-\text{O}^{(-)} \\ \\ \text{H} \\ \text{Va} \end{array}$ </div> <div style="text-align: center;"> $\begin{array}{c} \text{R}' \\ \\ \text{R}_3\text{Si}-\text{N}-\text{O}-\text{R}' \\ \text{Vb} \end{array}$ </div> <div style="text-align: center;"> $\text{R}_3\text{Si}-\text{N}=\text{N}-\text{R}'$ </div> <div style="text-align: center;"> $\begin{array}{c} \quad \\ -\text{Si}-\text{N}-\text{N}\equiv\text{N} \leftrightarrow -\text{Si}=\text{N}=\text{N}=\text{N} \\ \quad \end{array}$ </div> </div>										
No.	Compound	M.P.	B.P.	Torr	n_D	°C	D_4	°C	Prep. Eqn.	Ref.
Group V (R' = phNHCO—)										
1	me ₃ SiNH ₂ O ^a	−77°	100°	760	1.4051	20	0.8572	20	(63)	(154, 186)
2	et ₃ SiNH ₂ O ^a	−65°	172°	760	1.4392	20	0.8876	20	(63)	(154)
3	ph ₃ SiNH ₂ O	59°							(63)	(154)
4	me ₃ SiN(R')O(R')	128–138°							(B)	(154)
5	et ₃ SiN(R')O(R')	79–81°							(B)	(154)
Group VI ^b										
1	me ₃ SiNNph	(−72°	78°	6	1.5190	20	0.9304	29)	(64)	(158)
2	et ₃ SiNNph		(106°	8	1.5140	20)			(64)	(158)
3	pr ₃ SiNNph		(130°	4	1.5065	20	0.9061	24)	(64)	(158)
4	me ₃ SiNNC ₆ H ₄ ² me		(108°	7	1.5225	20)			(64)	(158)
Group VII										
1	H ₃ SiNNN	−81.8°	~28°	760					(69)	(36)
2	me ₃ SiNNN ^a	−95°	87–96°	760					(69) (70) (Dd)	(17, 27, 138)
3	meCl ₂ SiNNN	—	100.5°	760					(70)	(137)
4	me ₂ phSiNNN	—	70°	0.15					(70)	(173)
5	ph ₃ SiNNN	81°	—	—					(70)	(173, 178)

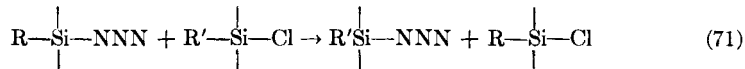
6	$\text{me}_2\text{Si}(\text{NNN})_2$	144.3°	760			(70) (71)	(138)
7	$\text{meClSi}(\text{NNN})_2$	47°	20			(70)	(137, 138a)
8	$\text{ph}_2\text{Si}(\text{NNN})_2$	85–90°	10^{-3}	1.5887	20	(70)	(138a, 177)
9	$\text{meSi}(\text{NNN})_3$	~70–73°	20			(70)	(137, 138a)
10	$\text{phSi}(\text{NNN})_3$	63°	0.01			(71)	(137)
11	$\text{Si}(\text{NNN})_4$	Crystalline				(70)	(175)
12	$(\text{me}_3\text{Si})_2\text{NNNN}$	40–42°	11			(D)	(179)

^a Vapor pressure curve (log P Torr): V/1 $-2011/T + 8,265$; V/2 $-2499/T + 8,500$; VII/2 $-1915/T + 8,102$. Heat of vaporization (kcal/mole): V/1, 9.2; V/2, 11.42. Trouton's Constant: V/1, 24.6; V/2, 25.7.

^b VI/1 contaminated with 25% me_3SiNHph ; VI/2 with 60% et_3SiNHph ; VI/3 with 10% pr_3SiNHph ; VI/4 with ca. 50% $\text{me}_3\text{SiNHC}_6\text{H}_4\text{CH}_3$.

in pyridine, tetrahydrofuran, benzene, or at 230–250° in ZnCl_2/KCl salt melts (138).

c. Exchange Reactions on Si Atoms. Exchange occurs according to the equation

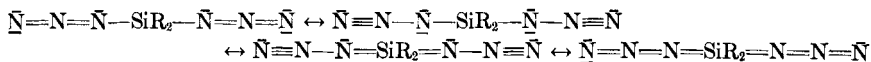


in presence of Al_2Cl_6 and under reflux quantitatively between me_3SiNNN and me_3SiCl_2 , as well as with phSiCl_3 (137, 138).

d. Thermal Decomposition of Tetrazoles. Thermal decomposition of 1-trimethyl-silylamino-3-trimethylsilyltetrazole leads, among other products, to me_3SiNNN and $\text{me}_3\text{SiNCNSi}(\text{me})_3$ (17).

Silicon azides with one or two azido groups are thermally stable up to 300°. As a rule they decompose slowly from 500° with loss of nitrogen. They are not sensitive to shock and explode only when ignited. Pyrolysis of me_3SiNNN or decomposition in the light from a mercury arc leads to H_2 , N_2 , CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , HCN , HN_3 , NH_4N_3 , and nonvolatile polymers (27). Nitrogen is split off in ultraviolet light even at room temperature. In contrast to the compounds VII/2–8, H_3SiNNN decomposes slowly on storage with evolution of SiH_4 (36). The compounds ph_3SiNNN and $\text{ph}_2\text{Si}(\text{NNN})_2$ react with triphenylphosphine in boiling ether with loss of N_2 and formation of the stable compounds $\text{ph}_3\text{Si}-\text{N}=\text{Pph}_3$, m.p. 211–213°, and $\text{ph}_3\text{P}=\text{N}-\text{Si}(\text{ph})_2-\text{N}=\text{Pph}_3$, m.p. 190–191° (177). Phenyltriazidosilane, $\text{phSi}(\text{NNN})_3$, may be distilled at 63° in high vacuum without decomposition; $\text{meSi}(\text{NNN})_3$ and $\text{Si}(\text{NNN})_4$, on the other hand, detonate (137, 175). All silicon azides are sensitive to hydrolysis.

The infrared spectrum of silicon azides shows a characteristic ν_s NNN frequency at 1290–1325 cm^{-1} ; SiN vibrations have not been recorded. From the microwave spectrum an angular structure for H_3SiNNN has been unexpectedly deduced (36); $p_\pi-d_\pi$ bonding between Si and N must therefore be either absent or only weakly developed. The thermal stability of mono- and bis(azido)silanes has been attributed to resonance between structures such as:

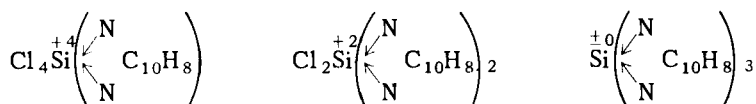


Reaction of lithium azide with bis(trimethylsilyl)chloramine (tetrahydrofuran, 20°, 2 days, high yield) gives bis(trimethylsilyl)azidoamine, $(\text{me}_3\text{Si})_2\text{N}-\text{NNN}$, a colorless liquid, b.p. 40–42°, which decomposes above 150° with evolution of nitrogen (179). It is the first stable inorganic compound to be prepared with four adjacent N atoms. The structure proposed is that of a tetrazadiene $(\text{me}_3\text{Si})_2\text{N}=\text{N}=\text{N}=\text{N}$; from the readiness of silyl migration and the stability of the compound, $\text{me}_3\text{Si}-\text{N}=\text{N}=\text{N}=\text{N}-\text{Si}(\text{me})_2$ should also be considered as a possible structure.

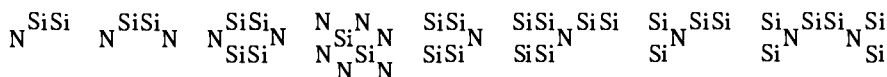
V. Silicon-Nitrogen Compounds with Silicon in a Lower Oxidation State Than +4

A. GENERAL SURVEY

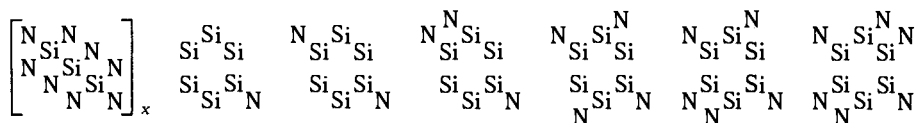
Silicon-nitrogen compounds with the Si atom in a lower oxidation state than +4 have been isolated by reducing complexes formed by silicon halides with α, α' -dipyridyl or as disilanyl derivatives. All other known compounds of this class have more complex structures: in the case of Si^{2+} each Si atom is linked to two others to form chain or ring structures; for Si^{1+} the Si atom is surrounded by three others to form ring structures of high molecular weight:



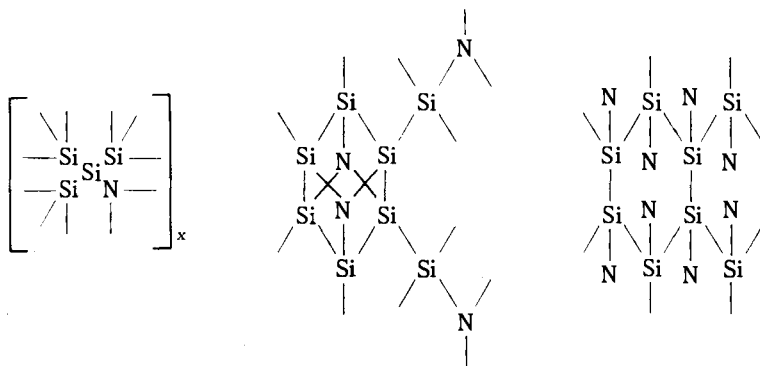
α, α' -Dipyridyl complexes



Disilanyl structures (with $\text{Si}^{+3} \text{—} \text{Si}^{+3}$ bonds)



Polysilane(+2) chains and aminosiloxenes (with $\text{Si}^{+2} \text{—} \text{Si}^{+2} \text{—} \text{Si}^{+2}$ bonds)



Polysilane(+1) rings

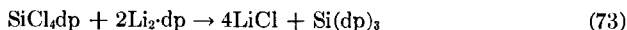
(N and Si are atoms saturated by H, R, or O; —N— and Si \leq are atoms bonded to further Si atoms.)

B. α, α' -DIPYRIDYL COMPLEXES OF Si(0) AND Si(+2)

When the white addition product of SiCl₄ with α, α' -dipyridyl (dp) (170) is reduced with two equivalents of dilithium dipyridyl in tetrahydrofuran, dark green crystals of silicon(II) dichloride-2- α, α' -dipyridyl separate from the deep green solution (60):



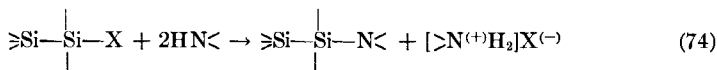
With 2 Li₂ · dp the violet solution yields black crystals of silicon(0)-3- α, α' -dipyridyl:



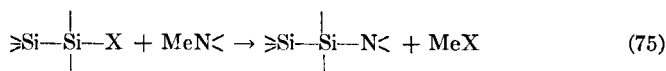
Si(dp)₃ is converted to SiCl₂(dp)₂ on treatment either with Cl₂ or with SiCl₄dp in tetrahydrofuran solution; with iodine it yields SiI₄(dp)₂. Both compounds with silicon in the oxidation state +2 or 0 are sensitive to air (60).

C. DISILANYL AMINES

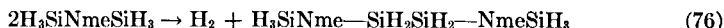
These compounds are formed by aminolysis of disilanyl halides such as Si₂H₅Cl, Si₂H₅Br, Si₂H₅I, Si₂Cl₆, Si₂me₅Cl, me₂ClSiSiClme₂ with NH₃ or me₂NH:



Alternatively, disilanyl halides may be reacted with metallated nitrogen derivatives such as NaN[Si(me)₃]₂ and Ag[NCO] (or Ag[NC]):



A third method is the coupling of Si—Si bonds by photolysis (6):



Ammonia reacts with Si₂H₅I to form tris(disilanyl)amine, N(Si₂H₅)₃, but with me₅Si₂Cl to form only bis(pentamethyldisilanyl)amine, HN(Si₂me₅)₂. This is analogous to the reactions of H₃SiI and me₃SiCl, which give N(SiH₃)₃ and (me₃Si)₂NH (139, 157, 171). With me₂ClSiSiClme₂ suitably diluted the tetrasilapiperazine ring system, [—me₂Si—me₂Si—NH—]₂, results (157). There is a tendency for Si₂H₅Nme₂ and Si₂Cl₅N[Si(me)₃]₂ to disproportionate into Si₂H₄(Nme₂)₂ and Si₂H₆ or into [(me)₃Si]₂N—Si₂Cl₄—N[Si(me)₃]₂

TABLE VI
DISILANYL AMINO COMPOUNDS (GROUP VIII)

No.	Compound	M.P.	B.P.	Torr	n_D	°C	D_4	°C	Prep. Eqn.	Ref.
1	(H ₃ Si-H ₂ Si) ₃ N ^a	-97°	176°	760			0.873	0	(74)	(45, 171)
2	H ₃ Si-H ₂ Si-Nme ₂ ^d		66°	760					(74)	(94)
3	me ₂ N-SiH ₂ SiH ₂ -Nme ₂ ^d		129°	760					(V) (C)	(94)
4	H ₃ SiNme-SiH ₂ SiH ₂ -NmeSiH ₃								(76)	(6)
5	(me ₃ Si-me ₂ Si) ₂ NH ^a	—	134°	40	1.4556	30	0.8053	30	(74)	(139, 157)
6	(me ₃ Si-me ₂ Si) ₂ NNa	62°	—	—	—	—	—	—	(V) (C)	(157)
7	me ₃ Si-me ₂ Si-NCO ^a	—	160°	760	1.4337	30	0.8537	30	(75)	(139)
8	me ₃ Si-me ₂ Si-CN ^b	—	176°	760	1.4374	30	0.8136	30	(75)	(29)
9	(-me ₂ Si-me ₂ Si-NH-) ₂	1°	61°	2	1.4760	20	0.8458	20	(74)	(157)
10	me ₃ Si-me ₂ Si-N[Si(me) ₃] ₂ ^c	< -70°	93°	14	1.442	20	0.822	20	(75)	(157)
11	(me ₂ N) ₃ Si-Si(Nme ₂) ₃	(subl. 270-280°, in high vac., 70-80°)							(74)	(176)

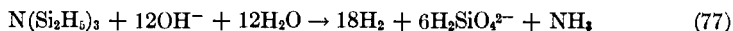
^a Vapor pressure (log P Torr): VIII/1 -2328,9/ T + 8,0645; VIII/5 9,0138 - 3021,16/ T ; VIII/7 8,2471 - 2309/ T ; VIII/8 8,3347 - 2452/ T . Heat of vaporization (kcal/mole): VIII/1, 10.66; VIII/5, 13.83; VIII/7, 10.57; VIII/8, 11.22.

^b Trouton's constant (cal/mole/deg): VIII/1, 23.7; VIII/5, 28.1; VIII/7, 24.5; VIII/8, 25.0 me₃Si₂CN and me₃Si₂CN.

^c 90% pure.

^d See Abedini, M., and MacDiarmid, A. G., *Inorg. Chem.* **2**, 608 (1963).

and Si_2Cl_6 (94, 157). The majority of disilanyl nitrogen compounds which have been prepared are quite stable. Thus, $\text{N}(\text{Si}_2\text{H}_5)_3$ decomposes slowly at $>110^\circ$ and $\text{Si}_2(\text{Nme}_2)_6$ sublimes without decomposition at $270\text{--}280^\circ$. Boron trifluoride cleaves $\text{N}(\text{Si}_2\text{H}_5)_3$ and $\text{HN}(\text{Si}_2\text{me}_5)_2$ forming $\text{Si}_2\text{H}_5\text{F}$ or $\text{me}_5\text{Si}_2\text{F}$. Whereas $\text{N}(\text{Si}_2\text{H}_5)_3$ inflames in air and is decomposed by aqueous alkali according to the equation



$\text{Si}_2(\text{Nme}_2)_6$ is not attacked by alkalis. The Si—Si bond is, however, cleaved in an unusual way by acids (176). The compound $\text{HN}(\text{Si}_2\text{me}_5)_2$ is much more difficult to metallate with NaNH_2 in benzene than is $\text{HN}[\text{Si}(\text{me})_3]_2$; the resulting $\text{NaN}(\text{Si}_2\text{me}_5)_2$ is sensitive to air and moisture (157). The individual compounds of group VIII are listed in Table VI.

D. IMINOPOLYSILANES(+2 TO +3)

Si_2Cl_6 and Si_3Cl_8 react with liquid ammonia or with gaseous ammonia in inert solvents in the same way as SiCl_4 . Ammonium chloride is produced together with amorphous white substances of high molecular weight, which are sensitive to moisture. These contain —NH— groups in place of the halogen atoms of the starting material (iminopolysilanes; "silicon imides"):

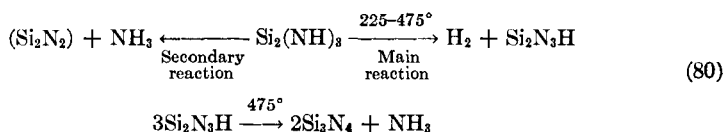


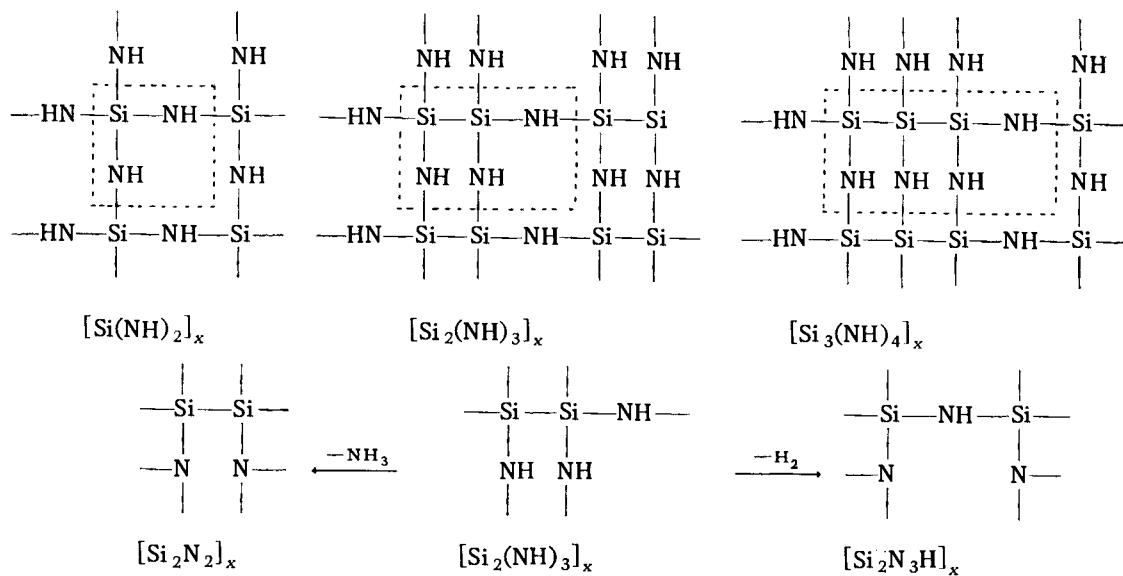
(where $n = 1, 2, 3$) (12, 13).

Using liquid ammonia at low temperatures substantially more ammonia is held because of ammoniates of NH_4Cl ; this is given off at higher temperatures (14):



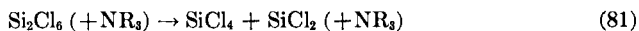
The ammonium chloride may be washed out with liquid ammonia, though $\text{Si}_2(\text{NH})_3$ adsorbs NH_3 strongly, just as amorphous SiO_2 adsorbs water (10, 125). Pure $\text{Si}_2(\text{NH})_3$ is obtained only on heating to 220° in vacuum (14). When more strongly heated, $\text{Si}_2(\text{NH})_3$ decomposes with loss of hydrogen to form $\text{Si}_2\text{N}_3\text{H}$ and subsequently loses ammonia to give Si_3N_4 . No silicodicyanogen, $(\text{SiN})_2$ (125), is obtained, even when the heating is done in vacuum, but a rearrangement occurs, giving 60% of SiNHSi— and 40% of NSiSiN— containing structures (14):





Structural units of silicon imides and the pyrolysis product of $\text{Si}_2(\text{NH})_3$

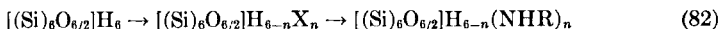
Catalytic quantities of tertiary amines or ammonium salts bring about disproportionation of Si_2Cl_6 at room temperature according to the equation (180):



These products react further to form $(\text{SiCl}_2)_x$ (180), $\text{Si}_5\text{Cl}_{12}$ (67), $\text{Si}_6\text{Cl}_{14}$ (66), or with pyridine, $\text{Cl}_4\text{Si}(\text{py})_2$ and $[\text{Cl}_2\text{Si}(\text{py})]_x$ (170).

E. AMINOSILOXENES

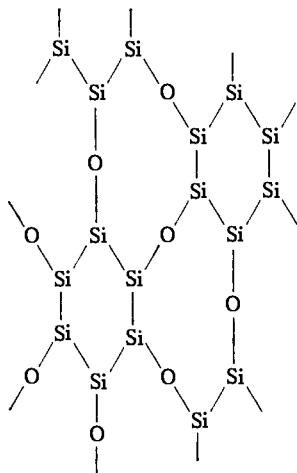
Siloxene, prepared from CaSi_2 by the action of hydrochloric acid in a water-alcohol mixture, may be converted into halogen-substituted siloxenes by the action of halogens or halogen hydrides, HX or H_2 being evolved. These, in turn, give aminosiloxenes and ammonium halides with ammonia or amines (68, 69, 70):



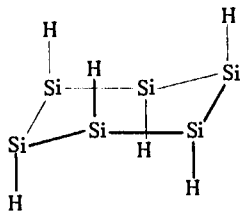
(where $\text{R} = \text{H}$, et , ph , $\text{CH}_2\text{CH}_2\text{NH}_2$.)

The siloxene framework consists of puckered six-membered rings of silicon atoms, with each Si linked to one H and also, by an oxygen bridge, to another Si hexagon, giving a giant two-dimensional molecule made up of $[(\text{Si})_6\text{O}_{6/2}]\text{H}_6$ units. The H atoms, which lie alternately above and below the siloxene plane, may be substituted under carefully controlled conditions. Ammonium halides formed in Reaction 82 may be washed out with liquid ammonia.

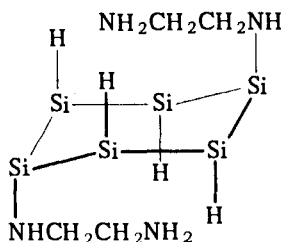
The following aminosiloxenes have so far been prepared, though not always in a pure state (the symbol $[]$ denotes $[(\text{Si})_6\text{O}_{6/2}]$): $[] \text{H}_5\text{NH}_2$,



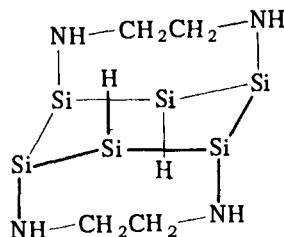
Siloxene structure (without H atoms)



Six-membered Si ring in siloxene with positions of the H atoms (without O atoms)



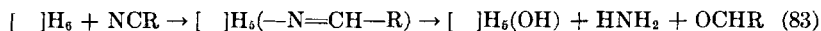
Bis(ethylenediamino)siloxene
(structural unit)



Bis(ethylenediamino)siloxene
(bridged structural unit)

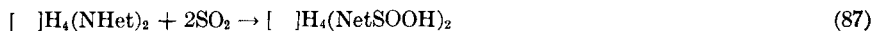
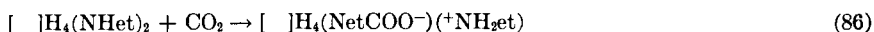
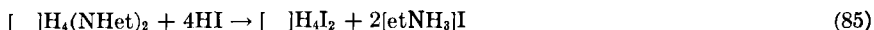
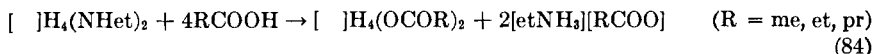
[] $\text{H}_4(\text{NH}_2)_2$, [] $\text{H}_3(\text{NH}_2)_3$, [] $\text{H}_2(\text{NH}_2)_4$, [] $\text{H}(\text{NH}_2)_5$, [] $(\text{NH}_2)_6$ (70), [] $\text{H}_4(\text{NHet})_2$, [] $\text{H}_2(\text{NHet})_4$, [] $\text{H}_4(\text{Net})_2$, [] $\text{H}_5(\text{NHph})$ (73), [] $\text{H}_4(\text{NHCH}_2\text{CH}_2\text{NH}_2)_2$, [] $\text{H}_2(\text{NHCH}_2\text{CH}_2\text{NH})_2$ (58), [] $\text{H}_5(\text{NCHR})$ (115), [] $\text{H}_4(\text{NetCOO})(\text{NH}_{2\text{et}})$, [] $\text{H}_4(\text{NetSOOH})_2$, [] $\text{H}_{1.7}\text{I}_2(\text{NHet})_{2.3}$ (73).

Aromatic nitriles add on to siloxenes, forming silicon imine structures, which are rapidly decomposed by water to aldehyde and ammonia (115):



Traces of water hydrolyze aminosiloxenes. Ammonia is split off, hydrogen is evolved, and Si—Si bonds are converted to Si—O—Si. Excess of water breaks down the siloxene structure to silicic acid. Liquid ammonia also destroys the aminosiloxene structure, especially in the light. Hydrogen is evolved and Si—Si bonds go to SiNHSi groups.

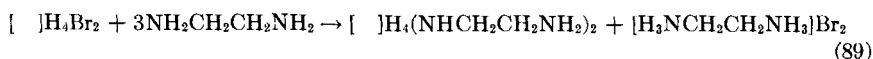
Bis(ethylamino)siloxene is cleaved by acids and will also add on CO_2 and SO_2 (73):



Diiodosiloxenes, which are not accessible by other routes, may be prepared by Reaction 85, while monoiodosiloxenes may be made from [] $\text{H}_5(\text{NHph})$ and HI. More highly substituted aminosiloxenes are also able to substitute only two iodine atoms on treatment with excess of hydriodic acid. This is because there is room for only one of the relatively large iodine atoms above and below the six-membered silicon ring:



In dibromosiloxene there is also one Br atom above and one below the plane, since it reacts with ethylene diamine according to the equation:

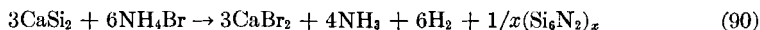


With tetrabromosiloxene all four Br atoms may be exchanged for ethylenediamine molecules, ring bridges being formed (58) (see diagram of structure).

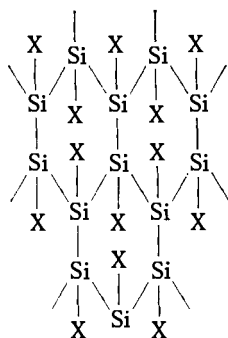
The carbamates formed by addition of CO_2 to aminosiloxene decompose in light or on access of small amounts of oxygen. Evolution of HCN and NH_3 occurs and the oxygen of the carbamate simultaneously transforms SiSi bonds into SiOSi (71, 72).

F. AMINOPOLYSILANES(+1)

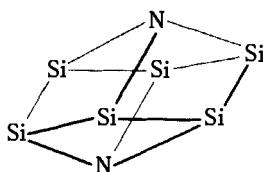
Calcium disilicide reacts with ammonium halides in a finely divided state when heated to the sublimation temperature (350–550°) according to the equation:



The solid swells to a loose brown powder which is insoluble and infusible. Calcium bromide may be washed out partially with acetone. The reaction occurs most readily with NH_4Br . It also occurs with alkyl or aryl ammonium halides, but not with $[\text{NR}_4]\text{X}$; with NH_4I , iodine is formed in secondary reactions and NH_4F gives silicon tetrafluoride. The silicon(+1) nitride, $(\text{Si}_6\text{N}_2)_x$, may be regarded as derived from a polysilane(+1), $[(\text{Si})_6\text{H}_6]_x$, by replacing three H atoms above and three below the puckered six-membered ring. The N atoms may then be arranged above and below the same but also a neighboring six-membered silicon ring (see diagram of structure).

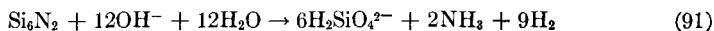


Polysilane(+1) structure
(X = H, Cl, NH_2 , etc.)



Structural unit of silicon(+1)
nitride $(\text{Si}_6\text{N}_2)_x$

(Si₆N₂)_x is, apart from Si₃N₄, the only definite binary silicon-nitrogen compound. It is amorphous to X-rays, stable in air and to heat, and reacts slowly with water or alcohol, but rapidly at pH > 7 according to the equation:

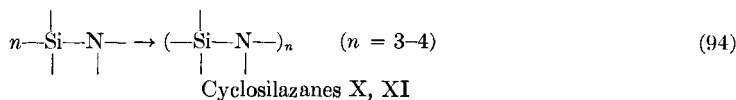
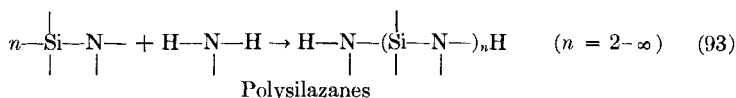
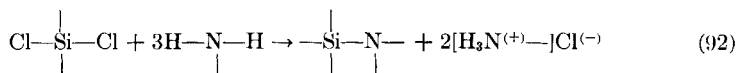


Boron trifluoride is not added (57).

When the chloropolysilane(+1), (SiCl)_x, which may be obtained by pyrolyzing the higher silicon halides Si_nCl_{2n+2} (*n* = 10), is treated with NH₃, the primary product at <0° is [Si(NH₂)]_x. This loses hydrogen at higher temperatures and each 6–8th Si–Si bond is converted to SiNHSi (126). Definite aminopolysilanes(+1), [Si(NHR)]_x, may be prepared from (SiCl)_x (59).

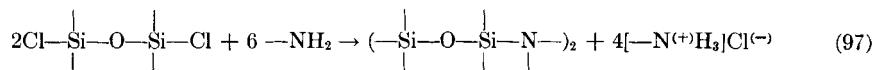
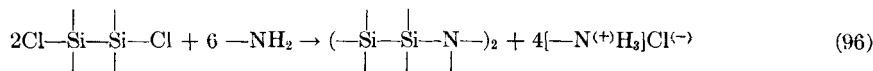
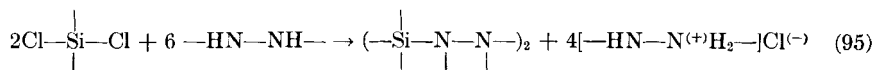
VI. Cyclic Silicon-Nitrogen Compounds

Ammonolysis or aminolysis of halogeno difunctional silanes gives polysilazanes only to a limited extent: the main products are cyclosilazanes in which 3 (preferably) or 4 SiN units are joined in a ring:

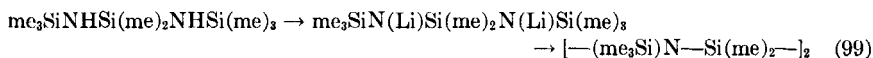
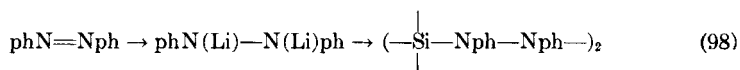


Monomeric units such as >Si=N— are excluded by the rules of silicon chemistry (the impossibility of having *p*_π—*p*_π bonds on silicon atoms) and have not been observed hitherto (cf. 45, 110).

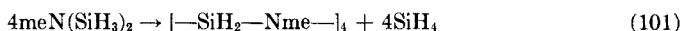
Analogously, hydrazines react to give disilatetrazacyclohexanes XII, 1,2-dihalogensilanes to give tetrasilapiperazines XIII, and α,ω-dihalogenosiloxanes to give cyclosiloxazanes XIV (79, 101, 157):



In those cases where the NH groups will no longer react, metallated amines are effective (41, 44, 47):

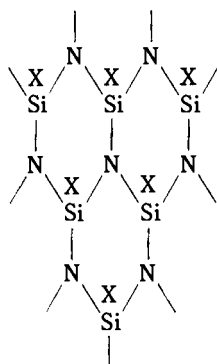


In addition to $\text{---Cl/---N}<$ exchange reactions, condensation reactions at elevated temperatures ($>200^\circ$) have been employed in the preparation of cyclic SiN compounds (6, 98):



Cyclodisilazanes IX may be obtained otherwise only from the breakdown products of the reaction of SiCl_4 with N_2 in glow discharges or by decomposition of the apparently unstable tetrasilylcyclotetrasilazanes (99).

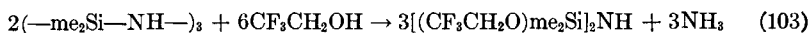
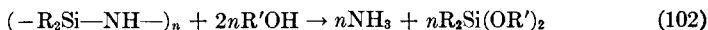
A large number of cyclotri- and cyclotetrasilazanes have been made by varying the substituents on the Si atom and to a less extent on the N atom, by use of $\text{NH}_3\text{---RNH}_2$ mixtures in aminolysis ($\rightarrow \text{Xd}/1$), by amine exchange reactions, or by *N*-metallation followed by silylation of cyclodisilazanes (cf. Table VII). A condensed six- and eight-ring product (XV) has also been described. High molecular cyclotrisilazanes, $(\text{XSiN})_x$, derived from polysilanes(+1) by replacing each second Si atom by N (see structure on p. 264), have been obtained in the ammonolysis of HSiCl_3 (111, 112) and SiCl_4 (124), and in discharge tube reactions with SiCl_4/N_2 mixtures (38, 105).



Structural formula for $(\text{XSiN})_x$ (idealized)

The cyclic silazanes are, broadly speaking, insensitive to water and particularly stable in the alkaline region. They are, however, rapidly broken

down by acids (1, 133, 161, 184). Derivatives of disilatetrazacyclohexane (XII) are more insensitive to moisture the more the H atoms or alkyl groups are replaced by phenyl groups (101). Alcohols also cleave the cyclosilazanes with evolution of ammonia. This is retarded by the presence of OH⁻ (1) and accelerated by acid OH groups such as occur in phenols (1, 97). Alkoxyorganodisilazanes, which are otherwise difficult to produce, are formed in good yield by the appropriate addition of alcohols (161):

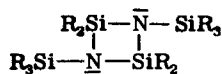


Equilibration of $(-me_2Si-NH-)_3$ with $(me_3Si)_2NH$ leads to trisilazanes in not particularly good yield. In the treatment of cyclosilazanes with amines, ring rearrangements or amino exchange reactions have been observed (1, 21). Warming of $(-me_2Si-NH-)_3$ with catalytic quantities of NH_4Br at 190–300° results in loss of ammonia and formation of oligomers and high molecular silazanes containing NSi_3 groups. They begin to decompose above 500° and are very stable to alkalis (80). Boron halides such as R_2BCl bring about cleavage of $(-me_2Si-NH-)_3$ to me_2SiCl_2 and $(R_2B)_2NH$ (103).

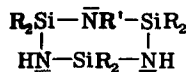
High molecular cyclotrisilazanes, $(XSiN)_x$, are insoluble in organic solvents; $(HSiN)_x$ is transformed by HCl into $HSiCl_3$ and NH_4Cl , by HI into $HSiI_3$ and NH_4I , and by NH_3 into $Si(NH)_2$ and H_2 (111, 112).

Cyclosilazanes undergo stepwise metallation of the NH groups by reaction with KNH_2 /liquid ammonia (120), $NaNH_2$ /benzene (149, 169), $NaN[Si(me)_3]_2$ (163), or LiC_4H_9 (41, 43). The alkali derivatives, which cannot be distilled and show no definite melting points, are thermally very stable, though some are sensitive to oxygen.

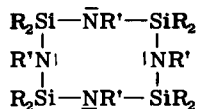
From electron diffraction measurements, cyclohexamethyltrisilazane, like cyclo-octamethyltetrasilazane, is found to be puckered, with $NSiN$, $111 \pm 5^\circ$; $SiNSi$, $117 \pm 4^\circ$; SiC , $1.87 \pm 0.05 \text{ \AA}$; SiN $1.78 \pm 0.03 \text{ \AA}$. Infrared spectroscopic data, however, have been interpreted in terms of a planar structure (77), with bond angles of 109° for $NSiN$ and 131° for $SiNSi$ (109). Other infrared measurements (81) tend to lead to confirmation of the electron diffraction results ($SiNSi$, 118.5°) and to determination of bond angles for XIVa of $SiOSi$, 124° ; $SiNSi$, 133.3° ; for XIVb/1, $SiOSi$, 132° ; $SiNSi$, 121.3° ; for XIVc, $SiOSi$, 137° , 125° ; $SiNSi$, 118.8° ; and for $(-me_2Si-NH-)_4$, $SiNSi$, 121.3° [123.4° according to reference (183)]. The $\nu_{as} SiN(Si)$ band in the infrared and Raman spectra of cyclotrisilazanes lies in the region $925\text{--}935 \text{ cm}^{-1}$, *N*-silyl-substituted cyclotrisilazanes show a characteristic band at $1005\text{--}1040 \text{ cm}^{-1}$. [For the PMR spectra of some cyclosilazanes see reference (81) and for electrical properties and dipole



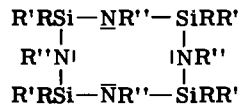
(IX)



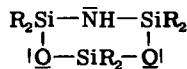
(Xd)



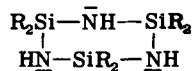
(XIa)



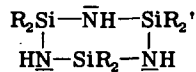
(XIe)



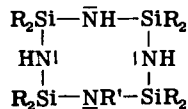
(XIVa)



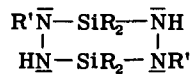
(Xa)



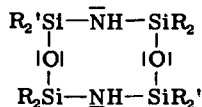
(Xe)



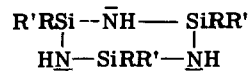
(XIb)



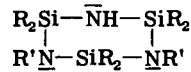
(XIIa)



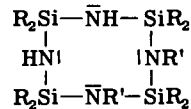
(XIVb)



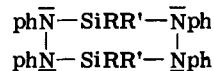
(Xb)



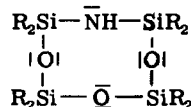
(Xf)



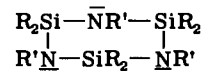
(XIc)



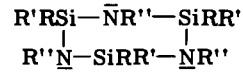
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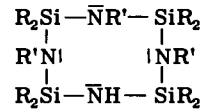
(XIVc)



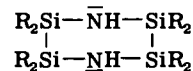
(Xc)



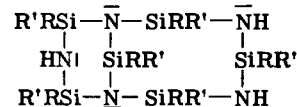
(Xg)



(XId)



(XIII)



(XV)

TABLE VII
CYCLIC SILAZANES

No.	R	R'	M.P.	B.P.	Torr	n_D	°C	D_4	°C	Prep. Eqn.	Ref.
Group IX: Cyclodisilazanes											
(IX)	1 Cl		84°	—	—	—	—	—	—	(VI)	(38, 105)
	2 me		39°	85°	7	1.4237	45	0.998	—	(99)	(42, 174)
Group X: Cyclotrisilazanes											
(Xa)	1 me		—10°	188° 112°	756 85	1.4448	20	0.9196	20	(92, 94)	(21, 22) (53, 104)
	2 et		—41°	150°	10	1.4670	20	0.9287	20	(92, 94)	(21, 32)
	3 ⁿ bu			193°	2	1.4654	20	0.8912	20	(92, 94)	(135)
	4 ph ^a		214°							(92, 94)	(91)
	5 meO		186°	(185°	10) ^b	—		(1.021	15) ^b	(92, 94)	(110, ^b 163)
	6 etO		89°	(220°	10) ^b	—		—	—	(92, 94)	(110, ^b 163)
	7 ⁱ prO		—	147°	4	—		—	—	(92, 94)	(127, 172)
	8 ⁿ buO		—	250°	12					(100)	(92)
	9 ^t buO		190°	—	—					(92, 94, 100)	(46, ^c 89, 98)
	10 chO		65–70°	—	—					(92, 94)	(163)
(Xb)	1 H	et	—	62°	0.5	1.4700	20	0.9596	20	(92, 94)	(131)
	2 me	et	—	115°	13	1.4564	20	—	—	(92, 94)	(61)
	3 me	ph	116°	220°	760	—	—	—	—	(92, 94)	(61)
	4 me	meO	217°	115°	1.5					(92, 94)	(163)
	5 me	etO	101°							(92, 94)	(163)
	6 me	ⁱ prO	45°							(92, 94)	(163)
	7 me	^t buO	44°							(92, 94)	(163)
	8 me	phO	95°							(92, 94)	(163)
	9 me	chO	77°							(92, 94)	(163)
	10 vi	meO	159°							(92, 94)	(163)
	11 ph	meO	157° (decomp)							(92, 94)	(163)

Continued

TABLE VII (Continued)

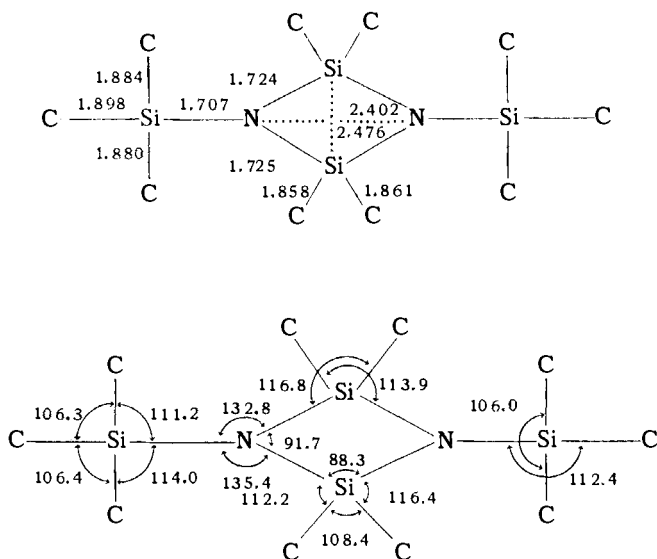
No.	R	R'	M.P.	B.P.	Torr	n_D	°C	D_4	°C	Prep. Eqn.	Ref.
(Xc)	1 me	ph	250°	190–193°	11	—				(100)	(2, 88)
	2 me	me ₃ Si	–43°	333°	723	1.4823	20	0.940	20	(VI)	(41, 43)
	3 et	me ₃ Si	–35°	362°	720	1.4868	20			(VI)	(41)
	4 ph	me ₃ Si	110–120°	422°	718	—				(VI)	(41)
	5 ph	me ₃ SiCl	90–100°	470–480°	720	—				(VI)	(41)
(Xd)	1 me	ph	37°	—	—	—				—	(2)
	2 me	am	—	87°	1	—				—	(2)
	3 ph	me ₃ Si	80°	293–300°	1	—				(VI)	(43)
(Xe)	1 me	et	–85°	58–59°	1	1.4540	20	0.9291	20	—	(185)
	2 et	me	–85°	78–80°	1	1.4630	20	0.9381	20	—	(185)
(Xf)	1 me	me ₃ Si	–74°	261°	730	1.4422	20	0.973	20	(VI)	(41, 43)
	2 et	me ₃ Si	–65°	333°	720	1.4751	20	—	—	(VI)	(41)
	R R'	R''									
(Xg)	1 H me	me	—	56°	5	1.4580	20	0.9297	20	—	(132)
	2 H et	me	—	74°	1.5	1.4680	20	0.9324	20	—	(132)
	3 H NHet	et	—	93–97°	11	1.4472	20	0.9229	20	—	(130)
Group XI: Cyclotetrasilazanes											
(XIa)	1 H	me	—	liquid	—					(101)	(6)
	2 me	H	97°	225°	756					(92, 94)	(21, 22)
			—	135°	35						(53, 104)
	3 et	H	16°	192°	10	1.4769	20	0.9521	20	(92, 94)	(21)
	4 'prO	H	—	191°	2					(92, 94)	(127, 172)
	5 phO	H	130°	—	—					(100)	(127)
	6 Cl	Cl ₃ Si	50°	103°	2					(VI)	(124)
(XIb)	1 me	me ₃ Si	–17°	107–108°	1.5	1.4613	20	—	—	—	(43)
(XIc)	1 me	me ₃ Si	–32°	122–124°	3	1.4497	20	0.901	20	—	(43)

(XId)	1 me	me ₃ Si	—55°	328°	718	1.4582	20	—	—	—	(42)
	R	R'	R''								
(XIe)	1 H	me	H	—	54°	1	1.4780	20	1.0069	20	(131)
	2 H	et	H	—	102°	0.5	1.4810	20	0.9767	20	(131)
	3 me	H	me	—	88°	2	1.4810	20	0.9776	20	(132)
	4 H	NHet	et	—	122°	11	1.4527	20	0.9231	20	(130)
Group XII: 1,4-Disila-2,3,5,6-tetrazacyclohexanes											
(XIIa)	1 ph	H	168–172°						(95)		(101, 143)
	2 ph	ph	254–257°						(98)		(101, 143)
	3 me	ph	oil						(95)		(101, 143)
(XIIb)	1 ph	ph	329–330°						(98)		(47)
	2 me	ph	240–243°						(98)		(47)
Group XIII: 1,2,4,5-Tetrasil-3,6-diazacyclohexanes											
(XIII)	1 me		1°	61°	2	1.4760	20	0.8458	20	(96)	(157)
Group XIV: Cyclotri- and -tetrasiloxazanes											
(XIVa)	1 me		10°	151°	760	1.4068	20	0.9895	25	(97)	(79, 81)
(XIVb)	1 me	me	40°	206–208°	760	—				(97)	(79, 133)
	2 me	et	<20°	70°	0.5	1.4308	20			(97)	(133)
	3 meO		—	173–175°	0.05	—				(97)	(120)
(XIVc)	1 me		20°	190–191°	760	1.4151	20	0.9921	26	(97)	(79)
Group XV: Condensed cyclotri- and -tetrasilazanes											
(XV)	1 H	me	—	116°	1.5	1.4860	20	1.0371	20	—	(131)

^a Compound adds one molecule CCl₄ when crystallizing from CCl₄.

^b Data for "(RO)₂Si=NH."

moments see reference (104).] A careful X-ray structural determination has been made on *N,N'*-bis(trimethylsilyl)cyclodisilazane (IX/2) (174). It is monoclinic with the space group $F2_1/n$ ($a = 6.75_9 \pm 0.02$ Å, $b = 13.18_1 \pm 0.04$ Å, $c = 11.22_6 \pm 0.03$ Å, $\beta = 104^\circ 23' \pm 0.5^\circ$, $U = 968.7$ Å³, D_c 1.003, D_m 0.998 (floatation in methanol/diethylene glycol). It has a planar SiNSi_2NSi framework.



Bond distances (in Å) and bond angles (in °) for *N,N'*-bis(trimethylsilyl)cyclodisilazane.

VII. Prospect

This article represents only an arbitrary section of current activity in the field of silicon-nitrogen compounds; a more complete treatment would have exceeded the available space. Some mention must, however, be made of other important sectors of Si—N chemistry and of the chief workers in each. These are: ammonolysis of SiCl_4 (Billy, Goubeau, Glemser); modifications of Si_3N_4 (Glemser, Popper, Ruddlesden); polyamino-substituted silanes (Tansjö); pseudohalogen derivatives with (NSiH_3) groups (Ebsworth); condensation reactions of silylamines with silanols (Pike); silyl-substituted amino acids (Rühlmann, Birkofer); silyl-substituted ureas, carbonic acid amides, and carbodiimides (Birkofer, Goubeau, Pump, Wannagat); polysilazanes (Rochow, Andrianov); bis(silyl)amines and their reactions (Becke-Goehring, Grosse-Ruyken, Wannagat); reactions of silyl-substituted alkali amides with organic compounds (Krüger); tris(silyl)amines (Wannagat); silylamino derivatives of the transition metals

(Bürger); phthalocyaninatosilanes (Kenney). It will be seen that the chemistry of silicon-nitrogen compounds, which occupied only a few pages of Gmelin's *Handbuch der anorganischen Chemie* ten years ago, has undergone an almost explosive development. Only the practical applications seem to be delayed. In brief, SiN compounds, thanks to the variety of types and reactions they show, may well challenge the leading place of SiC and SiO compounds in silicon chemistry, at least insofar as the scientific and preparative aspects of the subject are concerned.

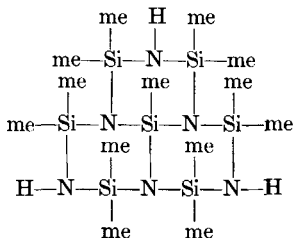
Addendum

During the past year nearly one hundred articles about SiN-chemistry have been published. Only a few of them could be woven into the text of the present review. Some of these additions to the chemistry of cyclosilazane compounds are noted here.

1. A three-membered Si_2N -ring system $[-(\text{me}_3\text{Si})\text{N}-\text{Si}(\text{me})_2-\text{Si}(\text{me})_2-]_{\text{ring}}$, m.p. -37° , b.p. 172.7° , n_D^{20} 1.4375, D_4^{18} 0.827, was synthesized by Fink (44a); a five-membered Si_3N_2 -ring system $[-\text{Si}(\text{me})_2-\text{Si}(\text{me})_2-\text{Nme}-\text{Si}(\text{me})_2-\text{Nme}-]_{\text{ring}}$, m.p. -12° , b.p. $70^\circ/13$ Torr, by Wannagat (170a); a cyclotrisildiazoxane $[-\text{Si}(\text{me})_2-\text{NH}-\text{Si}(\text{me})_2-\text{NH}-\text{Si}(\text{me})_2-\text{O}-]_{\text{ring}}$, m.p. $46-47^\circ$, by Andrianov and co-workers (2b); and a cyclohexasildiazotetroxane, $[-\text{Si}(\text{me})_2-\text{NH}-\text{Si}(\text{me})_2-\text{O}-\text{Si}(\text{me})_2-\text{O}-]_2$, m.p. -12° , b.p. $148-150^\circ/2$ Torr, n_D^{20} 1.4269, D_4^{20} 0.9756 by Sokolov (132b).

2. Four-membered rings with Si, N, and B or P were prepared by Fink (44): $[-(\text{me}_3\text{Si})\text{N}-\text{Si}(\text{me})_2-\text{N}(\text{me}_3\text{Si})-\text{P}(\text{ph})-]_{\text{ring}}$, b.p. $107^\circ/4$ Torr, n_D^{20} 1.5029, and $[-(\text{me}_3\text{Si})\text{N}-\text{Si}(\text{me})_2-\text{N}(\text{me}_3\text{Si})-\text{B}(\text{ph})-]_{\text{ring}}$, b.p. $90-91^\circ/1.2$ Torr, n_D^{20} 1.4783. The cyclodisilazane $[-(\text{me}_3\text{SiO})_2\text{Si}-\text{NH}-]_2$, m.p. 103° , b.p. 180° , was synthesized as early as 1961 by Andrianov and Delazari (1a). For other cyclodisilazanes of group IX see Fink (44) and for those of type $[-(\text{R}'\text{R})\text{Si}-\text{Nme}-]_2$ see Lienhard and Rochow (92a).

3. A triple condensated cyclotrisilazane with m.p. $165-167^\circ$ is derived from Xa/1 or XIa/2 by heating with KOH at $160-260^\circ$ (2a).



4. For some unreported derivatives of groups Xb and XIe see Andrianov and co-workers (2c), as well as Zhinkin (185a) and Tansjö (138b).

5. $(-\text{me}_2\text{Si}-\text{NH}-)_4$, XIa/2, crystallizes in space group $P2_1/c$ in a 1:1-chair and cradle structure with distance for Si-N of 1.708 to 1.750 Å and bond angles for SiNSi of 130.1 to 133.1° (132a).

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PEROXY COMPOUNDS OF TRANSITION METALS

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I. Introduction

It has been appreciated for at least 140 years that characteristic color reactions may occur when hydrogen peroxide is added to solutions of transition metal derivatives, and solid peroxy compounds of transition metals have been known for more than 100 years. These derivatives, besides having an intrinsic interest of their own, are of considerable and growing importance in relation to the catalysis of oxidations involving hydrogen peroxide or oxygen gas, the catalytic decomposition of hydrogen peroxide itself, and the storage and use of oxygen in biological systems; so we have sought to present a review of what is at present known of transition metal peroxides. We have included less than half of the references we have studied; we hope to have covered most of what is known about those peroxides that have been isolated as solid compounds, though the material is presented in a critical manner; some general principles of transition metal peroxide chemistry that have emerged are mentioned at the end of the article. We have considered the transition series as including scandium, the rare earths, the actinides, and the copper group, but the zinc group peroxides have been

omitted. Regarding applications of transition metal peroxides to analysis, and their use as intermediates in catalytic oxidation or decomposition, we have done no more than to include brief summaries and to give a number of further references; these topics demand (and in some cases have been given) reviews to themselves.

Nowadays, when it is sometimes considered safe to ignore work published before 1945, it is chastening to realize how large a proportion of the most convincing work dealing with transition metal peroxides was completed before 1914. It is clear that the broad range of physical and chemical methods available to the modern chemist should be able to extend and deepen our knowledge of these compounds, and we hope that this review may help to stimulate studies of this kind.

II. Detection and Estimation of Peroxide in Transition Metal Compounds

It is not always easy to prove that a particular compound contains peroxide oxygen, or to discover the amount of peroxide oxygen present; the only ultimate criterion is X-ray crystallography. In most cases chemical tests, coupled with elemental analysis, are capable of showing conclusively whether peroxide is present or not, but in some compounds, notably those in which other, readily oxidized groups are present as well as peroxide, chemical methods may not be very reliable. In the chemistry of "main group" peroxides, a distinction has been drawn between "bound" (or "true") peroxide and " H_2O_2 adducts" (or "false" peroxide); in transition metal derivatives, the former class are "complex" peroxides, while "ionic" peroxides behave in aqueous solution as do the H_2O_2 adducts. Attempts have been made to devise chemical tests to distinguish between these two classes; since such a distinction must depend on the resistance of the complex peroxide to hydrolysis, it is bound to be to that extent unreliable.

A. PHYSICAL METHODS

The only reliable method of determining peroxy groups in solids is that of X-ray crystallography. Few structures of transition metal peroxides have been determined and, of these, few have R values low enough to provide unequivocal proof that the structures are correct in detail.¹ Recent

¹ The R values used in this chapter in connection with crystallographic work represent the function

$$\frac{\sum | |F_{obs}| - |F_{calc}| |}{\sum |F_{obs}|}$$

this is a measure of the agreement between observed and predicted diffraction patterns. Ideally, this factor should be no larger than the experimental errors, which with normal photographic methods are of the order of 10–15%.

studies (137, 181, 182, 551) have shown that the infrared spectra of many transition metal peroxides contain strong absorption in the range 800–900 cm^{-1} , which has been assigned to stretching modes involving the peroxy group.

B. CHEMICAL METHODS

In a number of the simpler transition metal peroxides, the peroxide oxygen has been determined by measuring the amount of O_2 evolved on thermal decomposition. Where there is no other oxidizable group present, and where the transition metal does not change its oxidation state on thermal decomposition of the peroxide, half a molecule of O_2 is evolved to each peroxy group decomposed, the remaining oxygen atom remaining as a metal–oxygen system. This method is useful and reliable, provided the compound in question decomposes cleanly and simply (58, 59, 304, 504).

Acidified potassium permanganate solution is generally used in the determination of H_2O_2 (10), and its use in the analysis of transition metal peroxides seems to be accurate and reliable, so long as the necessary precautions are taken, particularly with respect to other redox systems that may be present. Cerium(IV) has been used similarly (181, 551). Both of these reagents give a measure of the total peroxide content.

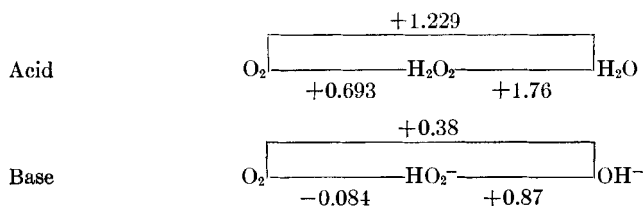
Acidified potassium iodide has been used in the presence of catalytic amounts of manganese(II) or magnesium ions to analyze peroxy compounds (343), but H_2O_2 gives no iodine with neutral potassium iodide solution (72); it has been claimed that bound peroxide liberates iodine quantitatively under these conditions, and the distinction has been made the basis of a method designed to determine bound peroxide. Riesenfeld (449) believed that addition of concentrated neutral potassium iodide solution to a true peroxycarbonate produces iodine immediately, while with H_2O_2 adducts of carbonates, only O_2 is evolved (presumably from decomposition of the H_2O_2). Subsequent discussion has shown that this view was oversimplified, and that the effects of pH and of the degree and rate of hydrolysis had not been considered (297, 306, 362, 443, 530, 531). The use of a phosphate buffer to maintain pH 7.5–8 was proposed by Liebhafski (311); under these conditions, the distinction between “true” and “false” peroxides seemed clearer, and the modified test was used to investigate a number of transition metal peroxides (492), though some of the results bear little relation to the structures of the compounds studied (as determined by other and more reliable methods). Other studies, however (245, 453), suggested that the test is only valid at pH 7; more recent and more exhaustive investigation of peroxycarbonates, using the Riesenfeld-Liebhafski test, have shown that its reliability is in doubt (384), while we have found that with such well-characterized systems as the tetra-

peroxychromate(V) anion, $[\text{Cr}(\text{O}_2)_4]^{-3}$, or the μ -peroxodicobalt cations the test either does not work at all or gives wildly varying and inconsistent results (101). The use of the test in transition metal compounds is further complicated by the range of possible redox reactions of the metal itself with iodide ion or with iodine; all in all, while in some cases the test has proved useful, its reliability even in qualitative analysis is questionable.

Potentiometric titration, using sodium hypochlorite and potassium ferrieyanide, of the H_2O_2 liberated from peroxy compounds on hydrolysis in alkaline solution has been used to estimate the amount of "active" oxygen in these compounds (452, 453). The use of acetone extraction at 0°C has been suggested (581), but this method is limited in scope, and has received little attention.

III. Some Physical Constants of H_2O_2 and Related Species

Pure hydrogen peroxide is a pale blue, syrupy, endothermic liquid. Its dielectric constant and proton dissociation constant indicate that the liquid is a good ionizing solvent, somewhat more dissociated than water. The redox potentials in acid and in base are summarized as follows:



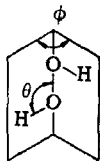
These figures show that hydrogen peroxide tends to act as an oxidizing or a reducing agent; the oxidizing power, i.e., the tendency to form water or OH^- , decreases with increasing pH, whereas the potential for oxidation of hydrogen peroxide, or the reducing power, increases with increasing pH. Other physical properties are set out in Table I.

IV. Scandium and the Lanthanides

Peroxy derivatives of scandium, lanthanum, praseodymium, and neodymium have been obtained at temperatures below 0° by treating a suspension of the metal hydroxide with H_2O_2 , or by adding alkali to a solution containing the metal cation and H_2O_2 (70, 71, 96, 361, 497). The compounds of scandium and lanthanum contain peroxide and the metal in the molar ratio 1:1 (as determined using potassium permanganate), even after treatment with 90% H_2O_2 , though it was suggested that the initial product with praseodymium was a triperoxide that subsequently decomposed (353). Elaborate phase studies (328-330) indicate the formation of compounds

TABLE I
SOME PHYSICAL CONSTANTS OF H_2O_2 AND RELATED SPECIES

A. Distances and angles



Species	$r(\text{O}-\text{O})$ (\AA)	$r(\text{O}-\text{H})$ (\AA)	θ	ϕ	Phase	Reference
H_2O_2	1.47 ± 0.02	—	—	—	Vapor ^a	(166)
	1.475 ± 0.004	0.96 ± 0.01	$94.8 \pm 2^\circ$	$119.8 \pm 3^\circ$	Vapor ^b	(433)
	1.49 ± 0.02	—	$96^\circ 52'$	$93^\circ 51'$	Solid ^c	(1)
F_2O_2	1.217	1.575 (O—F)	$109^\circ 30'$	$87^\circ 30'$	Vapor ^d	(233)

Species	$r(\text{O}-\text{O})$ (\AA)	Systems	Phase	Reference
O_2^-	1.49 ± 0.04	$\text{MO}_2(\text{M} = \text{Sr, Ba, Zn, Cd})$	Solid	(2, 146)
	1.48	$\text{M}_2\text{O}_2(\text{M} = \text{Li, Na, K, Rb, Cs})$		(222, 529)
O_2^-	1.31 ± 0.03	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$	Vapor	(209)
	1.28 ± 0.02	$\beta\text{-NaO}_2$		(595)
		$\alpha\text{-KO}_2$		(3)
O_2	1.2107 ± 0.0001	Oxygen gas	Vapor	(366)
O_2^+	1.1227 ± 0.0001		Vapor	(218)
	1.17 ± 0.17	$(\text{O}_2)\text{PtF}_6$	Solid	(26)

B. Vibrational properties: point group C_2

Mode, approximate description, and symmetry class			Frequency (cm^{-1})	Reference	Force constants ($\text{dyne/cm} \times 10^{-6}$)		Reference
ν_1	(O—H) stretch	a	3599.2	(433)	(O—H) stretch,	7.28	(164)
ν_2	(O—H) bend	a	1380	(433)	(O—O) stretch,	3.84	
ν_3	(O—O) stretch	a	890	(163)	(OOH) bend,	0.89	
ν_4	Torsion	a	314	(94)	(HO—OH) bend,	0.11	
ν_5	(O—H) stretch	b	3607.9	(433)			
ν_6	(O—H) bend	b	1266	(163)			

^a Electron diffraction.^b Infrared.^c X-ray.^d Microwave.

C. Some thermodynamic properties

For H_2O_2 , heat of formation $\Delta H_f^\circ = -32.52$ kcal/mole at 25°C (464)
 $\Delta G^\circ = -25.24$ kcal/mole at 25°C (464)

Bond dissociation energies

Bond	Species	Energy (kcal/mole)	Reference
(O—O)	H_2O_2	47.8	(312)
(O—H)	H_2O_2	90.0	(145)
(O—H)	OH	101.5	(25)
(O=O)	O_2	117.96	(116)

D. Other properties

Dipole moment $\mu = 2.13$ D in dioxane (314)

Dielectric constant $\epsilon = 84.9$ at 0°C (187)

Conductivity $\lambda = 4.0 \times 10^{-7}$ ohm cm^{-1} (467)

Molar diamagnetic susceptibility $\chi_m = -17 \times 10^{-6}$ cgsu/mole at 10°C (486)

Polarizability $\alpha = 2.3 \times 10^{24}$ cc/molecule at 25°C (162)

Barrier to internal rotation = 3.5 kcal/mole (165)

Proton dissociation constant $K = 2.24 \times 10^{-12}$ at 25°C (133)

of lanthanum, praseodymium, and neodymium that are formulated as $\text{M}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (at 0°) or $\text{M}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (at -20°), though the analytical data presented are not entirely convincing, and none of these substances was obtained pure; the molar ratio (peroxide:metal) seems to be 1:2, though evidence was also obtained for the formation of a 1:1 peroxide of neodymium, formulated as Nd_2O_5 (328). These solids are not very stable thermally, losing oxygen slowly at room temperature and rapidly at 100° ; they cannot be dehydrated without loss of peroxide oxygen. With dilute acids they give O_2 , and with concentrated sulfuric acid ozone is evolved. Little else is known of their properties; it is assumed that the metals are all in the +3 state.

Under the same conditions, cerium forms an apparently definite compound formulated as $\text{CeO}_3 \cdot 2\text{H}_2\text{O}$, in which the metal is in the +4 state and the ratio (peroxide:metal) is 1:1 (303, 327, 408, 409, 489); there is some evidence that an unstable cerium(III) peroxide is formed as an intermediate in the reaction between cerium(III) hydroxide and H_2O_2 (303). The heat of formation of the substance, often described as $\text{Ce}(\text{O}_2\text{H})(\text{OH})_3$, has been measured; the compound loses O_2 rapidly at 60 – 80° , and with dilute acids gives O_2 and Ce(III) .

Phase studies indicate the formation of $\text{Ce(O)(O}_2\text{)} \cdot \text{H}_2\text{O}$, $\text{Ce(O)(O}_2\text{)}$,

and $\text{Ce}(\text{O}_2)_2$ at low temperatures, though no anhydrous solids seem to have been isolated (327); the diperoxy derivative is extremely unstable.

In the presence of citrate, cerium(IV) forms a soluble complex with H_2O_2 ; the species is colored and contains two peroxy groups to each cerium atom (14, 539).

V. Titanium

The appearance of an orange color when H_2O_2 is added to an acid solution of Ti(IV) was noted as long ago as 1870: in the ninety-odd years since then, remarkably little has been established for certain about peroxy compounds of titanium. As several studies have made clear, the color of an aqueous solution of Ti(IV) in H_2O_2 depends on the pH, being orange in acid solutions, yellow in solutions of about pH 8, and colorless in strongly alkaline solutions. Several solid peroxy derivatives have been isolated, but there is little agreement about their formulas and structures.

A. REACTIONS AT HIGH pH

A spectrophotometric investigation of solutions containing Ti(IV), H_2O_2 , sulfate, and potassium carbonate indicates that at pH greater than 10, a colorless species containing two peroxy groups per titanium atom is formed; this is given the formula $[\text{Ti}(\text{O}_2)_2(\text{OH})_2]^{-2}$ (370). Different spectrophotometric studies (11, 13) indicate that under these conditions the complex formed contains peroxide and titanium in the ratio 1:1; at pH 10–13, the species is formulated as $[\text{Ti}(\text{O})(\text{O}_2)(\text{OH})_2]^{-2}$, though at pH 14 the species formed is given the structure $[\text{Ti}(\text{O})(\text{O}_2)_2]^{-2}$.

Solid tetraperoxytitanates of formulas $\text{M}_4'\text{Ti}(\text{O}_2)_4 \cdot 6\text{H}_2\text{O}$ have been obtained by adding ice-cold solutions of H_2O_2 and alkali metal hydroxide to peroxytitanium hydrate (see below) (489).^{1a} These compounds seem to be genuine complex peroxides, and not orthotitanates with H_2O_2 of crystallization (238), as had been suggested (492) on the basis of their behavior in the Riesenfeld-Liebhaufski test. These tetraperoxytitanates are decomposed by aqueous acid to peroxytitanium hydrate. At the same time, the differently hydrated compounds $\text{M}_4'\text{Ti}(\text{O}_2)_4 \cdot 2.4\text{H}_2\text{O}$ (where M is Na or K) behave in solution as if they should be represented by the formulas $\text{M}_4'\text{TiO}_6 \cdot 2\text{H}_2\text{O}$, the criterion being again the Reisenfeld-Liebhaufski test (32); in view of the spectrophotometric study mentioned above (370) it seems likely that, while tetraperoxytitanates may exist in the solid state, the species present in alkaline solution probably contains no more than two peroxy groups per titanium atom.

^{1a} The compounds described (355) as $\text{K}_4\text{TiO}_6 \cdot 10\text{H}_2\text{O}$ and as $(\text{Na}_2\text{O}_2)_4\text{Ti}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ have been shown (238) to be tetraperoxytitanates.

The yellow solid obtained by the reaction of ammonium hydroxide and ammonium fluoride with peroxytitanium hydrate, or by the decomposition of $(\text{NH}_4)_3\text{TiF}_6$ in air followed by dissolution of the resulting solid and saturation of the solution with ammonium fluoride, contains the $[\text{Ti}(\text{O}_2)\text{F}_5]^{-3}$ ion (400, 401, 404). When dissolved in a cold aqueous solution of potassium chloride this ion decomposes to the tetrafluoroanion $[\text{Ti}(\text{O}_2)\text{F}_4]^{-2}$, which may also be obtained by the action of H_2O_2 on K_2TiF_6 . Attempts to repeat the preparation of the $[\text{Ti}(\text{O}_2)\text{F}_4]^{-2}$ ion (489) have failed.

X-ray examination of the solid $(\text{NH}_4)_3[\text{Ti}(\text{O}_2)\text{F}_5]$ showed that it is isomorphous with $(\text{NH}_4)_3\text{ZrF}_7$ (397); calculations from the observed intensities indicate that the ion belongs to the asymmetric group $\text{O}_h^5\text{---Fm}3\text{m}$. This is an interesting example of seven-coordination which is rare in transition metal complexes and might well repay closer attention to determine the exact orientation of the peroxy group.

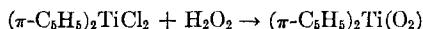
B. REACTIONS IN NEUTRAL SOLUTION

The several spectrophotometric studies made of the reaction between Ti(IV) and H_2O_2 in neutral solution for once agree in formulating the yellow species present as containing one peroxy group for each titanium atom (11, 13, 370, 469). A shift in the ultraviolet absorption maximum as the concentration of titanium increased was taken as showing that the species is polymeric (434), but the observation derives from a wrongly prepared starting material (309); there is no evidence to suggest that the species present in solution is not a monomer.

By the addition of alcohol to a solution of titanyl sulfate containing hydrogen peroxide and adjusted to pH 8.6 with potassium carbonate, a yellow solid of formula $\text{TiO}_3 \cdot 2\text{H}_2\text{O}$ has been obtained (11, 13, 309). Similar solids are precipitated by the addition of excess of base to an acid solution of Ti(IV) containing H_2O_2 (398, 399), and from the reaction between H_2O_2 and alkaline solutions of Ti(IV) (565); the material, which has strong oxidizing properties, has been called peroxytitanium hydrate. Analysis has established the presence of one peroxy group to each titanium atom (309, 356, 358, 398, 399, 434, 465, 489, 493, 505, 565), but there has been some discussion as to the number of molecules of water of crystallization; the most generally accepted number is two (489, 505), but the formula $\text{TiO}_3 \cdot \text{H}_2\text{O}$ has received some support (140, 256, 277, 456). It seems clear that the peroxy group is not present as H_2O_2 of crystallization, but in view of the uncertainty of formula it is not surprising that the relative arrangement of peroxy group and titanium atom is not known. The compound passed through cation- and anion-exchange columns and so is uncharged (370).

Peroxytitanium hydrate reacts with alkali and H_2O_2 to give tetraperoxytitanates, from which it may be obtained on hydrolysis (238, 489, 492). It may also be obtained by hydrolysis of complex peroxytitanyl sulfate (438, 487, 493) and perchlorate (238), and has been produced by ultraviolet and γ -radiolysis of solutions of Ti(IV) (16), presumably through intermediate formation of H_2O_2 .

The compound described by Billy (51–53) as $\text{Ti}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ was almost certainly a mixture of $\text{TiO}_3 \cdot \text{aq}$ and $\text{TiO}_2 \cdot \text{aq}$. An attempt to rationalize the triangular peroxytitanyl group by the reaction



has failed (102). There was no reaction with alkali metal peroxides; and the reaction with 10% H_2O_2 at 0°C was very vigorous—the only recoverable product was TiO_2 .

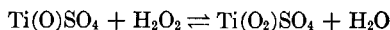
C. REACTIONS IN ACID SOLUTION

The reaction between Ti(IV) and H_2O_2 in acid solution, giving a red color, has been extensively studied because of its importance in analysis; even now, however, there is much uncertainty as to what the colored species may be. Spectrophotometric studies indicate that it contains one peroxy group to each titanium atom, but this is where general agreement ends.

In sulfuric acid solutions, it was originally suggested on the basis of transport studies that the colored complex is anionic, perhaps $[\text{Ti}(\text{O}_2)(\text{SO}_4)_2]^-$ (489); the analogous titanium peroxyoxalate anion $[\text{Ti}(\text{O}_2)(\text{C}_2\text{O}_4)_2]^-$ is formed by the reaction between H_2O_2 and the titanyl oxalate anion $[\text{Ti}(\text{O})(\text{C}_2\text{O}_4)_2]^-$ (345, 438). Hydrolysis of the sulfate complex gives peroxytitanium hydrate (51, 438, 487, 493). On the other hand, it has often been claimed that the ultraviolet absorption is unaffected, save in intensity, by charging the anion present (13, 156, 238, 370, 479) (though this has been contested) (386); because of this, and on the strength of dialytic experiments (238), the colored species has been formulated as a cation.

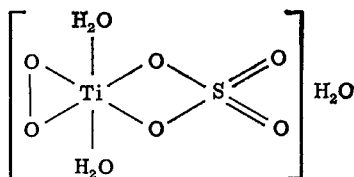
The species present at $\text{pH} < 3$ has been described as $[\text{Ti}(\text{O}_2) \cdot 3\text{H}_2\text{O}]^{+2}$ (370), as $[\text{Ti}(\text{H}_2\text{O}_2)]^{+4}$ (13), and as $[\text{Ti}(\text{OH})_2 \cdot \text{H}_2\text{O}_2]^{+2}$ (555); at pH between 3 and 6 the various formulas $[\text{Ti}(\text{O}_2)\text{OH} \cdot 2\text{H}_2\text{O}]^+$ (370) $[\text{Ti}(\text{O}_2\text{H})]^{+3}$ and $[\text{Ti}(\text{O}_2)]^{+2}$ (13) have been proposed, though it is hard to understand how the details of some of these structures could have been determined spectrophotometrically from the evidence presented. The addition of alcohol to solutions containing potassium sulfate, Ti(IV), sulfuric acid, and H_2O_2 leads to the precipitation of red solids of formulas $\text{K}_2\text{SO}_4 \cdot \text{Ti}(\text{O}_2)\text{SO}_4 \cdot 3\text{H}_2\text{O}$ (from solutions of $\text{pH} < 3$) or $4\text{K}_2\text{SO}_4 \cdot \text{Ti}(\text{O}_2)\text{OH} \cdot \text{SO}_4 \cdot 2\text{H}_2\text{O}$ (from solutions of $3 < \text{pH} < 6$) (51, 348, 370, 489, 493); these compounds are usually supposed to contain the peroxytitanium cation, and the peroxytitanium

species are held on cation-exchange resins (370), though it is perhaps worth noting that the former could well contain the anion $[\text{Ti}(\text{O}_2)(\text{SO}_4)_2]^{-2}$. Various measurements have been made of the dissociation constant of the red complex; these have been interpreted on the basis of equations such as



The results are wildly divergent (13, 47, 156, 217, 479).

If an excess of H_2O_2 is added to a solution of titanyl sulfate in concentrated sulfuric acid, a dark red amorphous solid is obtained when the solution is evaporated to dryness (*sic*). This solid analyzes as $\text{Ti}(\text{O}_2)\text{SO}_4 \cdot 3\text{H}_2\text{O}$; it gives a positive Riesenfeld-Liebhafski test and is freely soluble in both water and alcohol, though hydrolysis occurs in dilute (*sic*) aqueous solution. The complex shows only feeble cathodic migration when the solution in dilute sulfuric acid is electrolyzed, and so appears to be a nonelectrolyte; molecular weight determinations in aqueous acid solution indicate only 28% dissociation from the value for a monomer (*sic*), though the significance of this measurement is open to question since there is the possibility of some hydrolysis. These observations (387), coupled with somewhat inconclusive infrared spectroscopy (254, 255) and differential thermal analysis and with some differences between the ultraviolet spectra of this species and that formed in perchloric acid, which is formulated (386) as $\text{Ti}(\text{O}_2)(\text{ClO}_4)_2$, have been used by Patel to propose the structure given below for the sulfato compound



He has proposed similar structures for compounds obtained from solutions of $\text{Ti}(\text{IV})$, H_2O_2 , and certain dibasic organic acids such as oxalic (253, 254, 278, 279, 385), malonic (252, 253, 254, 257, 385), and maleic (252, 253, 254, 385). Similar preparative and analytical methods have been employed, and the oxalato species is probably the best characterized of these derivatives.

Thermal studies (253) indicating that the oxalate derivative is more stable than the malonate or the maleate compounds have been taken to imply that the five-membered ring of the oxalate derivative is under minimal strain, while the appearance of two bands in the infrared spectra of these compounds (385), which have been assigned rather tenuously to vibrations of the peroxy group, has been taken as showing that the $\text{O}-\text{O}$ bond

in these compounds is bent (whatever that may mean). The possible effects of crystal field splitting seem to have been ignored.

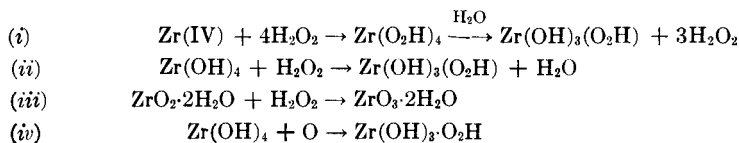
These conflicting observations seem to be almost impossible to interpret without the help of X-ray crystallography. At the same time if a cation were formed at all, it would be expected to be formed in concentrated sulfuric acid solution, unless dehydration greatly reduced the basic properties of the system; furthermore, it is hard to see why a compound obtained from so strongly dehydrating a solvent should have one molecule of uncoordinated water of crystallization.

The action of H_2O_2 upon Ti(IV) salts in phosphoric and acetic acids (134) and upon complex chlorides and pyrophosphates of Ti(IV) (348) has been shown to give peroxycomplexes, though the structures advanced for these are very doubtful. The addition of H_2O_2 to a solution of Ti(IV) and EDTA in perchloric acid has been shown to form the ion $[\text{Ti}(\text{H}_2\text{O}_2)(\text{OH})_2(\text{EDTA}^{4-})]^{-2}$; such solutions are pale yellow in color (555). The same spectrophotometric study has been used to evaluate various equilibria in this system and the Ti(IV)/ H_2O_2 system. Addition of a large excess of EDTA to these solutions precipitates a solid complex which is electrically neutral and which has been formulated as $[\text{Ti}(\text{O}_2\text{H})(\text{EDTA}^{3-})]$.

VI. Zirconium

Reaction of a Zr(IV) salt in acid or alkaline solution with H_2O_2 produces a white precipitate which has been formulated as $\text{ZrO}_3 \cdot n\text{H}_2\text{O}$, where n varies between 3 and 5 (18, 19, 20, 96). These compounds contain one peroxy group per zirconium atom.

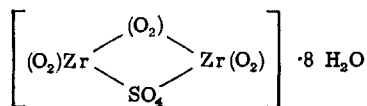
The reaction of Zr(IV) salts with an excess of H_2O_2 results in a peroxidic hydrolysis (212, 409); the final product is represented by the formula $\text{ZrO}_3 \cdot 2\text{H}_2\text{O}$, or perhaps $\text{Zr}(\text{OH})_3\text{O}_2\text{H}$. The possible reactions are described by the equations:



The application of phase diagrams and thermogravimetric analysis to the reaction between H_2O_2 and zirconium(IV) hydroxide in the range 0° to -20°C has shown (325, 326) that the primary product is $\text{ZrO}_3 \cdot 2\text{H}_2\text{O}$, which may then undergo successive dehydration to give ZrO_3 (though the anhydrous compound was not isolated). The peroxyzirconium hydrate is said to be obtained by the reaction of hydrated zirconia ($\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$) with NaOCl .

The reaction of $\text{ZrO}_3 \cdot 2\text{H}_2\text{O}$ with ice-cold alkali metal hydroxide in the presence of excess H_2O_2 produces a white solid (408, 489), which contains the tetraperoxyzirconate ion, $[\text{Zr}(\text{O}_2)_4]^{-4}$; a close physical study of the production of the reaction between $\text{Zr}(\text{IV})$ and alkaline H_2O_2 has shown (230) that the appearance and composition of the product depends upon the conditions of its formation. The compound may be the salt of an isopoly acid formed by the condensation of more highly peroxidized units; the presence of peroxy groups of three different levels of stability is indicated, and the polyacid is shown to contain hydroxyl groups and either 3 or 5 zirconium atoms in its basic unit. In solutions of pH 12–14 in the presence of an excess of H_2O_2 , analysis suggests that the zirconium is present as the anionic $[\text{Zr}(\text{O})(\text{O}_2)_2]^{-2}$ (12); studies using the ultraviolet absorption maxima at $465 \text{ m}\mu$ and $255 \text{ m}\mu$ have shown that, as the pH of such solutions decreases, anionic complexes in which the ratio of $\text{Zr}(\text{IV})$ to peroxide has the values 1:1 and 2:1 are formed. There appears to be no evidence as to whether these species are monomeric or condensed polyacid derivatives.

The reaction of H_2O_2 with ice-cold aqueous solution of zirconium(IV) sulfate produces a white solid of formula $\text{Zr}_2\text{O}_6\text{SO}_4 \cdot 8\text{H}_2\text{O}$ (489, 538). It is suggested that this is a basic peroxosulfate of structure



but there is no physical evidence to support this. The formation of this compound has been proposed as a method of separating zirconium from hafnium.

A complex peroxosulfatozirconate, analogous to that of titanium mentioned above, is formed when H_2O_2 is added to an ice-cold mixture of $\text{Zr}(\text{IV})$, potassium sulfate, and sulfuric acid (489). As previously, the formulation of this $[\text{Zr}(\text{O}_2)(\text{SO}_4)_2]^{-2}$ ion is not supported by any physical evidence.

Spectrophotometric studies have shown (15, 382) that zirconium does not form a peroxy species in concentrated acid solution. The product obtained by refluxing ZrO_2Cl_2 with urea and H_2O_2 , of composition H_3ZrO_4 , has found some application as a stationary phase oxidant in chromatography (155); peroxyzirconium hydrate has found application in analysis (158) and in the production of high purity zirconia (561).

VII. Hafnium

Little is known about the peroxide chemistry of hafnium. The addition of ice-cold H_2O_2 to hafnium sulfate produces a white insoluble precipitate

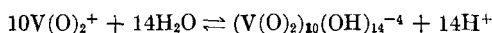
of composition $\text{HfO}_3 \cdot 2\text{H}_2\text{O}$ (220, 489) for which, by analogy with other elements, the structure denoted by $\text{Hf}(\text{OH})_3\text{O}_2\text{H}$ has been proposed.

Peroxyhafnium hydrate is insoluble in cold alkaline H_2O_2 , in contrast to its zirconium analog; this prevents the formation of the anionic tetra-peroxyhafnate $[\text{Hf}(\text{O}_2)_4]^{-4}$. However, the complex peroxysulfate hafnate anion $[\text{Hf}(\text{O}_2)(\text{SO}_4)_2]^{-2}$ is formed in a manner exactly similar to the analogous titanium and zirconium complexes (489).

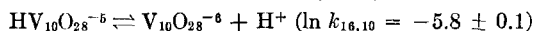
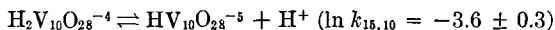
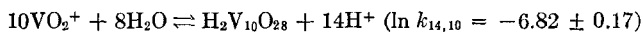
VIII. Vanadium

A. VANADIUM PENTOXIDE-WATER SYSTEM

Any discussion of the vanadium- H_2O_2 system should be prefaced by a short description of the vanadium pentoxide-water system. It has been shown (465) by means of potentiometry and absorption spectra that vanadium(IV) exists as VO^{2+} in the acidity range $2.95 M \geq [\text{H}^+] \geq 0.002 M$. Similarly (301, 466) V(V) exists as VO_2^+ in the acidity range $2.9 M \geq [\text{H}^+] \geq 0.05 M$; this formulation is preferred to $\text{V}(\text{OH})_4^+$. The hydrolysis of the VO_2^+ ion by acid was studied with various total concentrations of vanadium in perchlorate media of different ionic strength. In the range $3 < \text{pH} < 8$ the assembled data are consistent with the existence of $(\text{V}(\text{O})_2)_{10}(\text{OH})_{14}^{-4}$ over the biggest range of Z (the number of OH groups per VO_2^+ group) (509), so that initially hydrolysis occurs according to



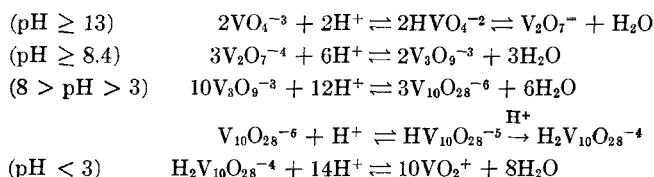
Conductometric and potentiometric titrations of vanadic acid (321), obtained by passing orthovanadate through an ion-exchange column, give support to its formulation as a decavanadate species. On the grounds of simplicity and from X-ray crystallography of isopolyvanadates (131), it is suggested that $\text{H}_2\text{V}_{10}\text{O}_{28}^{-4}$ is hydrolyzed successively to $\text{HV}_{10}\text{O}_{28}^{-5}$ and $\text{V}_{10}\text{O}_{28}^{-6}$; the hydrolysis constants are summarized below for 1 M perchlorate solutions.



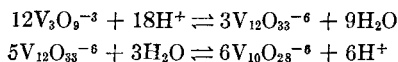
Further investigation (172, 243, 246-248, 350, 378, 415) using a variety of techniques has confirmed these results and shown that the conclusions are also correct for the concentration range $1.05 \times 10^{-3} > [\text{V}^V] > 1.05 \times 10^{-4}$ at an ionic strength of 3.0. As the pH of vanadium(V) solution increases beyond 6.5, a depolymerization occurs and the metavanadate ion species is formed. The exact nature of the metavanadate ion is still not satisfactorily elucidated. On the one hand Jahr (242, 243, 246) and

Glemser (172), as a result of cryoscopic studies, suggest that the metavanadate ion is tetrameric, $V_4O_{12}^{-4} \equiv (VO_3^-)_4$; on the other hand, Thilo (481) maintains the hypothesis of a trimer, $V_3O_9^{-3} \equiv (VO_3^-)_3$, on the basis of spectrophotometry. Thilo resolves this contradiction by suggesting that the polymerization number (n_v) is dependent on pH to such an extent that, unless the pH and concentration of metavanadate solutions are varied very considerably, the value $n \approx 4$ will inevitably result from the presence of small amounts of decavanadate in the solution, and the data he presents on the effect of small amounts of decavanadate on the observed value of n_v are certainly impressive.

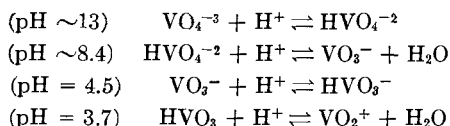
A further increase in pH leads successively to the formation of pyrovanadate and orthovanadate. In pyrovanadate solutions the dimer $V_2O_7^{-4}$ is in equilibrium with the monomeric form HVO_4^{-2} , the latter predominating in all but the most vanadium-rich solutions. In strong alkali, the orthovanadate ion VO_4^{-3} exists at all concentrations. The over-all picture of the vanadate system may be represented as follows (494):



Two further points are worth attention; the first is the description (172) of the transient red color observed when an orthovanadate solution is acidified. On the basis of a linear relation between extinction coefficient and n_v , this has been formulated as dodecavanadate, $V_{12}O_{33}^{-6}$, a conclusion which is supported by the R_f value from paper chromatography. Readjusting the data to fit the trimetavanadate hypothesis, we may visualize the formation of this ion in the following terms



This red dodecavanadate is the same as the octavanadate of Jander and Jahr (249). The second point is the observation (481) that monomeric vanadate and metavanadic acid exist in very dilute solutions of vanadates; in such dilute solutions ($< 10^{-4} M$) the predominant equilibria with changing pH are



In summary, the degree of condensation in the vanadium–water system is determined by two factors:

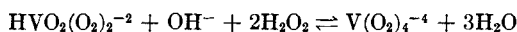
- (i) The concentration of free hydrogen ion.
- (ii) The concentration of vanadium.

Linked with these two, the ionic strength of the medium is obviously very important. It is reasonable to suppose that these same factors will affect the vanadium–H₂O₂ system and that for complete understanding of this system the same extensive variation of conditions will be necessary.

B. 4:1 PEROXYVANADATES: $V(O_2)_4^{-3} \equiv VO_3^{-3}$

The reaction of concentrated alkali hydroxide with concentrated solutions of V₂O₅ in H₂O₂ at temperatures below 0°C gives blue solutions which contain the ion VO₃³⁻. These salts, which can be precipitated by the addition of alcohol, can also be obtained by the addition of a large excess of H₂O₂ to a cold concentrated orthovanadate solution (239, 351). Reaction with permanganate shows these compounds to be tetraperoxy derivatives, and this has been confirmed by spectrophotometric studies (91, 239). Various other products of formulas such as M₃^IVO₆·2.5H₂O, M₃^IVO₇, M₄^IV₂O₁₂, and M₆^IH₂V₂O₁₈ have been obtained by this preparative reaction (42, 43, 351, 359), but it appears that these substances are mixtures of the tetraperoxy salt with decomposition products such as the [HVO₂(O₂)₂]⁻² ion (137, 239).

The salts are stable only at low temperatures, the stability decreasing with increasing cation size (239). The potassium salt, which is isomorphous with K₃[Cr(O₂)₄], has a magnetic moment of 0.6 B.M., consistent with the presence of vanadium(V), and the infrared spectra of the potassium and ammonium salts contain bands in the region 800–900 cm⁻¹ that have been assigned to vibrations of the peroxy group (137). It has been suggested (268) from spectrophotometric studies that in solution there is a hydrolytic equilibrium, involving hydroxyl ions and hydrogen peroxide, between the tetraperoxy species and a diperoxy anion as follows:

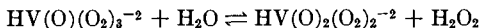


This explains the need for a high concentration of H₂O₂ to stabilize the blue tetraperoxy species. The reaction with acid potassium iodide has been used to confirm the formulation of a tetraperoxy species (239).

C. 3:1 PEROXYVANADATES: $V(O)(O_2)_3^{-3} \equiv VO_7^{-3}$; $HV(O)(O_2)_3^{-2} \equiv HVO_7^{-2}$

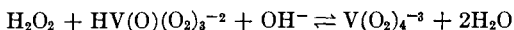
Cryoscopic titration of concentrated pyrovanadate solutions with excess concentrated H₂O₂ indicates the existence in solution of the yellow ion

$[\text{HV}(\text{O})(\text{O}_2)_3]^{-2}$, which contains three peroxy groups per vanadium atom (91). This ion is stable only in the presence of excess H_2O_2 , otherwise hydrolyzing to a diperoxy species:



Similar results are obtained for the orthovanadate- H_2O_2 system.

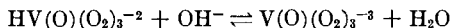
Spectrophotometric titration of the acid triperoxy species with base has been shown to produce the tetraperoxy anion $\text{V}(\text{O}_2)_4^{-3}$ so long as the base is not present in excess:



It is suggested that any slight excess of base causes the destruction of the tetraperoxy species and the formation of the yellow triperoxy anion $\text{V}(\text{O})(\text{O}_2)_3^{-3}$:

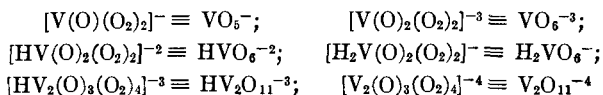


which is stable at room temperature. An acid-base equilibrium exists between the two triperoxy anions



The spectra of the two ions in the region 400–450 $\text{m}\mu$ are very similar.

D. 2:1 PEROXYVANADATES:



The yellow color produced by addition of H_2O_2 to a dilute solution of a metavanadate has been shown to be due to a diperoxy anion by cryoscopy and spectrophotometry (91) as well as by thermochemical studies (410); the same anion is apparently produced when an excess of H_2O_2 is added to vanadium pentoxide (363, 364), though decomposition to the red monoperoxy cation takes place in the absence of excess of H_2O_2 . There is some controversy, however, as to how the anion should be formulated. Potentiometric titration of lithium hydroxide against vanadium pentoxide dissolved in H_2O_2 (239) indicates that a tribasic anion, $[\text{V}(\text{O})_2(\text{O}_2)_2]^{-3}$, is formed, while the addition of alkali hydroxide to solutions of vanadium pentoxide in H_2O_2 has led to the formation of yellow crystalline solids of formulas $\text{M}^1\text{H}_2\text{V}(\text{O})(\text{O}_2)_2$. On the other hand, the cryoscopic and spectrophotometric studies have been interpreted in terms of the monobasic anion $[\text{V}(\text{O})(\text{O}_2)_2]^-$. This apparent contradiction can be resolved if the monobasic anion is

formulated with one molecule of water: $[(\text{H}_2\text{O})\text{V}(\text{O})(\text{O}_2)_2]^-$; this might well lose the two protons associated with the water molecule at high pH. In accordance with this view, the yellow anion $[\text{HV}(\text{O})_2(\text{O}_2)_2]^-$ is formed in the titration of solutions of pyrovanadates with H_2O_2 (91) and by the decomposition of ammonium tetraperoxyvanadate (38).

The equilibrium between the tribasic anion, the red monoperoxy cation, and H_2O_2 has been studied by dialysis (239) and by spectrophotometry (269, 270); dilute acid is necessary to stabilize the anion. A spectrophotometric study of the thermal decomposition of the "peroxyvanadium complex" formed by the action of H_2O_2 on an acid solution of a vanadate has also shown that the red peroxy cation is in equilibrium with a yellow diperoxy anion, though in this case the anion was not identified; various kinetic parameters were evaluated for the system (112). Orthovanadate may be formed as an intermediate in the decomposition of the diperoxy species of isopolyvanadate (235, 237).

At least two dimeric peroxyvanadate anions have been identified. Cryoscopic titration of an alkaline solution of a metavanadate with H_2O_2 indicates (91) the formation of the anion $[\text{HV}_2(\text{O})_3(\text{O}_2)_4]^{-3}$, formally derived by condensation of $[\text{V}(\text{O})(\text{O}_2)_2]^-$ and $[\text{HV}(\text{O})_2(\text{O}_2)_2]^{-2}$; this confirms earlier observations (33) on a compound previously described (359) as containing the anion $\text{V}_5\text{O}_{26}^{-8}$. Compounds that are supposed to contain the ion $[\text{V}_2(\text{O})_3(\text{O}_2)_4]^{-4}$ have been prepared by the action of aqueous ammonia on a solution of a metavanadate in H_2O_2 (359), by the action of H_2O_2 on a complex oxyfluoride of vanadium (352), and by the action of H_2O_2 on a melt of V_2O_5 and potassium hydroxide (183). The formulation of the potassium salt was supported by differential thermal analysis and by X-ray studies, but it should be noted that when sodium hydroxide was used the product was sodium tetraperoxyvanadate. It has been suggested that the species described as $[\text{V}_2(\text{O})_3(\text{O}_2)_4]^{-4}$ and $[\text{HIV}(\text{O})_2(\text{O}_2)_2]^-$ are really the same (91).

The salts described as containing the anions $[\text{V}(\text{O})_2(\text{O}_2)]^-$ (480) and $[\text{V}_2(\text{O})_4(\text{O}_2)_3]^{-4}$ (38, 45, 46) may have been partly decomposed samples of diperoxyvanadates (91).

E. 1:1 PEROXYVANADATES: $\text{V}(\text{O})(\text{O}_2)^+ \equiv \text{VO}_3^+$

The addition of H_2O_2 to V_2O_5 (24, 87, 239, 363, 365, 411, 574), to an acid solution of a metavanadate (91, 112, 469, 515), to a vanadium(V) salt in weakly acid solution (270), and to a decavanadate (321) produces a red color which has been shown by transport (363, 365), cryoscopic (91, 515), dialytic (239), spectrophotometric (91, 112, 270, 321, 469, 515), conductometric (270, 321), and pH (270, 321) studies to arise from the monomeric monoperoxyvanadate cation $\text{V}(\text{O})(\text{O}_2)^+$. The red color is stable in moderately acid media; in excess acid, condensation to isopolyvanadate

occurs, with subsequent production of V_2O_5 and VO_2^+ ; in strong acid, particularly if the solution is heated, the red cation is reduced to vanadium(IV), VO^{+2} (112, 270, 469). In excess H_2O_2 the red cation is converted to the yellow peroxy anion $V(O)(O_2)_2^-$ (91, 112, 239, 270, 321). Spectrophotometric studies (321) have shown that the red cation has $\lambda_{\max} = 560 \text{ m}\mu$, at which point the pH is 2.30. It has been suggested that the vanadate-catalyzed oxidation of iodide by acid- H_2O_2 involves the formation of an intermediate monoperoxyvanadium species, $V(O_2)OH$ (425). A study of the reduction of acid solutions of $V(O)(O_2)^+$ by γ -radiation has shown that the absence of H_2O_2 and $V(O)(O_2)^+$ when vanadium(V) is reduced by γ -radiation of acid solutions is due to reduction of these by $\cdot OH$, either of H_2O_2 before peroxidation of VO_2^+ can occur, or of $V(O)(O_2)^+$ as soon as it is formed (138, 418). A spectrophotometric study has been made (112) of the thermal decomposition of the red-yellow "pervanadium complex" and the kinetics of the process elucidated. The 1:1:1 complex formed between ammonium vanadate, pyridine-2,6-dicarboxylic acid, and H_2O_2 (211) has been obtained as a pure solid (210) and the structure of the anion has been proposed as $[V(O)(O_2) \cdot C_5H_3N(COO)_2 \cdot H_2O]^-$, but this suggestion awaits the application of physical methods for confirmation. Solutions of V_2O_5 in H_2O_2 have been used as oxidizing agents in organic chemistry (545-547, 553, 554).

Figure 1 shows the interrelation of the vanadium(V)-water and the vanadium(V)- H_2O_2 systems. We may make the following general observations:

(1) The number of peroxy groups per vanadium atom increases with alkalinity.

(2) Increasing acidity increases polymerization and decreases the number of peroxy groups per vanadium atom.

(3) Increasing the concentration of H_2O_2 decreases the degree of polymerization.

We may also make the more specific observations as follows:

(1) The 2:1 species $V(O)(O_2)_2^-$ has acidic properties, thus explaining the observed decrease in pH when H_2O_2 is added to a metavanadate; in the presence of excess of metavanadate, polymerization will occur due to the acidity of the medium. With increasing alkalinity this diperoxy anion is converted to the 3:1 species $HV(O)(O_2)_3^{-2}$ and $V(O)(O_2)_3^{-3}$ successively.

(2) The 2:1 species $HV_2(O)_3(O_2)_4^{-3}$ is favored by high concentrations of vanadium and is converted to the 3:1 species $HV(O)(O_2)_3^{-2}$ by high concentrations of H_2O_2 .

(3) The 4:1 species $V(O_2)_4^{-3}$ is favored by alkaline media of high ionic strength, rich in H_2O_2 . Under such conditions H_2O_2 functions as an acid; thus any excess of base causes all the H_2O_2 to be involved in the formation of HO_2^- , and consequently the 3:1 species $V(O)(O_2)_3^{-3}$ is formed.

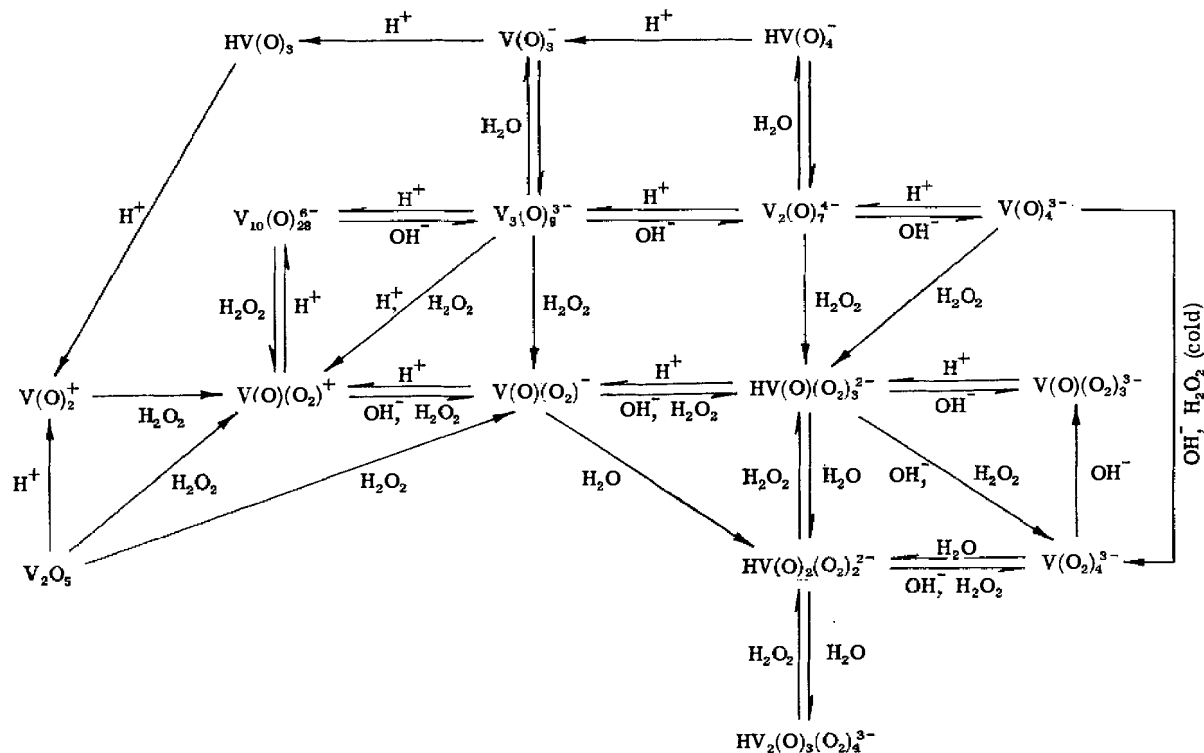
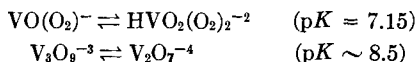
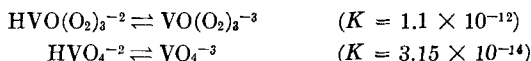


FIG. 1. Diagram showing the relationships between vanadium(V) oxy and peroxy compounds in aqueous solution.

(4) Comparison of the pK values of the transformations

and the dissociation constants



shows that the peroxy species are more acidic and less polymerized than the simple vanadates.

IX. Niobium and Tantalum

A. 4:1 PEROXY SPECIES: $\text{M}(\text{O}_2)_4^{-3} \equiv \text{MO}_8^{-3}$

The addition of ethanol to a solution containing H_2O_2 together with the metal pentoxide M_2O_5 ($\text{M} = \text{Nb}, \text{Ta}$) and an excess of an alkali metal hydroxide precipitates a white crystalline solid which contains the $\text{M}(\text{O}_2)_4^{-3}$ anion (21, 137, 182, 184, 360, 508). Salts of this anion are stable in air and dissolve in water without decomposition, although the tantalum derivatives are much less soluble and, in general terms, much more stable than their niobium analogs (360). The salts previously described (360) as containing the $\text{Nb}_2(\text{O})_3(\text{O}_2)_4^{-4}$ ion have been shown to be tetraperoxyniobates (21).

Hydrolysis of the tetraperoxy salts with dilute acid gives the monoperoxy anions $\text{MO}_2(\text{O}_2)^-$ (360). The tetraperoxy anions are isomorphous and isostructural with the tetraperoxy species of chromium (57); their salts are diamagnetic and conductivity measurements confirm the presence of a 3:1 electrolyte (137). Measurements of the infrared (137, 182) and Raman spectra (182) show the presence of strong absorption in the region 810–820 cm^{-1} which is assigned to ν (O-O). The compounds have been investigated by differential thermal analysis and by quantitative X-ray phase analysis (184).

B. 1:1 PEROXY SPECIES: $\text{M}(\text{O})_2(\text{O}_2)^- \equiv \text{MO}_4^-$

The reaction of the tetraperoxy anions $\text{M}(\text{O}_2)_4^{-3}$, either as solids or in solution, with dilute acids affords a gelatinous precipitate of the monoperoxy anion $\text{M}(\text{O})_2(\text{O}_2)^-$ (21, 184, 360, 508). The niobium compound is light yellow and the tantalum compound is white: both are insoluble in water and are decomposed by hot dilute acid (184). The free monoperoxy acid $\text{HMO}_2(\text{O}_2)$ is formed when an aqueous solution of M_2O_5 is warmed with H_2O_2 (21, 360).

The reaction of H_2O_2 with metaniobates gives salts of the corresponding monoperoxy compound, $\text{M}^{\text{I}}\text{Nb}(\text{O})_2(\text{O}_2)$, although it appears that some of these may contain hydrogen peroxide of crystallization, particularly when obtained by using high concentrations of H_2O_2 . These salts are not particularly stable at 0°C (185).

A spectroscopic study (4, 5) has shown by the method of continuous variations that a 1:1 peroxyniobate species having $\lambda_{\text{max}} = 256 \text{ m}\mu$ is formed in solutions of Nb_2O_5 in a large excess of H_2O_2 which contain less than 40% sulfuric acid. Increasing the acid concentration produces a diperoxy species. The 1:2 species described by earlier workers (479) has been shown to be the same as the 1:1 species.

C. OTHER PEROXYNIOBATE SPECIES

A spectrophotometric study (4, 5) of the species existing in solutions of Nb_2O_5 in H_2O_2 in which the acid concentration is varied over a wide range has shown that three complexes are formed. The first (I), having $\lambda_{\text{max}} = 365 \text{ m}\mu$ in 100% H_2SO_4 , is destroyed by the addition of less than 2% sulfur trioxide and exists throughout the range 50–100% H_2SO_4 . The second (II), whose absorption maximum is inaccessible, is important at acid concentrations of less than 60%. The third species (III) has an absorption maximum at $256 \text{ m}\mu$ and is important at acid concentrations less than 40%. The H_2O_2 :Nb ratios of these three complexes were determined to be:

I	3:2
II	2:1
III	1:1

A study (6) of the condensation equilibrium between I and II shows that its acid dependence is due to the additional equilibrium between H_2O_2 and its conjugate acid H_3O_2^+ which is not dissociated in strong mineral acids.

These results represent one of the few exceptions to the general rule that the number of peroxy groups per metal atom decreases with increasing acidity.

No comparable study has been made of the $\text{Ta}(\text{V})/\text{H}^+/\text{H}_2\text{O}_2$ system.

X. Chromium

The peroxides of chromium are probably better known and better characterized than those of any other transition element. Four different series of derivatives are known, formed under different conditions of pH, and solid members of each series have been prepared: they have the formulas $\text{M}_3^{\text{I}}[\text{Cr}(\text{O}_2)_4]$, $\text{M}^{\text{I}}\text{HCr}(\text{O})_2(\text{O}_2)_2$, $\text{BCr}(\text{O})(\text{O}_2)_2$ (where B is a nitrogen base), and $\text{D}_3\text{Cr}(\text{O}_2)_2$ (where D is a nitrogen base or cyanide ion). In addition to these, other peroxochromium compounds have been described, but

are less well characterized. In the account that follows, the series are considered in turn, after which an attempt is made to discuss the relationships between them.

A. THE RED TETRAPEROXYCHROMATES(V)

When an alkaline solution of a chromate is treated with H_2O_2 , it turns from yellow to deep red-brown; if the system is kept at 0° , dark brown crystals slowly precipitate (450). Analysis shows that the alkali metal derivatives have the formulas $\text{M}_3^{\text{I}}\text{CrO}_8$, while the amount of O_2 evolved on decomposition in acid or alkaline solution, together with the reaction with potassium permanganate, indicates the presence of four peroxy groups (441, 442). Acid salts of this series have not been prepared; the triammonium salt $(\text{NH}_4)_3[\text{Cr}(\text{O}_2)_4]$ is formed from solutions that are only weakly ammoniacal, provided enough H_2O_2 is present, though triamminodiperoxychromium(IV) is formed as well (446) if this condition is not fulfilled.

These red salts are relatively stable to heat, and may be kept for some months at room temperature without decomposition. The potassium salt decomposes relatively slowly even at 170° (450), but pure samples explode at 178° and the explosion temperature is apparently lowered by the presence of impurity. The sodium and ammonium salts are less stable (450).

The formula $\text{M}_3^{\text{I}}[\text{Cr}(\text{O}_2)_4]$ implies the presence of chromium(V), and in accordance with this the potassium salt has a paramagnetic susceptibility at 20° of 1.80 B.M. (280, 541, 542), while electron resonance spectra

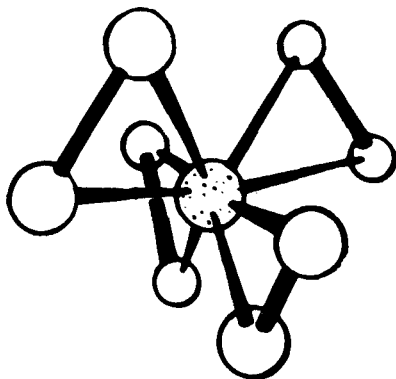


FIG. 2. The tetraperoxychromate(V) ion (232, 522a, 523). The structural parameters from a least-squares refinement (524) of earlier (523) experimental data are: $r(\text{Cr}-\text{O}_a)$, 1.846 ± 0.022 ; $r(\text{Cr}-\text{O}_b)$, 1.944 ± 0.024 ; $r(\text{O}_a-\text{O}_b)$, $1.405 \pm 0.039\text{\AA}$; $\angle \text{O}_a\text{CrO}_a = 86.8 \pm 1.4^\circ$; $\angle \text{O}_b\text{CrO}_b = 173.7 \pm 2.5^\circ$; three-dimensional analysis, $R = 0.1$. A different (522a) least-squares refinement gives parameters that differ insignificantly from these, but the value for $r(\text{O}_a-\text{O}_b)$, $1.472 \pm 0.025\text{\AA}$, is worth noting. Circle, O; dotted circle, Cr.

have been obtained from the powder (147, 232, 319, 524) (with $g_{\parallel} = 1.936 \pm 0.002$, $g_{\perp} = 1.983 \pm 0.002$) (524) and from aqueous and alkaline solutions (103). A recalculation (524) of data from an X-ray study of a single crystal of the potassium salt (523), which is isomorphous with the analogous derivatives of niobium and tantalum (57), shows that the chromium atom is surrounded by four equivalent peroxy groups, in an arrangement that could be described as a distorted dodecahedron of oxygen atoms (see Fig. 2); the two Cr—O distances are significantly different. Molecular orbital calculations have been made using parameters derived from the g values (524); the unpaired electron is assigned to a B_1 orbital of chromium. The O—O distance of 1.40 Å is rather less than the 1.49 Å found in alkali metal peroxides (2), perhaps because electrons that in the free peroxide ion are in antibonding π orbitals are partly delocalized in the complex into orbitals of chromium.² The crystal field parameter Δ has been calculated from two weak ultraviolet bands (which may be due to crystal field transitions) as $\sim 35,000 \text{ cm}^{-1}$ (524), while the infrared spectrum of the potassium salt has been recorded (137, 181) (see Table II).³

TABLE II
INFRARED FREQUENCIES ASSOCIATED WITH THE PEROXY GROUPS
IN SOME PEROXYCHROMIUM COMPOUNDS^a

Compound	Frequency (cm^{-1})	
	Reference (181)	Reference (137)
$(\text{NH}_3)_3\text{Cr}(\text{O}_2)_2$	865s	891s
$\text{En} \cdot \text{Cr}(\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$	—	880s
$\text{K}_3[\text{Cr}(\text{O}_2)_4]$	875s	975w, 875s, 675m ^b
$(\text{NH}_4)_3[\text{Cr}(\text{O}_2)_4]$	—	970w, 870s, 665m ^b
$\text{NH}_4[\text{HCr}(\text{O})_2(\text{O}_2)_2] \cdot \text{H}_2\text{O}$	980*s, 932s	980s, 937s
$\text{K}[\text{HCr}(\text{O})_2(\text{O}_2)_2]$	984*m, 924*s, 876s	—
$\text{Ti}[\text{HCr}(\text{O})_2(\text{O}_2)_2]$	970*w, 920*s, 870s	—
$\text{Cr}(\text{O})(\text{O}_2)_2$ (in ethyl acetate)	940*s, 864s	—
$\text{Py} \cdot \text{Cr}(\text{O})(\text{O}_2)_2$	937*s, 875m	950w, 942w, 934
$\text{Bipy} \cdot \text{Cr}(\text{O})(\text{O}_2)_2$	922*s, 890m	947m, 925m
$1,10\text{-phen} \cdot \text{Cr}(\text{O})(\text{O}_2)_2$	—	945m, 925s, 910w

^a All spectra save that of $\text{Cr}(\text{O})(\text{O}_2)_2$ in ethyl acetate were recorded as nujol mulls; the bands marked with asterisks were assigned to (Cr=O) modes, making a distinction that in these systems may be artificial; s = strong, m = medium, w = weak intensity.

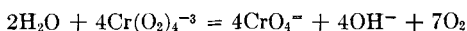
^b May be due to carbonate impurity.

² A different least-squares refinement of the same data (522a) gives a value for the O—O distance of $1.472 \pm 0.025 \text{ Å}$, not significantly different from that in the O_2^- ion.

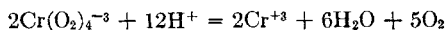
³ There are differences in detail in the reported ultraviolet spectra and electron resonance g values (319, 524), which may arise from differences in experimental conditions.

The red tetraperoxychromates(V) are slightly soluble in water and the solutions are stable for some days, particularly in the presence of free alkali (450). Freezing point measurements confirm that the potassium salt gives four particles in solution (442), while the molar conductivity is 252 ohm⁻¹mol⁻¹cm² at infinite dilution (442) (see also 137).

The course of decomposition in aqueous solution depends on the pH. In neutral or alkaline solution, chromate and oxygen are formed according to the equation (442, 450):



The decomposition is first order. In acid solution, Cr(III) is produced according to the limiting equation:



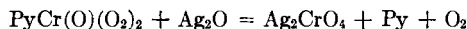
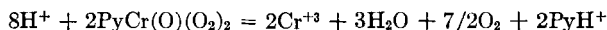
Under these conditions, the decomposition is second order (59). In practice, some chromate is always formed at the same time, the amount decreasing as the acidity rises (442, 450). The blue hydrated chromium pentoxide or the violet salts of diperoxychromic acid (see below) are formed as intermediates in this reaction: if an aqueous paste of ammonium tetraperoxychromate(V) is acidified, the violet $(\text{NH}_4)[\text{Cr}(\text{O})_2(\text{O}_2)_2\text{H}]$ is precipitated (447), while the amount of ether-extracted chromium pentoxide produced by the addition of various acids to cooled solutions of the tetraperoxychromates(V) varies with the strength of the acid (448). In the absence of water the sodium and potassium salts do not react with ethereal solutions of hydrogen chloride; decomposition, which is very slow, gives chromate. If a few drops of water are added, however, the solution turns an intense blue (448). When heated with an excess of ammonia solution, ammonium tetraperoxychromate(V) gives triamminodiperoxychromium(IV).

Several other red peroxychromates have been reported, with complex formulas (such as $\text{Li}_3\text{Cr}_2\text{O}_{15}$ or $\text{Mg}_2\text{K}_2\text{Cr}_2\text{O}_{15}$) that imply the presence of Cr—O₂—Cr bridges (37, 39–41, 44). In at least one case, magnetic measurements have shown that the compound really contains the tetraperoxychromate(V) ion (460); it seems very likely that this is true of all of them, the odd formulas arising from slight decomposition or from side reactions in the course of analysis.

B. DERIVATIVES OF BLUE CHROMIUM(VI) PENTOXIDE

The blue substance formed when hydrogen peroxide is added to an acid solution of a chromate, though very unstable in water, can be extracted with ether (24) or other oxygen-containing organic solvents in which it is much more stable (186). The ethereal solution reacts with electron-pair donors such as pyridine (575), aniline (575), quinoline (577), or 1,10-phen-

anthroline (130), and solid compounds of formulas BCrO_5 ($\text{B} = \text{base}$) have been obtained from the reaction mixtures by evaporating the excess solvent. The pyridine derivative was given the structure $\text{PyCr}(\text{O})(\text{O}_2)_2$ on the basis of its reactions with dilute sulfuric acid, with silver(I) oxide, and with neutral potassium permanganate (of which four equivalents were consumed per mole of pyridine complex) (490):



This structure implies that the chromium atom is in the (formal) +6 state, and that the compound is a molecular donor-acceptor complex; in keeping with this, the molecular weight in benzene is that of a monomer (442, 575), the conductivity in dimethylformamide is very small (137), while the small (and probably temperature-independent) paramagnetic susceptibility [$\mu = 0.4\text{--}0.8\text{B.M.}$ (137, 181, 280)] is consistent with the presence of $\text{Cr}(\text{VI})$. Moreover, careful analysis of the 1,10-phenanthroline derivative gave the hydrogen content expected for the adduct rather than for a salt, while there is no band in the infrared spectrum of the pyridine complex that is likely to be associated with a $\text{N}^+\text{--H}$ stretching mode (130). Physicochemical

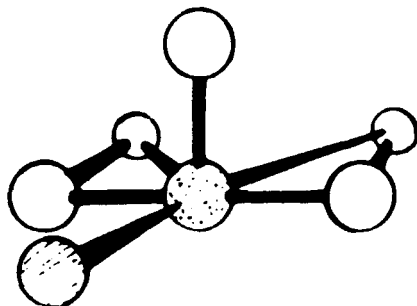
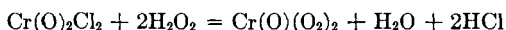


FIG. 3. Coordination around the chromium atom in pyridinechromium pentoxide (392, 522). A recent least-squares refinement of the three-dimensional analysis (522) gives the following structural parameters: $r(\text{Cr--O}_1)$, 1.794 ± 0.014 ; $r(\text{Cr--O}_2)$, 1.825 ± 0.014 ; $r(\text{Cr--O}_3)$, 1.796 ± 0.014 ; $r(\text{Cr--O}_4)$, 1.844 ± 0.014 ; $r(\text{Cr--O}_5)$ (chromyl oxygen), 1.576 ± 0.018 ; $r(\text{Cr--N})$, 2.047 ± 0.013 ; $r(\text{O}_1\text{--O}_2)$, 1.407 ± 0.016 ; $r(\text{O}_3\text{--O}_4)$, $1.400 \pm 0.016\text{\AA}$; $\angle \text{O}_1\text{CrO}_2 = 45.7 \pm 0.7^\circ$. In this determination the R value for the refined determination is 0.11. Circle, O; dotted circle, Cr; lined circle, N.

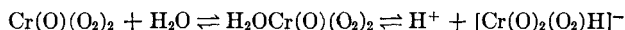
studies of the preparative reaction in a variety of solvents (130, 456, 468, 469) confirm that the formation of CrO_5 involves two molecules of H_2O_2 to each chromate ion, with an equilibrium constant for formation of 5.4×10^7 at 10° in water of $\text{pH} \sim 1.5$ (130); the conclusion from an earlier spectrophotometric study (168) that the blue compound was the monoperoxy acid $\text{HCr}(\text{O})_3(\text{O}_2)$ has since been abandoned (171). Two X-ray studies of

the pyridine complex confirm this view. The chromium atom, the two peroxy groups, and the nitrogen atom of the pyridine molecule are all nearly coplanar, while the fifth oxygen lies above the chromium atom (392, 522) (see Fig. 3).

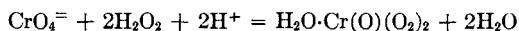
The blue pentoxide has never been isolated. Attempts to prepare it directly from chromyl chloride and H_2O_2 gave an equilibrium mixture that retained some chromyl chloride and from which no definite compound was isolated (488):



From a solution of the pentoxide in dimethyl ether, an etherate has been obtained by careful evaporation of the excess solvent at -50° (488); the crystals, which were originally mistaken for the free acid $\text{H}_3\text{Cr}(\text{O}_2)_4$ (448), exploded if allowed to warm to -30° . By analogy with the etherate, it seems likely that in water the species present should be written $\text{H}_2\text{O}\cdot\text{Cr}(\text{O})(\text{O}_2)_2$ or $\text{H}_2\text{Cr}(\text{O})_2(\text{O}_2)_2$. Aqueous solutions decompose rapidly to Cr(III) and O_2 at $\text{pH} < 4$ (55); as the pH rises, the amount of Cr(VI) formed in the decomposition increases (55, 444, 516). When the ethereal solution is treated with less than the calculated amount of ethereal ammonia, alcoholic potassium hydroxide (440, 576), or concentrated aqueous potassium cyanide (578), the violet salts of diperoxychromic acid, $\text{M}^+\text{HCr}(\text{O})_2(\text{O}_2)_2$, are precipitated; ammonium tetraperoxychromate has been obtained from ethereal chromium pentoxide and saturated aqueous ammonia (442) and, with an excess of aqueous ammonia (575), triamminodiperoxychromium(IV) is formed. Aqueous potassium hydroxide, aqueous or alcoholic sodium hydroxide (576), or aqueous sodium carbonate (439) decomposes the ethereal solution to chromate, while solid sodium acetate reacts to give a purple substance that is probably $\text{Na}[\text{Cr}(\text{O})_2(\text{O}_2)_2\text{H}]$ (388). With organic nitrogen bases, either adducts or salts of diperoxychromic acid are formed: aniline (575), quinoline (577), pyridine (575), dipyridyl (137), 1,10-phenanthroline (130), and probably strychnine (24) give adducts, while tetramethylammonium hydroxide, trimethylamine, and piperidine give what appear to be salts (577). All these reactions imply, as was suggested many years ago (10), that in aqueous solution the blue pentoxide is the parent acid of the violet salts, and that in water it can act as either a protonic or a Lewis acid:



The rise in pH on formation of chromium pentoxide in aqueous solution (55) implies that its formation involves removal of protons



and that if it is a protonic acid it must be a weak one. No thorough study seems to have been made of the competing reactions of salt and adduct formation; on the basis outlined above, it seems likely that the stronger bases would give adducts rather than salts.

The reaction between alkali metals and ethereal solutions of chromium pentoxide gives purple-red solids that have been formulated as $M_2Cr_2O_8$, but which are probably diperoxychromates (81) (see below). The reaction between chromium pentoxide and such compounds as nitrophenols led to little or no hydroxylation (219).

The adducts with amines are rather more stable than the etherates, though the pyridine derivative explodes when heated to 70° or when treated with concentrated sulfuric acid (442).^{3a} The suggestion that it exists in stereoisomeric forms (445) has not apparently been pursued. The adducts with bidentate ligands seem to be rather more thermally stable than those with monodentate bases (130, 137); this raises an interesting question of structure. In the pyridine derivative, the chromium atom is in a sense six-coordinated, but the ligands form a pentagonal pyramid, so that there is what might be called a vacant coordination position axial to the unique oxygen atom (see Fig. 3). In the adducts of bidentate diamines, this position might well be filled. There is little direct evidence, however, for such a structural difference. The ultraviolet spectrum of the 1,10-phenanthroline derivative is rather different, it is true, from that of the pyridine compound; it shows, in place of the two peaks at ~ 5800 and 7000 \AA ($\epsilon \sim 500$), two bands of about this intensity but at ~ 6300 and $\sim 8300 \text{ \AA}$. The infrared bands assigned to modes of the peroxy groups in the spectra of the two compounds in the NaCl region, however, are at very similar frequencies (137).

The decomposition of chromium pentoxide has been the subject of some unconvincing kinetic studies. One series of experiments has led to the conclusion that the rate of decomposition in aqueous solution, like the rate of formation, is independent of the concentration of H_2O_2 , is first order in chromium pentoxide, and at a given concentration of H_2O_2 and of dichromate is first order in sulfuric acid (176). In organic solvents, the decomposition is unimolecular with rate constants at 10° and 20° of 0.002125 and $0.005273 \text{ sec}^{-1}$, respectively (414).

In papers (414, 419-424) in which many details appear to conflict with other published work, it has been proposed that the blue compound decomposes to give chromium(III) chromate, though it seems to be generally agreed (55, 444, 516) that the amount of Cr(III) formed depends on the pH of the solution. On the basis of some low analytical results, it is proposed that the blue compound should be described as chromium(III) perchromate,

^{3a} The pyridine adduct, when dry, has been known to explode violently at room temperature.

$\text{Cr}_2^{\text{III}}(\text{Cr}_2^{\text{VI}}\text{O}_{10})_3$, while the pyridine adduct is regarded as containing a complex chromium(III)-pyridine cation. It must be admitted that the numerical results obtained by Schwarz and Giese (490) in their analysis of the pyridine complex are not very impressive, but this is a reflection of the instability of the compound rather than an indication that the formula is more complicated. The suggested structure is not consistent with the results of the X-ray studies (392, 522) and the ethereal solution gave no electron resonance spectrum (123) such as would be expected for a derivative of chromium(III). Finally, evidence is presented (421, 423) to show that Cr(III) is an intermediate in the formation of the blue compound. The reader is referred to the original papers to form his own judgment.

C. THE VIOLET DIPEROXYCHROMATES(VI)

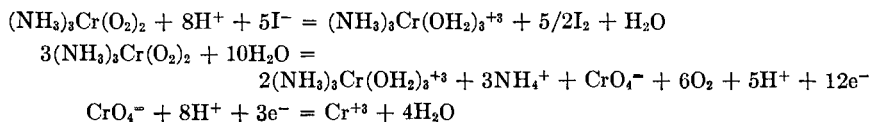
These salts, which have been given a number of different formulas (see Subsection E), are obtained either by the action of H_2O_2 on weakly acidic solutions of alkali metal chromates (450) or by treating an ethereal solution of chromium pentoxide with less than the calculated amounts of ethereal ammonia, alcoholic potassium hydroxide, or aqueous potassium cyanide (576). The salts are soluble in water; the ammonium salt dissolves in alcohol, though not in other organic solvents; the aqueous solutions are conducting, (137, 181, 450) and the molar conductivity of a solution of the ammonium salt has been given as 67 (at 5°) (137) and as $111 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$ (181). The instability of these solids makes analysis difficult; the composition was long believed to be represented by the formula $\text{M}^{\text{I}}\text{CrO}_6$, usually with one molecule of water of crystallization (491), but careful analysis of the anhydrous potassium salt has shown that it contains one hydrogen atom per molecule (181) and the presence of $-\text{OH}-$ groups is confirmed by the infrared spectrum (181). Treatment with potassium permanganate, ceric sulfate, or silver(I) oxide shows that there are two peroxy groups to each chromium atom; it was also established that the number of peroxy groups per chromium was the same in the violet salts and in chromium pentoxide (181). Since physicochemical studies (456, 468, 469) of the reaction between H_2O_2 and chromate in neutral solution had already indicated this conclusion, and since the salts show the small (and probably temperature-independent) paramagnetism ($\mu \sim 0.6 \text{ B.M.}$) associated with Cr(VI) (137), the structural formula $\text{M}^{\text{I}}[\text{Cr}(\text{O})_2(\text{O}_2)_2\text{H}]$ seems well established for these compounds. It is probable that the peroxy groups are laterally coordinated to chromium; since no acid salts of tetraperoxychromic(V) acid have been obtained, the proton seems most likely, as Griffith (181) concluded on other grounds, to be associated with one of the Cr—O groups. Until recently, the anion has been described as a dimer, $[\text{Cr}_2(\text{O})_4(\text{O}_2)_4]^-$, because it was not realized that

an atom of hydrogen was present in the anion; the correctness of the monomeric formulation has been confirmed by cryoscopic measurements (181). It is remarkable that no authentic derivative of the fully substituted acid has been described, though the brick-red solids of formulas K_2CrO_6 (59) and $CaCrO_6$ (68) could be such compounds (see below). Aqueous solutions of the violet salts are neutral to litmus; the relatively low conductivity suggests that the proton in the anion is not particularly mobile.

The violet salts are all extremely unstable, exploding when struck or warmed, "*z.B. mit dem Hand*". They decompose in water or in the solid state to give oxygen and chromic acid or chromate (576). The aqueous solutions give unstable precipitates with soluble salts of lead, barium, or silver(I), while solutions of iron(III) turn green (576). The action of alkali leads to the formation of some of the red tetraperoxychromate(V), with some decomposition to chromate and oxygen (450); with acid, chromium pentoxide hydrate is produced (225), while the main product of reaction with aqueous ammonia is triamminodiperoxychromium(IV) (447).

D. DERIVATIVES OF DIPEROXYCHROMIUM(IV)

When a tetraperoxychromate(V) (450), a diperoxychromate(VI) (450), or an ethereal solution of chromium pentoxide (575) is treated with an excess of aqueous ammonia, a brown-red crystalline solid is formed, of composition $Cr(O_2)_2 \cdot 3NH_3$; the same substance has been obtained by direct reaction of ammonium dichromate, aqueous ammonia, and H_2O_2 (226). In water, in which it is slightly soluble, its molecular weight (determined cryoscopically) is roughly the same as its formula weight (442) and the solution is almost nonconducting (137), while the ammonia content is unaffected by treatment with acetic acid (226); evidently the compound is not an ammonium salt. Five electron equivalents of iodine are liberated per formula weight on treatment with potassium iodide (575), while reaction with potassium permanganate gives a net consumption of three electron equivalents of oxidizing power per mole (130); these observations can be explained if the substance is a diperoxy derivative of chromium(IV):



In agreement with this view, the paramagnetic moment of the compound is 2.8 B.M., consistent with the presence of the two unpaired electrons associated with chromium(IV) (49, 137). In the crystal (320), the chromium atom may be described as seven-coordinated (see, however, Section XXIV) with a roughly T-shaped arrangement of nitrogen atoms round it; the

peroxy groups lie with the O—O axes in the plane of the downstroke of the T, so that they and one nitrogen atom form an irregular plane pentagon around the chromium atom (see Fig. 4). The O—O distance of 1.31 Å is some 0.18 Å less than in the peroxide ion (2), so the compound was described as a superoxide of Cr(II); since the infrared frequencies probably

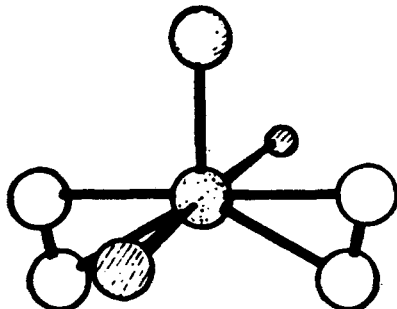


FIG. 4. The arrangement of the heavy atoms in triamminodiperoxychromium(IV). In the orthorhombic form, the structural parameters are: $r(\text{Cr—O}_1)$, 1.891 ± 0.020 ; $r(\text{Cr—O}_2)$, 1.879 ± 0.021 ; $r(\text{Cr—O}_3)$, 1.858 ± 0.020 ; $r(\text{Cr—O}_4)$, 1.867 ± 0.019 ; $r(\text{Cr—N}_1)$, 2.147 ± 0.025 ; $r(\text{Cr—N}_2)$, 2.084 ± 0.020 ; $r(\text{Cr—N}_3)$, 2.110 ± 0.022 ; $r(\text{O}_1\text{—O}_2)$, 1.414 ± 0.026 ; $r(\text{O}_3\text{—O}_4)$, 1.424 ± 0.024 Å. $\angle \text{O}_1\text{CrO}_2 = 44.0^\circ$, $\angle \text{O}_3\text{CrO}_4 = 45.0^\circ$, both $\pm 0.8^\circ$; three-dimensional analysis, $R = 0.11$ (522b). A two-dimensional analysis of the monoclinic form (320) indicates that the atomic arrangement is the same, but the structural parameters are less precise, even when refined by a least-squares analysis (522a,b). Circle, O; dotted circle, Cr; lined circle, N.

associated with vibrations of the peroxy group are very similar in this and in other peroxychromium compounds, the short O—O distance is surprising (181).⁴ The compound is polymorphic, and two forms (226, 446) were described wrongly as isomers; its ultraviolet spectrum has been recorded (506).

Analogous derivatives of ethylenediamine, $\text{en} \cdot \text{Cr}(\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, and of hexamethylenetetramine, $\text{C}_6\text{H}_{12}\text{N}_4 \cdot \text{Cr}(\text{O}_2)_2$, have been made by treating solutions of the appropriate amine and chromic acid with 30% H_2O_2 (223); their structures have not been determined.

Triamminodiperoxychromium(IV) is a relatively stable compound, which when dry may be kept at room temperature for months without decomposition (442), though it explodes when ground up or when heated with a flame (226). The products of decomposition include ammonia, chromium(VI), and chromium(III) possibly as hexammine chromium(III) chromate (442). It is insoluble in alcohol and in ether, but gives a violet-

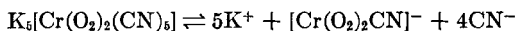
⁴ A least-squares refinement of the data (522c) indicates that the limits of error of this value are ~ 0.1 Å; a more precise study of the orthorhombic form (see Fig. 4) gives O—O distances of $1.41\text{--}1.42 \pm 0.025$ Å (522b).

red solution in water, which decomposes on heating, giving off oxygen (575). Treatment with acid induces decomposition to chromium(III), chromium(VI), and oxygen, the speed of decomposition depending on the strength of the acid; in dilute acid, most of the peroxy oxygen is evolved as O_2 (442), while with acid and ether some chromium pentoxide may be extracted (226, 575). With concentrated hydrochloric acid, the main chromium-containing product is aquotriamminechlorochromium(III) chloride (567, 569); with concentrated sulfuric acid the compound explodes (226), and when warmed with alkali it decomposes to give chromate (575).

The reaction with potassium cyanide solution at 60° leads to the formation of a compound of formula $CrO_4 \cdot 3KCN$ (578). This compound probably contains the complex anion $[Cr(O_2)_2(CN)_3]^{-3}$, at least in the solid state⁵; it gives about six electron equivalents of iodine with potassium iodide, as against a calculated five for the above formula (578). It is fairly stable at room temperature, though exploding at 115°C^{5a}; it is soluble in water, giving a brown solution that slowly decomposes with evolution of oxygen. When the aqueous solution is treated with sulfuric acid, the brown color turns a deep violet, and the colored component can be extracted with ether; the ethereal extract contained a cyanoperoxy derivative of chromium, but no definite compound was isolated (578). Wiede suggested that the violet species was the free acid $H_3[Cr(O_2)_2(CN)_3]$, but offered no evidence for this view (578).

When an aqueous solution of potassium tricyanodiperoxychromium(IV) is heated with dilute sulfuric acid, O_2 and hydrogen cyanide are evolved, leaving chromium(III). The aqueous solution of the peroxycyanide gives unstable precipitates with soluble salts of silver(I), thallium(I), lead(II), or copper(II); the formation of a brown rather than a white precipitate with silver(I) implies that the solution contains little cyanide ion (578).

When a mixture of potassium cyanide and chromic acid in appropriate concentrations is treated with 30% H_2O_2 , a pentacyanide derivative, of formula $Cr(O_2)_2 \cdot 5KCN \cdot 5H_2O$, is formed (440). This compound, which is dark red, is hygroscopic, and dissolves in water to give a conducting solution; some rather unsatisfactory cryoscopic measurements suggest that ten particles are formed in solution:



though dissociation to two cyanide ions and the complex $[Cr(O_2)_2(CN)_3]^{-3}$, giving eight particles, seems more reasonable if the tricyano complex exists

⁵ This has been confirmed by X-ray crystallography (522c); refinement of the structure is not complete, but with $R = 0.125$, $r(O-O) = 1.445-1.446 \pm 0.016$, and $r(C \equiv N) = 1.133 \text{ \AA}$.

^{5a} Griffith, however, found that the compound is dangerously explosive at room temperature (182a).

in solutions of the tricyanide derivative. The aqueous solution, which is alkaline, gives the reactions of cyanide ion; with concentrated ammonia it forms the dark red solid $K_2[Cr(O_2)_2(CN)_2NH_3]$, which is also hygroscopic; the solution of this in water is conducting, and cryoscopic measurements are consistent with dissociation according to the equation (440):



E. OTHER PEROXYCHROMIUM COMPOUNDS

$(NH_4)_2CrO_6$. Attempts to repeat the preparation of this compound, described in two different communications (224, 379), have led either to the formation of $NH_4[Cr(O)_2(O_2)_2H]$, or to a mixture of ammonium tetraperoxychromate(V) and ammonium chromate (181).

$K_2CrO_{10} \cdot nH_2O$, K_2CrO_6 (60). The dark violet compound described as K_2CrO_{10} was made by treating 60% H_2O_2 , cooled by solid CO_2 , with a saturated solution of potassium chromate and adding a large excess of cooled ethanol. The compound was extremely unstable at room temperature; its formula was deduced from the ratio of O_2 evolved to potassium chromate formed on decomposition with (finally) gentle warming; it should apparently be written $K_2[Cr(O_2)_5]$. Such a formula implies the presence of Cr(VI) with a coordination number of 5 (see Section XXIV); perhaps some of the peroxide was present as H_2O_2 . The compound dissolves in water, with evolution of oxygen; when dispersed on a watchglass at room temperature, it decomposes to form the stabler solid K_2CrO_6 , formulated as $K_2[Cr(O)_2(O_2)_2]$. The former compound sounds in some ways like $K[Cr(O)_2(O_2)_2H]$, but in the absence of physical data no further conclusions can be drawn. The existence of these two compounds was deduced from catalytic studies.

$CaCrO_6 \cdot nH_2O$, $CaCrO_5 \cdot nH_2O$. If 55% H_2O_2 is added to freshly prepared calcium chromate at -80° and the resulting solution treated with an excess of alcohol, a brick-red compound is formed of formula $CaCrO_6 \cdot nH_2O$; it decomposes at room temperature to the stabler $CaCrO_5 \cdot nH_2O$, which itself gives calcium chromate on prolonged standing (68). The former compound apparently contains two peroxy groups per mole, and so might well be a disubstituted salt of diperoxychromic acid, $H_2[Cr(O)_2(O_2)_2]$, but it is not clear if either of these substances is a definite compound. Analogous derivatives of sodium (66a), cobalt (396), and nickel (67) have been obtained; all were prepared as a result of kinetic studies.

$M^1H_2CrO_7$, $M^1CrO_5 \cdot H_2O$, $M_2^1Cr_2O_{11}$. These are all formulas applied to the violet salts of diperoxychromic acid.

$Ca_3Cr_2O_{12} \cdot 12H_2O$ (431). This buff-colored fluffy solid, made by the action of H_2O_2 on calcium chromate at room temperature, contained three

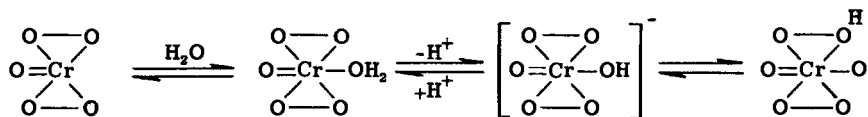
peroxy groups per chromium atom, and was probably a partly decomposed or otherwise impure sample of calcium tetraperoxychromate(V).

$M_2^{II}Cr_2O_8$. Purple solids of this composition were obtained by treating an ethereal solution of chromium pentoxide with potassium metal (81) or with the solid acetates of lithium, sodium, zinc, or other metals (388). The salts were analyzed by a method that may well have allowed the escape of some peroxy oxygen, and were found to contain one peroxy group to two chromium atoms. They were formulated as probably analogous in structure to perdisulfates, but it is not clear whether they are true chemical individuals. Their properties suggest that at least the potassium salt may have been the diperoxychromate, $K[Cr(O)_2(O_2)_2H]$.

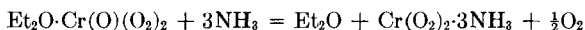
Besides these compounds, it has been suggested on the basis of oxygen exchange studies that a peroxy cation of chromium may be formed as an intermediate in the action of O_2 on solutions of chromium(II) (267). A blue-green peroxychromium derivative seems to have been formed by the reaction between chromic acid and H_2O_2 in trifluoroacetic acid, but nothing further is known about it (153).

F. DISCUSSION AND INTERPRETATION

One of the remarkable things about the peroxy compounds of chromium is their similar, but different, conditions of preparation and products of decomposition. In this context, it is interesting to bear in mind that for Cr^{+6}/Cr^{+3} , E° is +1.33 volt and E_B° is -0.13 volt; the potentials for H_2O_2 are given in Section III. With increasing pH, the reducing power of H_2O_2 rises, but the ease of reduction of chromium(VI) falls more rapidly. It is therefore a little surprising that the immediate product of the reaction between H_2O_2 and Cr(VI) at pH < 7 contains Cr(VI), while in alkaline solution the peroxy compound formed is a derivative of Cr(V); the Cr(V) derivative on decomposition in alkaline solution reverts to chromate, while it is only in acid solution that reduction occurs to Cr(III). The difference in products of decomposition of aqueous solutions of chromium pentoxide on the one hand, and of the violet salts $M[Cr(O)_2(O_2)_2H]$, on the other, is also strange, particularly since the hydrated pentoxide appears to be the parent acid of the violet salts; the latter compounds decompose to chromate and oxygen, while the former gives a proportion of Cr(III) that increases as the pH drops. This suggests that protonation of a peroxy group may be an important part of the reductive decomposition; if this is so, the relationship between the blue pentoxide and the violet salts may be explained in terms of a tautomerism:



This is not the only anomaly; treatment of the peroxychromates with alkali gives chromate, but treatment with ammonia gives triamminodiperoxychromium(IV). The stability of this substance, which can be regarded as containing five-coordinated chromium, is in itself a little surprising; the mechanism of its formation from the etherate of chromium pentoxide is interesting, since both the starting material and the product contain two peroxy groups per molecule:



It is not clear whether the oxygen is liberated as such, or whether it is involved in oxidizing ammonia (in which case the above equation would be a purely formal representation of part of the over-all reaction); what is clear is that, unless some most unusual rearrangement takes place, the oxygen atom that is eliminated is the chromyl oxygen atom, and is not derived from one of the peroxy groups.

There is much to be discovered about the peroxides of chromium; in particular, it would be interesting to have more structural information about some of the derivatives that seem well characterized, while new compounds may be obtained from reactions using very concentrated hydrogen peroxide. The oxidation-reduction relationships among the compounds already known are summarized in Fig. 5.

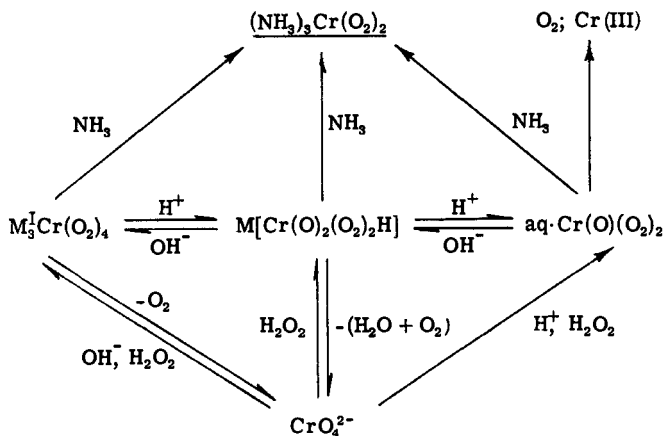


FIG. 5. Relationships among the best known peroxychromium species.

XI. Molybdenum and Tungsten

The known peroxides of molybdenum and tungsten are all apparently derived from the +6 states; nonetheless, their chemistry is complicated and in some places obscure. Alkali and alkaline earth metal salts have been prepared in which the ratio of peroxide to molybdenum or tungsten is

4:1, 3:1, 2:1, and 1:1, besides less well-defined derivatives in which the ratio is not integral; in some cases there is uncertainty as to the degree of polymerization. Peroxypolymolybdates and tungstates are also known, though it is clear that in these systems, as with vanadates (see above), the extent of polymerization is reduced by hydrogen peroxide. There is some evidence to suggest that peroxy cations exist in strongly acid media; complex peroxyoxalates, -tartrates, -phosphates, and -fluorides are formed, and in many cases have been isolated as solids. In the account that follows, a description of the various species in order of decreasing peroxide content is prefaced by a short account of the oxyanions.

A. OXY ANIONS

As far as tungsten is concerned, it now seems to be generally agreed that in solution the two simplest species formed are the 1-tungstate, WO_4^{2-} , and the hexatungstate, $\text{HW}_6\text{O}_{21}^{5-}$ (436, 473). The hexatungstate, formed at $\text{pH} < 10$, polymerizes further when boiled with acid, and may exist in two forms; in recent studies no evidence has been obtained to support the suggestions (50, 150, 383) that di- or tritungstates are formed in appreciable concentration.

With molybdenum the position is less clear. An elaborate study of changes in pH using glass electrodes, in the way developed by Sillén and his school, has been interpreted in terms of the formation of the 1-molybdate ion, MoO_4^{2-} , the acid 1-molybdate ion, HMoO_4^- , and a heptamolybdate species, $\text{Mo}_7\text{O}_{24}^{6-}$ (474). Other investigators believe that a tetramolybdate anion, $\text{Mo}_4\text{O}_{13}^{3-}$, and perhaps the free acid $\text{H}_2\text{Mo}_4\text{O}_{13}$ can be obtained in solution (88, 115, 436).

B. 4:1 PEROXY SPECIES: $\text{M}(\text{O}_2)_4^{2-} \equiv \text{MO}_8^{2-}$

Red salts of the cations Na^+ , K^+ , Ca^{+2} , Sr^{+2} , Ba^{+2} , Co^{+2} , and $\text{Zn}(\text{NH}_3)_4^{+2}$ have been obtained by the action of excess H_2O_2 on neutral or slightly alkaline solutions of 1-molybdates, or by double decomposition reactions (62, 63, 173, 284, 293, 357, 463, 502, 504). These substances (save for the tetrammino-zinc derivative, whose decomposition is more complicated) give almost two moles of O_2 per gram-atom of molybdenum on thermal decomposition, leaving a residue of molybdate, and so are believed to contain four peroxy groups per molybdenum atom; it is not certain, however, that all of these peroxy groups are directly bound to molybdenum. The sodium salt $\text{Na}_2\text{MoO}_8 \cdot 2\text{H}_2\text{O}$ cannot be dehydrated further without loss of peroxide oxygen, from which it was concluded that the substance contains two molecules of H_2O_2 of crystallization (293). On the other hand, an anhydrous potassium salt has been obtained (173) which must contain four directly bound peroxy groups; a spectrophotometric study indicates

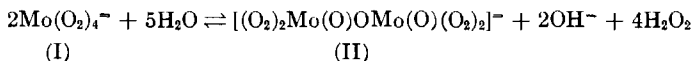
that $\text{Mo}(\text{O}_2)_4^-$ groups are present in solution, and it would be difficult to explain the difference in color between the yellow 2:1 (see Subsection D) and the red 4:1 compounds if the additional peroxide in the latter were present merely as H_2O_2 of crystallization. While the question will only be answered conclusively by crystallography, it seems likely that the $\text{Mo}(\text{O}_2)_4^-$ ion exists in the solid state, though it may be readily hydrolyzed in solution.

Analogous derivatives of tungsten are formed under conditions like those used in making the tetraperoxy-1-molybdates, and have been analyzed similarly (61, 64, 65, 244, 293, 417, 463). The salts of colorless cations are yellow; experiments involving the calcium salt indicate that some peroxide oxygen is lost on dehydration, from which it has been concluded that at least some of the peroxide oxygen is present as H_2O_2 (65), while one spectrophotometric study indicated that the yellow species is formed in solution from two peroxy groups per tungsten atom (470). A different study, however, using (among other techniques) spectrophotometry, suggested that a peroxytungstic acid containing four peroxy groups per tungsten atom is formed in solution (437), while a potassium salt containing one half a molecule of water of crystallization in its formula has been obtained (463). Thus it seems likely that, as with molybdenum, a tetraperoxy-1-tungstate anion is formed, though it may be unstable to hydrolysis. The powder photograph of $\text{K}_2[\text{W}(\text{O}_2)_4]$ has been recorded (58).

These compounds are all extremely unstable, exploding when struck or warmed; the most stable seems to be tetramminozinc tetraperoxy-1-molybdate, which has been kept unchanged over solid alkali in an atmosphere of ammonia for some weeks (463). Though the ultimate products of decomposition of the salts of simple cations are the 1-molybdates or 1-tungstates, a number of intermediate decomposition products have been described, containing 3, 2, or 1 atom of peroxy oxygen per atom of molybdenum or tungsten (62, 63, 65, 284, 293, 417, 502). The sodium salt $\text{Na}_2[\text{Mo}(\text{O}_2)_4] \cdot 4\text{H}_2\text{O}$, for example, gives as immediate decomposition product the yellow diperoxyspecies formulated as $\text{Na}_2[\text{Mo}(\text{O})_2(\text{O}_2)_2] \cdot 2\text{H}_2\text{O}$ (see below), though the dihydrate decomposes directly to the 1-molybdate (293). The heats of decomposition of some of these tetraperoxy salts have been measured (294, 295, 591) and have been used to calculate a quantity described as the energy of the bond between the molybdate or tungstate group and the peroxy oxygen atom. It is not easy to see what physical significance to give to this quantity, which is presumably meant to represent $E(\text{MoO}_4\text{-O})$. The kinetics of decomposition of sodium tetraperoxy-1-molybdate (283, 292) and of calcium tetraperoxy-1-tungstate (64) have been studied, using the rate of oxygen evolution as a measure of the rate of reaction.

Potassium tetraperoxymolybdate gives a deep red solution in water,

which slowly turns yellow with evolution of oxygen (173) though at pH greater than 7 the ion is apparently stable in the presence of excess H_2O_2 ; an equilibrium with the dimeric tetraperoxy-1,2-molybdate anion has been suggested:



In strong alkali, decomposition to the 1-molybdate is rapid, though the compound $\text{K}_2[\text{Mo}(\text{O})_3(\text{O}_2)]$ has been obtained from an alkaline solution of the tetraperoxy-1-molybdate (34); with dilute acid, a yellow solution results with vigorous evolution of oxygen, the yellow species being most probably the dimeric tetraperoxy-1,2-molybdate (compound II) (92). The solution in concentrated aqueous ammonia is more stable. Tetraperoxy-1-tungstates behave similarly; in acids they give tetraperoxy-1,2-tungstates (in compound II, $\text{Mo}=\text{W}$), but in alkali they are said to give colorless solutions with only slight evolution of oxygen (244).

Both series of salts react almost quantitatively with acid potassium permanganate solution, though the last stages of the reaction with tetraperoxy-1-molybdates are very slow (173, 284); Rosenheim found that only one fourth of the peroxide oxygen of the molybdates oxidized iodide ion (463), but Gleu was able to determine the peroxide content of tetraminozine tetraperoxy-1-molybdate iodimetrically (173, 174). The difference between these two results may arise from different conditions of pH.

C. 3:1 PEROXY SPECIES: $\text{M}(\text{O})(\text{O}_2)_3^- \equiv \text{MO}_7^-$

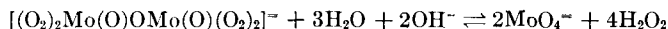
Peroxymolybdates (504) and -tungstates (65, 417) of calcium and strontium that contain three peroxy groups per atom of molybdenum or tungsten have been obtained from the thermal decomposition of the tetraperoxy-1-molybdates or -tungstates; strontium triperoxymolybdate is brick-red, while the tungsten derivatives are pale yellow; all are thermally unstable at room temperature, and were formulated as $\text{M}^{\text{II}}[\text{MoO}_7]\cdot\text{aq}$ or $\text{M}^{\text{II}}[\text{WO}_7]\cdot\text{aq}$. There is little to suggest that these compounds are true chemical species rather than mixtures of salts of the $\text{M}(\text{O}_2)_4^-$ and $[(\text{O}_2)_2\text{M}(\text{O})\text{OM}(\text{O})(\text{O}_2)_2]^-$ anions.

Compounds that appear to be pyridinium salts of composition $\text{PyH}_2\text{MO}_7\cdot 2\text{H}_2\text{O}$ (M is Mo or W) have been obtained by treating pyridinium tetraperoxy-1,2-molybdate or -tungstate with hydrogen peroxide (29). Attempts to repeat the preparation of the tungsten derivative have not been successful (182), the maximum amount of peroxide oxygen per atom of tungsten being 2.5 atoms. Pyridinium triperoxymolybdate decomposes at 100°C , but since it only loses oxygen and is not de-

hydrated, it has been argued that the peroxide cannot be present as H_2O_2 of crystallization (29). On the other hand, the ease with which the peroxide oxygen can be removed has been taken as showing that H_2O_2 of crystallization is present in the solid, so that the molybdenum and tungsten compounds are formulated as $(\text{PyH})_2[(\text{O}_2)_2\text{Mo}(\text{O})\text{OMo}(\text{O})(\text{O}_2)_2] \cdot 2\text{H}_2\text{O}_2$ and $(\text{PyH})_2[(\text{O}_2)_2\text{W}(\text{O})\text{OW}(\text{O})(\text{O}_2)_2] \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$. In support of this view (182), the infrared and ultraviolet spectra (the former measured for the solids, the latter for solutions) are the same as those of the tetraperoxy-1,2-molybdate or -tungstate ions.

D. 2:1 PEROXY SPECIES: $\text{M}(\text{O})_2(\text{O}_2)_2^- \equiv \text{MO}_6^-$; $[(\text{O}_2)_2\text{M}(\text{O})\text{OM}(\text{O})(\text{O}_2)_2]^- \equiv \text{M}_2\text{O}_{11}^-$

From acid solutions containing alkali metal molybdates and a high concentration of H_2O_2 , alkali metal salts may be obtained in which there are two peroxy groups and one alkali metal cation to each atom of molybdenum or tungsten (36, 92, 182, 244, 463). The anions were formulated by Rosenheim as the dimeric tetraperoxy-1,2 species $[(\text{O}_2)_2\text{M}(\text{O})\text{OM}(\text{O})(\text{O}_2)_2]^-$ (where M is Mo or W), and these dimeric anions are certainly formed under most conditions. A careful study of the changes in pH with volume for the molybdenum system (514) supported this view, as did an interpretation of the neutralization curves of mixtures of molybdic acid and H_2O_2 (544). A cryoscopic determination of the ionic weight of the tungsten species, formed *in situ* by adding sodium tungstate, nitric acid, and H_2O_2 in appropriate ratio to the sodium nitrate/water eutectic, gave the value expected for the dimer (241) and was considered more reliable than an earlier estimate based on dialysis, which indicated a monomeric structure (236, 240). The infrared spectra of the sodium and potassium salts of both the molybdate and the tungstate as solids and in solution in D_2O , together with Raman data from solutions, have been interpreted in terms of the dimeric structure; several coincidences were observed in the infrared and Raman spectra, making a centrosymmetric structure unlikely (182). Finally, a crystallographic study (126) of the potassium salt shows that the anion is dimeric, with the structure given in Fig. 6. It is particularly interesting that the O—O distance is very close to that for the free peroxide ion. Csanyi (109) found two neutralization points on titrating a solution of the parent acid (prepared by passing a solution of the monosodium salt through an acid ion-exchange column) against alkali, at $[\text{Mo}]:[\text{OH}]$ ratios of 1:1 and 1:2; he interpreted this as showing that there were two acid protons per molybdenum atom, and that the ion is monomeric. The second neutralization point, however, could arise from hydrolysis of the dimer:



(The H_2O_2 will react with some of the molybdate ion under these conditions, forming tetraperoxy-1-molybdate.) Support for the monomeric structure was also adduced from R_f values obtained by paper chroma-

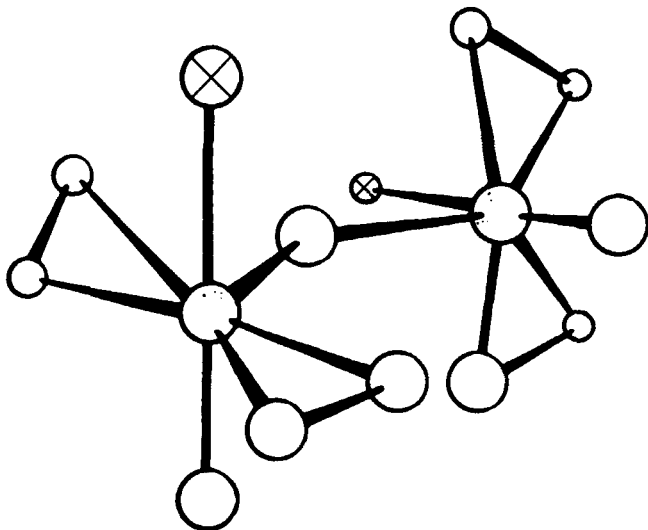
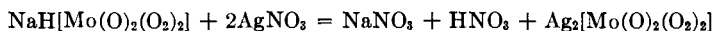


FIG. 6. Structure of the tetraperoxyditungstate ion in $\text{K}_2[(\text{O}_2)\text{W}(\text{O})\text{OW}(\text{O})(\text{O}_2)] \cdot 4\text{H}_2\text{O}$. One molecule of water is coordinated to each tungsten atom. Mean structural parameters are: $r(\text{W}-\text{O})$, peroxy, 1.91; $r(\text{W}-\text{O})$, apical, 1.68; $r(\text{W}-\text{O})$, bridge, 1.93; $r(\text{W}-\text{O})$, water, 2.36; $r(\text{O}-\text{O})$, peroxy group, 1.50 Å; $\angle \text{WOW}$ (bridge) = 138° ; $\angle \text{OWO}$ (peroxy group) $\sim 46^\circ$. Three-dimensional analysis, $R = 0.17$ (126). Circle, O; dotted circle, W; crossed circle, O of H_2O .

tography (110), though this is not particularly convincing evidence. With neutral silver nitrate solution, a neutral solution of the sodium peroxy-molybdate reacted to give a precipitate, leaving a solution of pH 3.7; this was explained in terms of the reaction (108):



Unfortunately, the solid does not seem to have been analyzed (108). Finally, the molecular weight of the sodium salt in solution in fused Glauber's salt ($\sim 32^\circ$) was determined cryoscopically, and gave the value expected for the monomer (110). In view of the instability of these compounds, the reliability of the last measurement is open to question; at the same time, there is nothing in any of the experiments so far described that precludes the formation of small amounts of the monomer in equilibrium with the dimer in solution:



Removal of the proton from the monomeric anion might lead to the formation of derivatives of the doubly charged monomeric anion by displacing the equilibrium. Compounds whose formulas are consistent with the presence of such an anion have been prepared by neutralizing solutions of the free peroxy acids or the monosubstituted salts (34, 35), by thermal decomposition of the tetraperoxy-1-molybdates (284) or -tungstates (58, 65), or by the action of H_2O_2 on molybdates (504) or tungstates (417) at temperatures below 0° . If, as indicated in at least one case by X-ray powder photography (58), these materials are compounds and not mixtures, they may contain the monomeric, doubly charged diperoxy anion; it has been suggested, though, that at least those substances which are obtained from strongly alkaline solutions are mixtures of the salts of the tetraperoxy-1,2 anions with alkali (182), while it is not impossible that even some of the salts of formulas $\text{M}_2[\text{MoO}_6]\cdot\text{aq}$ or their tungsten analogs contain polymeric anions. This question is unlikely to be settled without crystallographic data.

It should be added that the discussions of the neutralization curves mentioned above, and the investigation of pH changes in the system (92, 109, 514, 544), were made on the assumption that a tetramolybdate species, $\text{H}_2\text{Mo}_4\text{O}_{13}$, is formed in solution; since it has been suggested that the simplest molybdates in aqueous solution are the 1-molybdate and the heptamolybdate ions $\text{Mo}_7\text{O}_{24}^{-6}$ (474), some of these results may need reinterpretation (though see 50, 436, 437).

The dissociation constant of the tetraperoxy-1,2-tungstate ion to a tungstate species and H_2O_2 has been estimated spectrophotometrically (470) as 9.74×10^{-2} ; the salt $\text{K}_2[(\text{O}_2)_2\text{W}(\text{O})\text{OW}(\text{O})(\text{O}_2)_2]\cdot 4\text{H}_2\text{O}$ has been dehydrated at 100° without loss of peroxide oxygen (276) so that the coordinated water molecules in the crystal (see Fig. 6) cannot be essential to the stability, while all of the peroxide oxygen was found to be active in the Riesenfeld titration (245).

These 2:1 peroxy salts are more stable thermally than the mononuclear tetraperoxy compounds, though some may explode on heating (182, 244, 463); the tungsten compounds are apparently more stable to decomposition at room temperature than their molybdenum analogs. Thermal decomposition gives molybdate or tungstate, perhaps through intermediate formation of monoperoxy species; the heats of decomposition of some of the disubstituted salts have been measured, from which the usual "bond energies to peroxide oxygen" have been calculated (282, 417, 591), and the kinetics of the decomposition of " $\text{Na}_2[\text{Mo}(\text{O})_2(\text{O}_2)_2]$ " have been investigated (283). The free acids are stronger acids than molybdic or tungstic acid (78, 92, 437); the dissociation constant of $\text{H}_2\text{Mo}_2\text{O}_{11}$, for example, is about 8×10^{-3} (109, 437). The magnetic moments of the sodium and potassium salts of the molybdenum and tungsten anions are less than 0.5 B.M., as expected

for derivatives of Mo(VI) or W(VI), while the electrical conductivities have been measured for aqueous solutions at 25° (137). The vibrational spectra have been analyzed in terms of a reasonable structure (182), which is essentially the same as that found for the hydrated potassium tungstate (126).

In solution, the salts react with acid permanganate to give O₂ (244, 295, 463) and in some cases the heat of this reaction has been determined (294, 295, 417); the reaction with potassium iodide, which has been mentioned, depends markedly upon pH (245). A study of the hydrolysis of the peroxy groups suggests that there is little hydrolysis at pH < 7, that the degree of hydrolysis at pH ~ 9 is 0.26 for the molybdenum anion and 0.5 for the tungsten species, and that the alkaline hydrolysis is unimolecular (454, 455); it is not clear, however, how reliable the methods are that led to these results. It has been shown spectrophotometrically that the equilibrium shown below is set up in solutions rich in H₂O₂ (92):

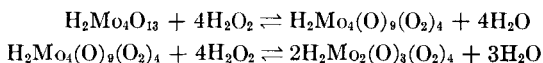


Although it appears that in acid solutions, or with less than one mole of alkali per gram-atom of molybdenum, the sole peroxy-molybdate species is the dimeric tetraperoxy-1,2-molybdate (92), Jahr detected the formation of a peroxyhexamolybdate in the presence of excess acid (234). In sulfuric acid more concentrated than 4.5 *M*, there is evidence that a complex peroxy-molybdenum cation is formed, containing a sulfate group, two molybdenum atoms, and two peroxy groups (92). This is discussed further in Subsection F.

E. 1:1 PEROXY SPECIES: M(O)₃(O₂)⁼ or MO₅⁼

Several compounds of formulas M₂^I (or M^{II}) [Mo (or W) (O)₃(O₂)]·aq have been obtained by neutralizing solutions of molybdic or tungstic acid containing H₂O₂ (34, 35), by treating a red tetraperoxy-1-molybdate with alkali (35), by the action of H₂O₂ on molybdates (504) or tungstates (65), or as decomposition products of other peroxy-molybdates or -tungstates richer in peroxide (391, 504). The free monoperoxy-molybdic acid H₂[Mo(O)₃(O₂)] has also been described (74, 391, 542); it may be prepared by dissolving molybdic acid in H₂O₂ solution, evaporating excess water, and drying the product at 110°. There is, however, some doubt as to whether a monoperoxy species exists in solution (92, 234, 437, 542). It was concluded from studies of the neutralization curves of H₂[Mo(O)₃(O₂)] that the species present were tetraperoxy-1,2-molybdic acid and a condensed species that contained no peroxide oxygen (542), while one spectrophotometric study gave no indication of the formation of a 1:1 peroxy species in solution (92); it was suggested that the free acid is in fact a salt, [Mo₂(O)₆H]⁺

$[\text{Mo}_2(\text{O})_3(\text{O}_2)_4\text{H}]^- \cdot 3\text{H}_2\text{O}$. Richardson, however (437), using spectrophotometry supplemented by studies of conductivity and pH, has obtained clear evidence for the formation of soluble monoperoxy species of both molybdenum and tungsten. The conductivity of a solution of what was believed to be tetramolybdic acid, $\text{H}_2\text{Mo}_4\text{O}_{13}$, decreased slowly on addition of H_2O_2 until a peroxide:molybdenum ratio of 1:1 was reached, while over the same range the pH rose slowly. At peroxide:molybdenum ratios between 1:1 and 2:1, however, the conductivity increased quite sharply, while the pH dropped. These observations, taken with the spectrophotometric results, were interpreted as showing the presence of a 1:1 peroxymolybdic acid of the same degree of complexity as the parent molybdic acid, depolymerization occurring with the addition of the second peroxy group:



No evidence was found to support the suggested salt-like structure for $\text{H}_2\text{Mo}(\text{O})_3(\text{O}_2)$. Attempts to replace the cation $[\text{HMo}_2(\text{O})_6]^+$ by H^+ , using a protonated ion-exchange column, were not successful, while ion migration studies supported by experiments using paper electrophoresis gave no evidence that molybdenum-containing cations were present. These results make it seem very probable that a 1:1 peroxymolybdic acid is formed in solution under the right conditions. With tungsten, the evidence obtained for the formation of a monoperoxy species was rather less decisive. A plateau of conductivity was found at a peroxide:tungsten ratio of 1:1, and from the over-all results it was concluded that peroxytungstic acids were formed in solution at all peroxide:tungsten ratios (437).

"Monoperoxymolybdic acid" was found to react very slowly with neutral potassium permanganate solution, though the reaction was much faster in the presence of sulfuric acid (437). The compound oxidized buffered potassium iodide solution (437). The degree (454) and rate (455) of hydrolysis of the potassium derivatives of both molybdenum and tungsten have been measured, but here again it is not clear how reliable the results are.

F. SPECIES CONTAINING LESS PEROXIDE

From solutions of molybdates or tungstates that are poor in hydrogen peroxide, many solids have been isolated that contain between 0 and 1 mole of peroxide oxygen to each atom of molybdenum or tungsten; formulas such as $5\text{BaO} \cdot 12\text{MoO}_3 \cdot 3\text{O} \cdot 18\text{H}_2\text{O}$ (or $\text{Ba}_5\text{Mo}_{12}\text{O}_{38} \cdot (\text{O}_2)_3 \cdot 18\text{H}_2\text{O}$) are to be found in several of the earlier papers, and ratios of peroxide oxygen to molybdenum or tungsten such as 2:3, 1:3, 2:7, and 1:4 have been reported (82, 358, 373, 374, 463). Many of these compounds were obtained by the

action of hydrogen peroxide upon solutions of polymolybdates. Unfortunately, however, there have been few recent studies of these compounds, and it is by no means clear how many of them are chemical individuals. Jahr concluded from his experiments using dialysis that at least some peroxy polymolybdate and -tungstate species were formed in solution (234, 240, 244); he described the golden yellow molybdate species as a peroxy-hexamolybdate. Richardson's work (437) indicates that the 1:1 peroxy species are polymeric, but does not afford evidence for the formation of species containing smaller proportions of peroxide in solution.

G. COMPLEX PEROXY SPECIES

1. Fluorides

Complex peroxyfluorides of both molybdenum and tungsten (402, 403) were prepared by Piccini by dissolving oxyfluoromolybdates or -tungstates in warm H_2O_2 , or by treating solutions of molybdates or tungstates in dilute hydrofluoric acid with H_2O_2 ; he obtained products with formulas $2\text{M}^{\text{I}}\text{F}\cdot\text{MoO}_3\text{F}_2\cdot\text{H}_2\text{O}$ (or $\text{M}_2^{\text{I}}[\text{Mo}(\text{O})(\text{O}_2)\text{F}_4\cdot\text{H}_2\text{O}]$), $2\text{M}^{\text{I}}\text{F}\cdot\text{WO}_3\text{F}_2\cdot\text{H}_2\text{O}$, and $3\text{NH}_4\text{F}\cdot\text{MoO}_3\text{F}_2$. The potassium peroxyfluoromolybdate, which is described as being isomorphous with the oxyfluoromolybdate $\text{K}_2\text{MoO}_2\text{F}_4\cdot 2\text{H}_2\text{O}$, decomposed on heating, giving (ultimately) O_2 and potassium molybdate; the compound could be recrystallized from dilute hydrofluoric acid, but was decomposed by dilute sulfuric acid or potassium permanganate solution.

2. Oxalates

Peroxyoxalates of molybdenum (338, 344, 349, 463) and tungsten (338, 347, 463) were prepared by dissolving oxalatomolybdates or -tungstates in 30% H_2O_2 at 0° . Analysis indicates that these compounds contain a dibasic anion in which there are one oxalate and two peroxy groups to each atom of molybdenum or tungsten, though compounds in which there is one peroxy group per heavy metal atom have also been described (338). The molybdenum derivatives are deep yellow, while the tungstates are colorless. The peroxy and oxalate groups react with acid permanganate solution; when these compounds were first prepared, their peroxide contents were determined by heating with potassium iodide solution (344, 347, 349), which gave results that were much too low (463). The degree and extent of hydrolysis has been studied (454, 455).

3. Tartrates

Evidence has recently been presented to indicate the formation of tungsten peroxy complexes with *d*-tartaric acid (76). Spectrophotometric measurements, combined with potentiometry, polarography, and optical

rotation studies, suggest that both the tetraperoxy-1-tungstate and the dimeric tetraperoxy-1,2-tungstate anions form complexes, probably with free tartaric acid rather than with the anion.

4. Phosphorus Compounds

A series of compounds has been obtained (143) by allowing molybdic acid and H_2O_2 to react with trialkyl phosphates, dialkyl phosphites, dialkyl phosphonates, alkylphosphonic acids, or triphenylphosphine. Orange-red products were obtained either as crystals or oils; they contained one or two peroxy groups per molybdenum atom, and on heating gave blue products with the loss of some of their peroxide oxygen. Structures for the compounds were suggested on the basis of measurements of molecular weight, combined with infrared studies.

5. Sulfates

Spectrophotometric studies of solutions of molybdic acid and H_2O_2 in strong sulfuric acid ($>4.5\text{ }M$) suggest that a sulfatoperoxy complex is formed (92, 382, 479). In dilute solution at least, it seems likely that the species formed contains one peroxy group per molybdenum atom, though in more concentrated solutions a higher peroxy compound may be formed. It has been suggested that the formation of the species may be described by the equation:

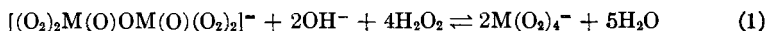


This means that the complex must be cationic; on the other hand, transport studies in sulfuric acid as solvent showed no signs of migration (479).

H. RELATIONSHIPS IN SOLUTION

In the absence of clear evidence to the contrary, it is assumed in the discussion that follows that peroxymolybdates and -tungstates are chemically similar; unless specifically stated, "M" stands for molybdenum or tungsten. The most convincing of the evidence set out in the preceding paragraphs may be summarized as follows:

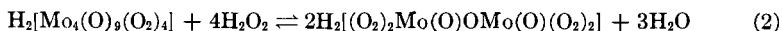
(1) In peroxide-rich solutions of molybdates or tungstates, there is an equilibrium between the 2:1 and the 4:1 species:



The 4:1 species are present in appreciable concentration only in weakly alkaline solution, decomposing to the 1-molybdate (or tungstate) in strong alkali, and dissociating to the 2:1 species at low pH.

(2) In peroxide-poor solutions, there seems to be an equilibrium be-

tween the dimeric 2:1 species and a 1:1 species (which for molybdenum has been described as a tetramer) at $\text{pH} < 7$:



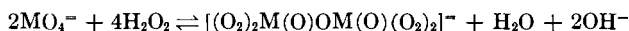
At high pH, the 2:1 species hydrolyzes, giving the 4:1 species and 1-molybdate or tungstate:



The relationship between the 2:1 and the 1:1 compounds is not as well-defined for tungsten as for molybdenum.

(3) When H_2O_2 is added to a solution of a polymeric molybdic or tungstic acid, there is a decrease in pH when the (peroxide:molybdenum or tungsten) ratio is greater than 1:1, indicating depolymerization; this follows from Eq. (2) above. For molybdenum, there is a slight increase in pH for peroxide:molybdenum ratios between 0 and 1, implying that the 1:1 peroxy-molybdic acid is of the same degree of complexity as the parent molybdic acid, which was believed to be a tetramer. For tungsten, there may be depolymerization over the whole range of peroxide concentration.

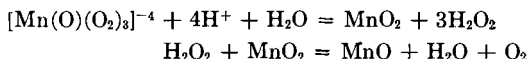
(4) The addition of H_2O_2 to a solution of an alkali metal 1-molybdate or 1-tungstate leads to an increase in pH, due to the formation of the dimeric 2:1 anion:



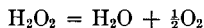
In the presence of large concentrations of H_2O_2 , the pH falls again [Eq. (1) above].

XII. Manganese

When a solution of potassium permanganate in 30% potassium hydroxide is treated with H_2O_2 at temperatures below 0° , the color turns to deep red-brown; by working at -18° , a dark red-brown crystalline solid was obtained (484), which was digested with alkaline H_2O_2 at -12° and washed with 3% methanolic potassium hydroxide. Manganese and potassium were present in the solid in the atomic ratio 1:2. Treatment with dilute acid decomposed the compound; for each gram-atom of manganese, 2.5 gram-atoms of oxygen were evolved as gas, while the residual solution contained about 1.5 moles H_2O_2 . On this basis, the compound was formulated as a triperoxymanganate(IV), $\text{K}_2\text{H}_2[\text{Mn}(\text{O})(\text{O}_2)_3]$; the decomposition by acid was explained in terms of an initial hydrolysis to $\text{Mn}(\text{IV})$ and three molecules of H_2O_2 , one of which reduced the manganese to $\text{Mn}(\text{II})$:



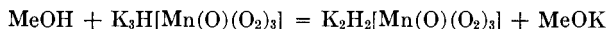
There are thus two gram-atoms of "O₂" formed in the reaction. The extra half gram-atom was put down to catalytic decomposition of some of the residual H₂O₂:



Since one mole of H₂O₂ gives one gram-atom of oxygen as gas on decomposition in this way, loss of half a mole of H₂O₂ from the hydrolysis products would be associated with the formation of half a gram-atom of "O₂," as was observed. This interpretation was further substantiated when hydrolysis at low temperatures was found to form up to two moles of H₂O₂, but no more, per gram-atom of manganese.

The solid gives a red-brown solution in water that slowly evolves O₂ and precipitates MnO₂; with acids, the compound is at once decomposed to O₂ and manganese(II). When dry, it may explode at temperatures above 0°, but it may be kept under acetone for at least 2 days at temperatures of about -60° to -70°.

Evidence was also presented (485) to indicate the formation of two other potassium peroxymanaganates in the preparative reaction; the compounds were formulated as K₃H[Mn(O)(O₂)₃] and K₂H₂[Mn(O₂)₄], but neither was isolated; it was suggested that the former reacts with methanol according to the equation:



It has been suggested that manganese(II)-phthalocyanine is an oxygen carrier (128), but this suggestion has been questioned (129). There is evidence that manganese forms a soluble, colored peroxy complex in the presence of citrate (539).

XIII. Rhenium

Red salts, formulated as containing the peroxy anion [Cl₅Re(O₂)ReCl₅]⁻⁴ (with rhenium in the +4 state) are formed by oxidizing the analogous μ -oxo derivative, [Cl₅ReOReCl₅]⁻⁴, with such oxidizing agents as cerium (IV), iodate, bromate, dichromate, iron(III), nitrite, H₂O₂, or molecular oxygen (which is only effective in the presence of a catalyst, such as nitrite or nitrate ions) (258, 259, 261). The reaction has been studied spectrophotometrically; the complexes are formed by most of the oxidizing agents in a combining ratio (chlororhenate:oxygen atom equivalents) of 1:2, but with H₂O₂ the ratio is 1:3, when the red species has a formation constant of 10¹⁴. The kinetics of the reaction between H₂O₂ and the μ -oxochlororhenate ion have also been investigated (260). Solid cesium, rubidium, and quinolinium salts of formulas M₂¹H₂[Cl₅Re(O₂)ReCl₅] have been obtained and analyzed. They all decompose slowly at room temperature to the μ -oxo compounds, the rubidium salt being the least stable, and dissolve

in acids giving solutions that are red at $\text{pH} \leq 2$ but yellow in less acid systems; it has been suggested that the red species contain protonated peroxy bridges. The quinolinium salt has a paramagnetic susceptibility μ_{eff} of 3.56 B.M. (259).

The total oxidizing power of the anion was determined by treatment with excess iron(III) followed by titration with permanganate, and the result was consistent with the presence of two rhenium(IV) atoms and a peroxy bridge; it was claimed that titration against permanganate of a solution in 2 *M* hydrochloric acid containing H_2O_2 and the μ -oxo derivative in the molar ratio 3 H_2O_2 to 1 chlororhenate established the presence of the peroxy bridge, but this evidence seems indecisive. These compounds are most interesting, but some of the ways in which they may be prepared are unusual for peroxy compounds, and more structural information is needed.

The compound previously reported as Re_2O_8 seems to have been per-rhenic acid (583).

XIV. Iron

Only one solid substance has been described that seems at all likely to be a peroxide of iron (394). This material, which is deep red, is formed by the action of 30% H_2O_2 on a suspension of ferrous hydroxide in alcohol at -20° to -60° ; when the equivalent amount of alcoholic potassium hydroxide was added to a solution of iron(II) or iron(III) chloride in alcohol mixed with 30% H_2O_2 , an apparently similar precipitate was formed, though no such substance was obtained by the action of H_2O_2 on a suspension of iron(III) hydroxide. The red solid was analyzed for peroxide oxygen by treatment with potassium iodide solution that contained a little sulfuric acid, and ratios of peroxide:iron of between 0.8 and 1 were obtained.⁶ The substance, which contained water, was unstable at room temperature, evolving O_2 ; when treated with water or acids, it gave H_2O_2 . It was formulated as $\text{Fe}(\text{O}_2)$. The true nature of this substance must be considered in serious doubt until its properties have been investigated again; at the same time it is unlikely to be iron(II) ferrate, as has been suggested (317), in view of the oxidation potentials of the ferrate ion [$\text{Fe}(\text{VI})\text{Fe}(\text{III})$, $E^\circ > 1.9$; $E_B^\circ > 0.9$ volt] (302). Rather surprisingly, ferrate has been identified spectrophotometrically in solutions of iron(III) ($\sim 10^{-3}$ *M*) in 2–7 *M* potassium hydroxide containing ethylenediaminetetraacetic acid (EDTA) and H_2O_2 , though no ferrate was detected in the absence of EDTA (285).

Peroxy derivatives of iron are generally considered to be formed as intermediates in the catalytic decomposition of H_2O_2 by ferrous or ferric salts. Although some of the early evidence for this view is open to question (75, 332, 333), a spectrophotometric study (132) indicates the forma-

⁶ This method of analysis depends on the iron being in the ferrous state.

tion of a peroxyferric species at $\text{pH} \sim 1.5$, containing iron and peroxide in the ratio 1:1 and formulated as $\text{Fe}(\text{O}_2\text{H})^{+2}$. Similar 1:1 complexes are formed in the presence of EDTA (28, 451) or 1,1-diaminocyclohexanetetraacetic acid (28) at $\text{pH} > 9$, with formation constants of $\sim 4 \times 10^3$ for the EDTA complex and $\sim 7 \times 10^2$ for the diaminocyclohexane derivative. Peroxide-iron(III) complexes may well be of major importance in mechanisms of catalysis (202, 310) or of the operation of iron(III)-containing enzymes such as peroxidase or catalase (159); they are also clearly related to the oxygenated compounds of the ferrous species called oxygen carriers. The ferrous oxygen carriers include ferrous dimethylglyoxime (117) and derivatives of heme (iron(II) protoporphyrin) such as hemoglobin, and hemerythrin (which despite its name does not contain heme); these compounds all take up O_2 reversibly. Hemoglobin itself contains four heme groups, and can combine with up to four molecules of O_2 , though the four dissociation constants are not the same (161); it appears that the oxygen molecules displace water ligands (275), and can in turn be displaced by carbon monoxide; oxyhemoglobin and carboxyhemoglobin are low-spin complexes, in contrast to the high-spin hydrated hemoglobin. The stereochemical arrangement of the oxygenated complex is not yet known. The non-heme derivative hemerythrin may take up one molecule of O_2 to each pair of iron atoms (334); here again oxygenation reduces the paramagnetic susceptibility.

Heme itself is not an oxygen carrier; it is fairly readily oxidized by O_2 to hemin (ferri-heme). Imidazole-protohemochrome (106) (heme with one imidazole ligand) and diimidazole-protohemochrome (107) are oxygen carriers, the latter combining with O_2 in the absence of solvent, though heme itself when dissolved in pyridine does not take up O_2 unless imidazole is added (106). In neutral or alkaline solution, many derivatives of iron(II) take up O_2 , but are oxidized rapidly to iron(III). The oxygen carriers are remarkable, not because of the ease with which they take up oxygen, but because the process of dissociation with electron transfer from the metal to the O_2 group has somehow been inhibited.

XV. Cobalt

The best known peroxy compounds of cobalt are binuclear, and usually cationic. Two series of these derivatives have been described, in each of which the cobalt atoms are linked through a peroxy bridge (though other bridging groups, such as $-\text{NH}_2$, may also be present). Salts of the one series are usually red or brown; they are diamagnetic, and have formulas that can be expressed in terms of two cobalt(III) atoms connected by a peroxide ion:

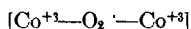
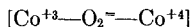


TABLE III
Conventional Labeling Adopted for Some of the
Peroxycobalt Species

$[(H_3N)_5Co(O_2)Co(NH_3)_5]^{4+}$	P_a^1	$[(H_3N)_5Co(O_2)Co(NH_3)_5]^{4+}$	D_a^1
$\left[\begin{array}{c} (O_2) \\ (H_3N)_4Co \quad Co(NH_3)_4 \\ \quad \quad \quad N \\ \quad \quad \quad H_2 \end{array} \right]^{4+}$	P_a^2	$\left[\begin{array}{c} (O_2) \\ (H_3N)_4Co \quad Co(NH_3)_4 \\ \quad \quad \quad N \\ \quad \quad \quad H_2 \end{array} \right]^{3+}$	D_a^2
$\left[\begin{array}{c} (O_2) \\ en_2Co \quad Coen_2 \\ \quad \quad \quad N \\ \quad \quad \quad H_2 \end{array} \right]^{4+}$	P_{en}^2	$\left[\begin{array}{c} (O_2) \\ en_2Co \quad Coen_2 \\ \quad \quad \quad N \\ \quad \quad \quad H_2 \end{array} \right]^{3+}$	D_{en}^2
$\left[\begin{array}{c} (O_2) \\ en_2Co \quad Coen_2 \\ \quad \quad \quad N \\ \quad \quad \quad H \end{array} \right]^{3+}$	$[P_{en}^2]'$	-	-
$\left[\begin{array}{c} Cl \quad Cl \\ H_3N \quad NH_3 \\ \quad \\ Co \quad Co \\ \quad \\ H_3N \quad NH_3 \\ \quad \\ H_3N \quad NH_3 \\ \quad \quad N \\ \quad \quad H_2 \end{array} \right]^{2+}$	$[P_{a,2Cl}^2]_s$	-	-
$\left[\begin{array}{c} H_3N \quad Cl \\ H_3N \quad NH_3 \\ \quad \\ Co \quad Co \\ \quad \\ N_3N \quad NH_3 \\ \quad \\ H_3N \quad NH_3 \\ \quad \quad N \\ \quad \quad H_2 \end{array} \right]^{2+}$	$[P_{a,2Cl}^2]_a$	-	-
$\left[\begin{array}{c} (O_2) \\ (H_3N)_3Co-OH-Co(NH_3)_3 \\ \quad \quad \quad OH \end{array} \right]^{3+}$	P_a^3	-	-
$\left[\begin{array}{c} H_2O \quad OH \\ H_3N \quad NH_3 \\ \quad \\ Co \quad Co \\ \quad \\ H_3N \quad NH_3 \\ \quad \\ H_3N \quad NH_3 \\ \quad \quad N \\ \quad \quad H_2 \end{array} \right]^{3+}$	$[P_{a,ol}^2, aq, ol]$	-	-
$\left[\begin{array}{c} Cl \quad Cl \\ H_2O \quad NH_3 \\ \quad \\ Co \quad Co \\ \quad \\ H_3N \quad NH_3 \\ \quad \\ H_3N \quad NH_3 \\ \quad \quad N \\ \quad \quad H_2 \end{array} \right]^+$	$[P_{a,3Cl,aq}^2]$	-	-
$[(NC)_5Co(O_2)Co(CN)_5]^{5-}$	P_{CN}^1	$[(NC)_5Co(O_2)Co(CN)_5]^{5-}$	D_{CN}^1
-	-	$\left[\begin{array}{c} (O_2) \\ (nprNH_2)_3Co-OH-Co(NH_2npr)_3 \\ \quad \quad \quad nprNH_2 \end{array} \right]^{2+}$	D_{npr}^2, ol

The remaining 5 coordination positions on each cobalt atom are filled by amino, chloro, cyano, or other ligands. Members of the second series are usually green; they are paramagnetic, and can in many cases be obtained as one-electron oxidation products of the diamagnetic derivative. Werner formulated them as containing two nonequivalent cobalt atoms:



More recent work, however, has shown that their electronic structures cannot be described in simple terms; the cobalt atoms are equivalent, and of oxidation state between 3 and 4. We have labeled the paramagnetic derivatives "P" salts, in contrast to the diamagnetic (D) derivatives (see Table III).

Besides these compounds, several complexes of cobalt have been prepared which act as oxygen carriers; these are briefly considered in this section. Finally, an ill-defined "simple" peroxide has from time to time been mentioned in published work.

A. PREPARATIONS

In the synthetic reactions that are described below, the peroxy bridge is introduced using air, ozone, or H_2O_2 , but changes in the remaining ligands are achieved by a variety of methods.

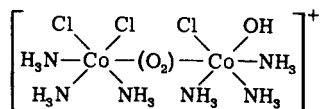
1. Monobridged Species

The brown salts obtained by air oxidation of ammoniacal solutions of cobalt(II) salts (151, 265, 335, 559, 573), and called oxocobaltiates by Frémy (151), were shown by Werner to contain the (diamagnetic) cation $[(\text{H}_3\text{N})_5\text{Co}(\text{O}_2)\cdot\text{Co}(\text{NH}_3)_5]^{+4}$, D_a^1 ; salts of the green paramagnetic ion $[(\text{H}_3\text{N})_5\text{Co}(\text{O}_2)\cdot\text{Co}(\text{NH}_3)_5]^{+5}$, P_a^1 , which is formally a one-electron oxidation product of D_a^1 , may be prepared similarly (151, 265, 335, 559, 573). It appears that the complex $[(\text{H}_3\text{N})_2\text{Co}(\text{OH}_2)_4]^{+2}$, which is formed initially, is further substituted until the pentammine $[(\text{H}_3\text{N})_5\text{Co}(\text{OH}_2)]^{+2}$ is produced, and that this then reacts with molecular oxygen (266). Preparation by this method, however, is slow and inefficient, and ozone (177) or H_2O_2 and ammonium persulfate (175) have been used in making salts of the green cation. Among the anions in these salts may be noted thiocyanate (339), perchlorate (124), permanganate (124), dichromate (124), and bromide (124) obtained by double decomposition.

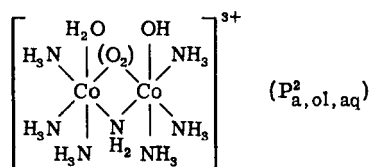
The action of air on a solution containing cobalt(II) and cyanide ion at 0° gives a brown crystalline solid containing the diamagnetic anion $[(\text{NC})_5\text{Co}(\text{O}_2)\cdot\text{Co}(\text{CN})_5]^{-6}$, D_{CN}^1 (203); oxidation of this species with bromine in alkaline solution gives the paramagnetic $[(\text{NC})_5\text{Co}(\text{O}_2)\cdot\text{Co}(\text{CN})_5]^{-5}$,

P_{CN}^1 , which is red, an unusual color for a P-type derivative. The potassium salt of this anion was originally described as $K_3[Co(CN)_5(OH)] \cdot H_2O$ (513).

A dark green salt which Werner (570) believed to contain the unsymmetrical cation



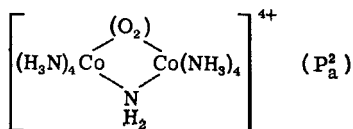
was obtained by the action of cold dilute acetic acid on the dibridged species



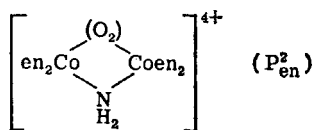
followed by concentrated hydrochloric acid. The structure implies that the salt should be paramagnetic.

2. Dibridged Species

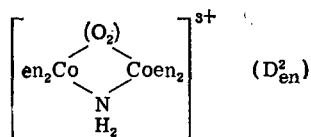
Oxidation by air of an ammoniacal solution of cobalt(II) sulfate gives a red solid, which Vortmann (559) called "fusco-salt" and which is a mixture of complex cobalt species (572); from it the green paramagnetic dibridged cation



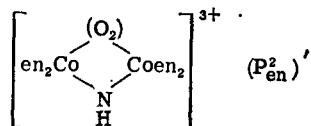
can be extracted (568, 570). The yield is very poor, but may be improved by using ozonized air (177, 525). This cation may be reduced to its diamagnetic analog in a one-electron step (570). When treated with ethylenediamine (570), the ammonia ligands are replaced, giving



In the presence of excess of base, reduction occurs to the diamagnetic analog

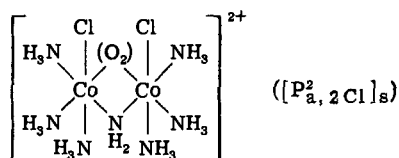


which is usually obtained from nitrate solution as an acid salt of formula $\text{D}_{\text{en}}^{2+} \cdot (\text{NO}_3)_3 \cdot \text{HNO}_3 \cdot 2\text{H}_2\text{O}$ (537). The cation

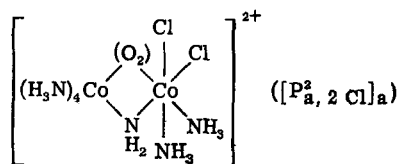


which was described by Werner (570) as formed by the action of aqueous ammonia on $\text{P}_{\text{en}}^{2+}$, is perhaps identical with $\text{D}_{\text{en}}^{2+}$ (537).

The insoluble chloride of the dark green paramagnetic cation formulated by Werner as the symmetrical dichloro species

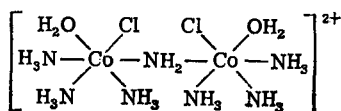


is precipitated by the action of ammonium chloride and hydrochloric acid on $\text{P}_{\text{en}}^{2+}$ (570). If, however, ammonium carbonate is used instead of ammonium chloride, another dark green salt is obtained, which was formulated as containing the isomeric unsymmetrical cation

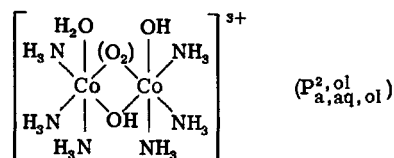


on the basis of degradative experiments (570) (see below).

One other green salt, which is probably paramagnetic, is obtained from the so-called "melanochloride" shown by Werner to have the structure



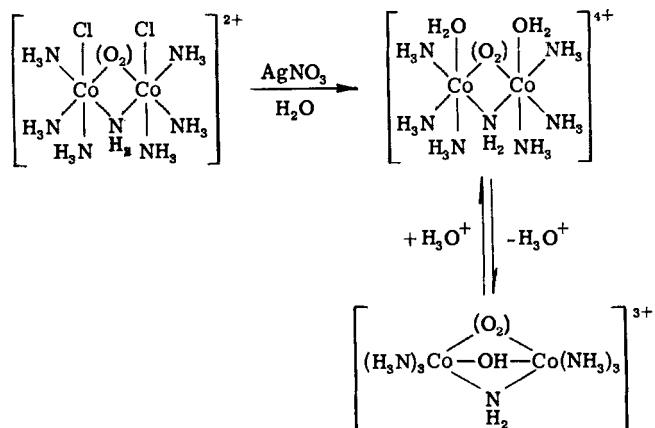
by treatment with silver nitrate and dilute nitric acid (570); the cation of the product was described as



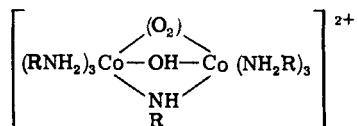
but it is not clear where the oxygen for the peroxy bridge came from.

3. Tribridged Species

Treatment of the symmetrical dichlorodibridged cation $[\text{P}_{\text{a,2Cl}}^2]_s$ with acidified silver nitrate solution gives the symmetrical diaquo complex $[\text{P}_{\text{a,2aq}}^2]_s$, which appears to be in equilibrium with the tribridged species P_a^3 (570):



It may also be prepared from melanochloride (570). Red salts, formed by the action of air on solutions of cobalt(II) chloride in ethanol containing *n*-propylamine or allylamine (79, 395, 405, 406), are believed (101) to contain tribridged diamagnetic cations where R is allyl or *n*-propyl:



4. The Simple Peroxide

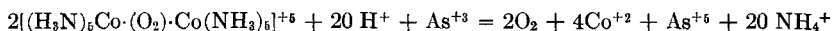
A cobalt peroxide was obtained by adding H_2O_2 to a solution of cobalt(II) chloride in alcohol at -20° , followed by the slow addition of dilute

sodium hydroxide solution. The material apparently has the formula $\text{Co}(\text{O}_2)$ (503). Other higher oxides of cobalt have been reported, but there is no evidence to suggest that they are peroxides.

B. STRUCTURES

1. General Features

The presence of peroxide oxygen in these salts was first inferred from their reaction with acids to give oxygen (151, 265, 335, 559, 573), though their behavior in the Riesenfeld titration is erratic (101). Reduction of the monobridged species $[(\text{H}_3\text{N})_5\text{Co}(\text{O}_2)\cdot\text{Co}(\text{NH}_3)_5]^{+5}$, P_a^1 , with arsenic(III) oxide in the presence of traces of osmium tetroxide catalyst established the presence of five oxidizing equivalents per mole, four of which were liberated as oxygen gas (175):



This showed there was an odd number of electrons associated with the cation; this, the red cyanide, and others of the green salts have paramagnetic moments close to 1.73 B.M. (30, 175, 203, 331, 342), indicating the presence of one unpaired electron to each pair of cobalt atoms; the Curie-Weiss law is obeyed between 77° and 273° (331). Several of the brown D-type cations have been shown to be diamagnetic (139).

These observations, coupled with the results of chemical analysis, establish the stoichiometry of the compounds concerned; the questions that are not solved in this way are: How are the nuclei arranged? Where is the unpaired electron located?

The best crystallographic data available indicates that (549), as suggested by Vlcek (556), the O_2 group lies with its axis perpendicular to the Co—Co axis (see Fig. 7) with distances and angles as shown⁷; the bonding may then be regarded as analogous to that found in platinum-ethylene complexes. At the same time, such a description no more than establishes the equivalence of the cobalt nuclei. Electron resonance studies (48, 124, 177, 482, 483) confirm this conclusion, and show that there is appreciable unpaired electron density at the cobalt nuclei in the monobridged and dibridged species studied, while work on dilute single crystals of P_{en}^2 in a matrix of μ -aminotetrakisethylenediaminecobalt(III,III) nitrate (177) has shown that the unpaired electron behaves as a spin arising from a *d*-like hole in an otherwise filled molecular orbital. At the same time, the magni-

⁷ It is most interesting that an analysis of the structure of D_a^1 , though still incomplete, indicates a "skewed" arrangement for the peroxy group; the cobalt and the peroxide oxygen atoms are coplanar, with Co—O—O angles of $\sim 122^\circ$ and $\sim 31^\circ$ (548).

tudes of the cobalt hyperfine interaction tensors were best explained in terms of a structure in which the O—O axis was skewed relative to the Co—Co axis (177). These results indicate that in the green salts the unpaired electron is in an antibonding molecular orbital with appreciable density on both cobalt nuclei (177). While this conclusion may depend to

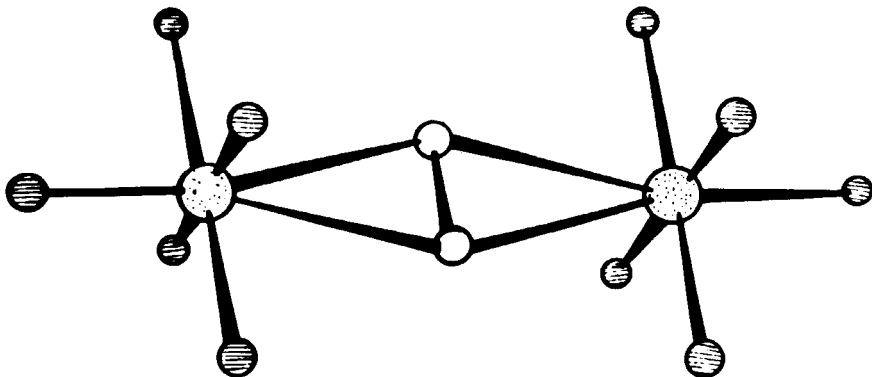
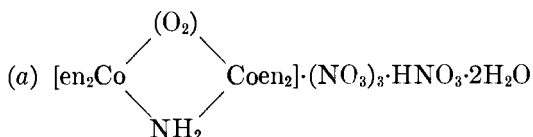


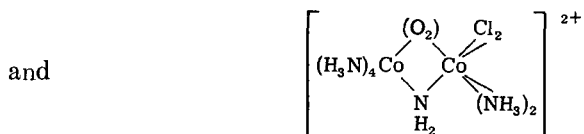
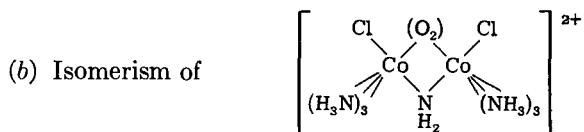
FIG. 7. The heavy atoms in the cation $[(\text{H}_3\text{N})_6\text{Co}(\text{O}_2)\cdot\text{Co}(\text{NH}_3)_6]^{+5}$ from a study of the anhydrous pentanitrate (549). The structural parameters are: $r(\text{Co}-\text{N})$, 1.96–2.01 (three different values, all ± 0.04); $r(\text{Co}-\text{O})$, 2.38 ± 0.04 ; $r(\text{O}-\text{O})$, $1.45 \pm 0.06 \text{ \AA}$; $\angle \text{NCoN}$, $84\text{--}96^\circ$, all $\pm 4^\circ$; $\angle \text{CoOC}$, 144° , $\angle \text{CoOO}$, 72° , both $\pm 4^\circ$. Three-dimensional analysis, $R = 0.2$. Circle, O; dotted circle, Co; lined circle, N.

some extent on the other ligands, it appears to hold for mono-, di-, and tribridged amino species P_a^1 , P_a^2 , P_a^3 , for P_{en}^2 , and for P_{CN}^1 (48, 124, 125, 177, 562). Polarographic studies support this view (557), while the absence of semiconducting properties (141, 142) is also in accordance with the equivalence of the cobalt atoms.

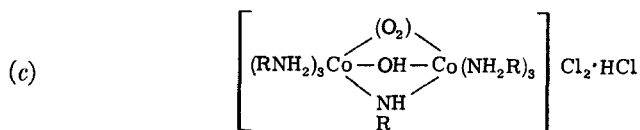
2. Particular Cases



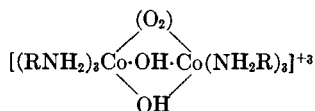
This was described by Werner (570) in terms suggesting that he regarded it as analogous to the paramagnetic P_{en}^2 . The compound, however, is diamagnetic and the ultraviolet spectrum strongly suggests that the cation present is the diamagnetic D_{en}^2 . The additional proton may be coordinated to the peroxy bridge (537).



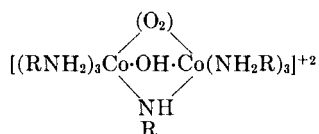
The structure of the symmetrical species seems to have been decided on the basis of its hydrolysis to the tribridged species (570). The unsymmetrical compound, on the other hand, decomposed when heated with hydrochloric acid to give cobalt(II) and chloropentamminecobalt(III) species, from which it was concluded that the cation had the unsymmetrical structure (570). Analogous symmetrical and unsymmetrical dibromides have also been prepared, and the evidence as to their structures is much the same as for the chlorides; the symmetrical dibromide was made by the action of hydrogen bromide on the tribridged P_a^3 , which is further evidence for the symmetrical structure. The symmetrical and unsymmetrical isomers differ in solubility; nonetheless, the evidence as to their structures is not decisive, and there is room for further investigation before Werner's suggestion can be accepted with confidence (570).



(where R is *n*-propyl or allyl.) The cation in these salts was formulated (79, 395) as



but salts of such a cation should be paramagnetic; the *n*-propylamino derivative, however, is diamagnetic (101), hence this structure cannot be right. The analytical data are most satisfactorily reconciled with the magnetic measurements if the compound is regarded as an acid salt of the diamagnetic cation



rather like the acid salt of the ethylenediamine derivative D_{en}^2 mentioned above (537).

C. OTHER PHYSICAL PROPERTIES

The absorption spectra of several of the complexes of both P and D series have been recorded, sometimes without agreement as to the details of the spectra, in a number of media, as shown in the tabulation.

Cation	Range (m μ)	References
P_a^1	200-700	(89, 313, 500, 590)
D_a^1	200-750	(89, 500, 590)
P_a^2	200-750	(500, 525)
P_{en}^2	400-750	(341, 537)
D_{en}^2	300-750	(537)
$[\text{P}_{\text{en}}^2]'$	450-700	(341)

The spectra have not been analyzed in detail in terms of electronic structure, though in some cases (313, 341) comparison is made with the spectra of related derivatives, and some very general assignments are made. The circular dichroism of P_a^1 , D_a^1 (590) P_{en}^2 , and $[\text{P}_{\text{en}}^2]'$ (341) have been investigated; the refractive indices of D_a^1 (587) and P_a^2 (587) have been measured. Werner (571) succeeded in obtaining *d* and *l* forms of the cations P_{en}^2 , D_{en}^2 , and $[\text{P}_{\text{en}}^2]'$ as the bromcamphorsulfonates, and their rotatory dispersions have been measured (341). The X-ray powder photographs of P_{en}^2 and D_{en}^2 nitrates were recorded, as was that of the acid nitrate $\text{D}_{\text{en}}^2(\text{NO}_3)_3 \cdot \text{HNO}_3 \cdot 2\text{H}_2\text{O}$ (537), while parts of the infrared spectrum of P_a^1 (549) and P_a^2 have been briefly described (90, 157). There is a band at $\sim 820\text{--}840\text{ cm}^{-1}$, a region often associated with coordinated peroxide, in the spectrum of P_a^1 , but other absorptions might also be expected in this region. The molar conductances of a number of P_a^1 salts have been measured (435).

D. CHEMICAL PROPERTIES

1. Stability

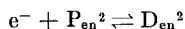
These salts are most stable when dry, but they all decompose slowly at room temperature or more quickly on heating. Derivatives of the dia-

magnetic cation $[(\text{H}_3\text{N})_5\text{Co}(\text{O}_2)\cdot\text{Co}(\text{NH}_3)_5]^{+4}$, D_a^1 , are particularly unstable, being difficult to obtain quite free from paramagnetic impurities, for they are decomposed by water or acids (203, 500, 570, 573). The decomposition in dilute sulfuric acid is extremely complicated, one gram-ion of D_a^1 reacting with 2.9 moles of acid to give at least 8 cobalt-containing species, including P_a^1 ; a mechanism has been proposed for the process that invokes formation of the intermediate $[(\text{H}_3\text{N})_5\text{Co}(\text{O}_2\text{H})]^{+3}$ (59). Acidification of aqueous solutions of D_{CN}^1 , $[(\text{NC})_5\text{Co}(\text{O}_2)\cdot\text{Co}(\text{CN})_5]^{-6}$, leads to the formation of $[(\text{NC})_5\text{Co}(\text{OH}_2)]^{-2}$ (203).

Salts of P_a^1 dissolve in concentrated sulfuric or phosphoric acid to give solutions stable for some weeks at room temperature (48, 124), but decomposition begins after a few minutes in water (being fast once begun) and is rapid in alkali (125, 570, 573). The dibridged species P_a^2 and P_{en}^2 give more stable solutions in water, though P_a^2 decomposes irreversibly in alkali; P_{en}^2 is reduced to the diamagnetic D_{en}^2 by base (537), but the peroxy framework is preserved. This implies that ionization of a proton from a coordinated amino group may be an important step in the irreversible decomposition, though it has also been suggested that P_a^1 is stabilized in acids by hydrogen bonding to the peroxy bridge (313). The perchlorates of P_a^1 and P_a^2 are soluble in acetone, and many P_a^1 and P_a^2 salts give solutions in liquid ammonia that are stable for a few minutes at least at -35° (124); liquid ammonia reacts with the halogenated species to replace the coordinated halogen atoms by ammonia (570).

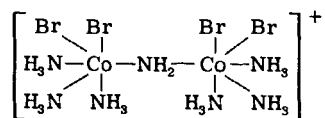
2. Oxidation-Reduction Reactions

The reduction of P salts and of their D analogs has been studied polarographically (30, 435, 557); from the chemical point of view, the most thoroughly studied P-D change is in the system (537):

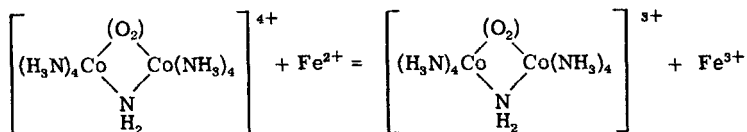


The reductive step is achieved rapidly by hydrazine, nitrite, ferrocyanide, arsenite, thiosulfate, or hydroxyl ions (537); tin(II), iron(II), iodide, or sulfite ions destroy the peroxy bridge. The reverse reaction is brought about rapidly by permanganate, nitrate, or bromate ions, hypochlorous acid, or bromine, but there is no immediate reaction with H_2O_2 , iron(III), silver(I), mercury(II), or dichromate ions. This rather oddly assorted collection of effective and ineffective oxidizing and reducing agents makes it clear that the process is very much influenced by activation effects; it was suggested that an even more unexpected reaction, the apparent one-electron oxidation of D_{en}^2 by bromide ion, was really a catalytic disproportionation (537), though little direct evidence was presented to support this view. The action

of bromine and sulfur dioxide on the tribridged P_a^3 breaks the peroxy bridge, giving the cation (570):



Attempts to prepare the diamagnetic D_a^1 by reducing P_a^1 in solution have led to the formation of decomposition products, probably because of the instability of D_a^1 in solution, but the intermediate formation of D_a^1 in the reduction is suggested by the polarographic results; intermediate formation of D_a^1 has also been postulated in the cathodic reduction of P_a^1 at a platinum electrode (23), in the reduction of P_a^1 by iron(II), vanadium(IV), tin(II), thiosulfate, or iodide ion (501) (though with iodide ion the mechanism is more complicated) (528) and in the reduction by arsenic(III), both uncatalyzed and in the presence of silver powder (23). It is proposed that attack by the peroxy group at the reducing center is the step that precedes electron transfer, and which prevents the protonation of the bridge that is the preliminary step in the complex decomposition in acid solution; the stoichiometry of the reactions shows that there is a one-electron transfer, with evolution of O_2 . The reaction with iron (II) is catalyzed by anions, an effect that has been discussed in terms of ion pair formation (527). A study of the kinetics of the reduction of P_a^2 by ferrous ion (525) indicates that here too the initial step is the one-electron reduction to the diamagnetic cation D_a^2 :



The effect of acid on the reaction rate is consistent with extensive protonation of the peroxy bridge in solutions of D_a^2 ; it is suggested that the dissociation constant of the protonated species is less than 10^{-3} . The reaction between P_a^1 and sulfite or nitrite ions appears to follow a different mechanism (526).

3. Other Chemical Properties

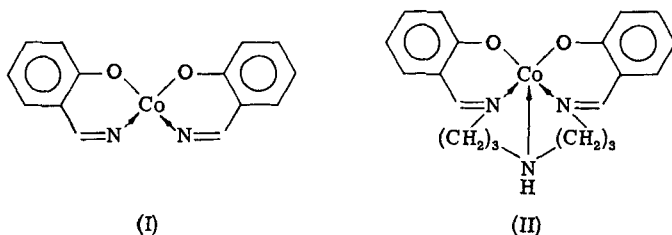
It has been claimed that in aqueous solutions of sulfate or oxalate ions, P_a^1 and D_a^1 give complex anionic species formulated on the basis of studies of ion migration and of dialysis (73) as $[D_a^1 \cdot 4L \cdot 18H_2O]^{-4}$ or $[P_a^1 \cdot 4L \cdot 18H_2O]^{-3}$, where L is sulfate or oxalate. Though some of the evidence is impressive,

the conclusions are hard to reconcile with the observation (48) that the ultraviolet spectra of P_2^{1-} in concentrated sulfuric acid and in a potassium bromide disc are virtually the same. This matter requires further investigation.

Various ligand-exchange reactions are mentioned in the section dealing with preparations. In particular, ammine and halogen ligands in dibridged species can be exchanged under appropriate conditions (570); halide ligands can be hydrolyzed and ammonolyzed (570) without disrupting the peroxy bridge, while the hydrolysis can be reversed by hydrogen halide. Ligand-exchange reactions have been less extensively studied for the monobridged species, probably because of their greater tendency to decompose in solution.

E. COMPLEXES OF BIOLOGICAL INTEREST

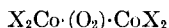
Certain complexes of cobalt with chelating ligands can behave as oxygen carriers. Among derivatives of a substituted salicylaldehyde and an amine, two types of complex emerge as being able to carry oxygen both in the solid state and in solution (17, 22, 84, 85, 208, 229, 580); they may be represented as



Complexes of type I have paramagnetic susceptibilities corresponding to the presence of one unpaired electron to each cobalt atom, and can absorb up to half a mole O_2 per mole; absorption of O_2 leads to a linear decrease in paramagnetism. Complexes of type II, on the other hand, have magnetic moments close to 3.8 B.M., indicating the presence of three unpaired electrons per mole; in absorbing one mole O_2 per cobalt atom, the magnetic moment decreases to a value corresponding to one unpaired electron. The oxygenated products are brownish red in color, and are unstable in solution at low pH (for review see 336).

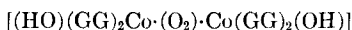
Studies involving peptides and a number of amino acids (80, 167) have shown that yellow-brown complexes of cobalt(II) with glycylglycine (GG) and with histidine (H) are reversibly oxygenated, and undergo spontaneous conversion to pink, irreversibly oxidized forms. Two moles of GG and half a mole of O_2 combine with one mole of Co(II) to form a red-brown crystal-

line complex, which is not formed under anaerobic conditions and which is formed irreversibly at pH less than 2. Once the complex is formed, part of the constituent chelating peptide cannot be enzymatically hydrolyzed, whereas in the free state GG is very rapidly hydrolyzed under similar conditions. The oxygenated complex is reminiscent in many of its properties of the D-type peroxy complexes discussed in Subsection B, and was consequently formulated as having the structure



where X represents the chelating peptide or amino acid (83).

This reversible binding of oxygen has been studied (215, 511, 512) by a variety of physical methods. The red-brown oxygenated form is probably diamagnetic (83, 511, 512); it has a strong charge-transfer band ($\lambda_{max} = 29,000 \text{ cm}^{-1}$, $\ln \epsilon = 3.47$) in its ultraviolet spectrum, and it is polarographically reduced to H_2O_2 . A kinetic study of the absorption of O_2 by cobalt(II)-glycylglycine in the pH range 7–12.5 indicates that an intermediate is formed containing hydroxyl ions, which is of the form

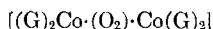


and is obtained by the addition of O_2 to $[Co(GG)_2(OH)_2]^-$ (532). It has been shown polarographically that the product of the irreversible reaction does not contain peroxide oxygen, but corresponds to the general formula $[CoX_2(OH)_2]^-$ or $[CoX_2(OH)]$; the red complex $[Co^{III}(GG)_2(OH)]_2 \cdot H_2SO_4$ has been isolated and characterized (83).

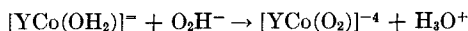
Bishistidinatocobalt(II) also takes up O_2 in the molar ratio $O_2:Co$ of 1:2; the oxygenated species is diamagnetic, in contrast to the parent complex, and slowly changes to a red cobalt(III) derivative (215, 336). The solid oxygenated species has recently been isolated, and from the infrared spectrum it has been deduced that each cobalt atom is six-coordinated, with a peroxy bridge like that in the perdisulfate ion (472).

Vitamin B_{12a} , containing cobalt(III), also takes up oxygen, apparently dimerizing in the process (251); it is not clear whether the oxygenation is reversible.

The decomposition of H_2O_2 by catalytic amounts of cobalt(II)-glycinate complexes (589) results in the formation of stable red-violet cobalt(III) complexes which have been shown to be mixtures of *cis*- and *trans*-hydroxo-aquobis(glycinate)cobalt(III), but unstable amber-colored solutions are produced in the formation of these compounds. A careful investigation of the amber-colored solution has shown it to contain μ -peroxotetrakisglycine-dicobalt(III):



H_2O_2 is also decomposed by solutions of aquo(ethylenediaminetetraaceto)-cobalt(II), $[\text{YCo}(\text{OH}_2)]^-$; a kinetic study of this reaction (588) suggests that a μ -peroxo complex is formed as an intermediate. It is suggested that the first step is

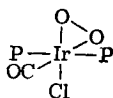


followed by fast reactions which include the formation of the oxidized dimer containing a μ -peroxo group, $[\text{YCo}(\text{O}_2)\cdot\text{CoY}]^{-4}$.

XVI. Iridium

The iridium complex $(\text{Ph}_3\text{P})_2\text{Ir}(\text{CO})\text{Cl}$ (552) does not react with O_2 as a solid, but in solution in benzene it takes up one mole of O_2 per iridium atom; the oxygenation is associated with a color change from yellow to red (550, 551). The oxygenated species, $(\text{Ph}_3\text{P})_2\text{Ir}(\text{O}_2)(\text{CO})\text{Cl}$, may be obtained as a crystalline solid by evaporating the solvent.

The oxygenated solid is quite stable at room temperature in an atmosphere of O_2 in the dark, though an irreversible photochemical oxidation occurs in the light. The O_2 may be removed in solution by lowering the pressure; the oxygenated solid loses O_2 only slowly in vacuum unless the temperature is raised. Treatment with acid gives H_2O_2 ; the molecular weight in benzene or chloroform shows that in these solvents the compound is monomeric. The infrared spectrum contains no absorption associated with OH groups, but there is a band at 860 cm^{-1} , a frequency associated with a coordinated peroxy group (181); it is interesting that the CO stretching frequency drops on oxygenation. The oxygenated solid is diamagnetic; from these data and from the dipole moment (5.9 D), the oxygenated species has been described as a *trans*-bis(triphenylphosphine) derivative of iridium(IV):



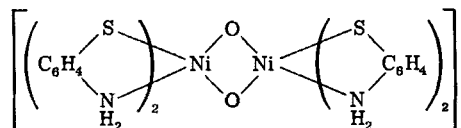
This most interesting compound is the simplest oxygen carrier yet described.

XVII. Nickel

There is no well-characterized peroxide of nickel. A gray-green crystalline solid was obtained by treating a solution of nickel(II) chloride with 30% H_2O_2 and the equivalent amount of alcoholic potassium hydroxide, at -50° ; this product, which gave H_2O_2 when treated with water or acids at room temperature, was found iodimetrically to contain up to two oxidizing equivalents per nickel atom and was formulated as $\text{Ni}(\text{O}_2)\cdot\text{aq}$. The solid

decomposed in a desiccator and more rapidly in air, losing most of its oxidizing power in air in 11 days at room temperature. The substance is regarded as distinct from black NiO_2 (393). Evidence has also been obtained to indicate that nickel peroxides are formed in the catalysis by nickel(II) hydroxide of the decomposition of H_2O_2 (66), while there is some suggestion (318) that soluble peroxynickel species may be formed.

By the action of oxidizing agents, including O_2 , on an alkaline suspension of bis(*o*-aminothiophenol)nickel(II), a blue solid has been obtained, which is formulated as a dimeric derivative of nickel(IV) (221):



It seems possible that there may be a bond between the two oxygen atoms, and that the substance should be regarded as a binuclear peroxide, analogous to the cobalt peroxides, but a decision on this point must await structural studies.

XVIII. Copper

A dark-colored solid containing peroxide oxygen has been obtained by the action of H_2O_2 on solid copper(II) hydroxide (299, 371) or by adding H_2O_2 and alcoholic potassium hydroxide in equivalent amounts to a solution of a copper(II) salt in alcohol at low temperatures (372, 536, 579); the reaction between copper(II) ion and H_2O_2 at room temperature and low pH causes a color change, but no precipitate is formed (7, 371, 457), while at high pH the decomposition of the added H_2O_2 is rapid and violent. No product containing peroxide oxygen was obtained by treating copper(II) acetylide with ethereal H_2O_2 (372) or from sodium peroxide and copper(II) sulfate, from potassium perdisulfate and copper(II) sulfate, or from copper(II) sulfate and ozone (371).

There is little agreement as to the formulas and properties of the product or products. The dark brown solid obtained by Moser from copper(II) hydroxide and H_2O_2 at 0° (371), like the product of the reaction between alcoholic copper(II) chloride, alcoholic potassium hydroxide, and H_2O_2 at -40° (372), contained copper, peroxide oxygen, and water in the approximate molar/atomic ratios 1:1:1; the peroxide oxygen was determined by using acid hydrolysis, measuring the amount of O_2 evolved, and using permanganate to estimate the H_2O_2 formed in solution. This product should therefore be described as $\text{Cu}(\text{O}_2) \cdot \text{H}_2\text{O}$, or $\text{Cu}(\text{OH})(\text{O}_2\text{H})$, a formula corresponding with that suggested by Krüss (299, 368); the water was not removed by vacuum drying. It has, on the other hand, been suggested (536)

that the product obtained from ethanolic copper(II) nitrate and H_2O_2 at -10° is always a mixture of $\text{Cu}(\text{O}_2)$ with varying proportions of CuO formed by thermal decomposition, while phase studies indicate (324) that at temperatures between -36 and $+20^\circ$ the solid phase $\text{Cu}(\text{O}_2) \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ exists, as well as the 1:1 phase $\text{Cu}(\text{O}_2) \cdot \text{H}_2\text{O}$. By working at -79° and using 30% H_2O_2 an olive-green solid has been obtained, which (after being washed until the washings were peroxide-free) was found to contain 1.5 atoms of peroxide oxygen per copper atom, and hence was given the structure $\text{Cu}_2(\text{O}_2)(\text{O}_2\text{H}) \cdot \text{aq}$.

This uncertainty as to composition of the product (or products) obtained in the preparative reactions is reflected in the descriptions of its properties. The solid is variously described as yellow-brown (536), olive-green (457), and black (579). There is general agreement that peroxide oxygen is lost slowly at room temperature and more rapidly on heating (372) and that the loss is least rapid when the solid is dry, but differing impressions are given as to the speed of thermal decomposition (299, 536). The compound is decomposed to H_2O_2 by dilute acid, only a little O_2 being evolved (372); it is also decomposed by dilute ammonia or sodium hydroxide (286); with hydrochloric acid, H_2O_2 and a little O_2 are formed (566).

When H_2O_2 is added to a solution of copper(II) sulfate containing citrate, an unstable brown color is produced, but no precipitate comes down (169); the brown color is probably due to a complex peroxycitrate, tentatively formulated as $[\text{cit-Cu}(\text{O}_2)]^-$.

Copper is also the metal in the naturally occurring oxygen carrier hemocyanine. In this system, the copper seems to be in the $+1$ state (160) and neither oxygenated nor deoxygenated species give electron resonance spectra at room temperature (375), though on acid hydrolysis some copper(II) is formed (160). One molecule of O_2 is taken up to each two copper atoms (214, 430, 432).

XIX. Silver

It has been clearly established that the solid of formula AgO is not a peroxide of silver (377, 477, 478); other higher oxides of silver have been reported (271, 499), but there is no evidence that any of them contains a peroxy group. The solubility of silver(I) in concentrated H_2O_2 has been measured (322) and used to calculate a solubility product for silver(I) hydroperoxide, which may be an intermediate in the catalytic decomposition of H_2O_2 by silver ions, but the solid material has not been isolated.

XX. Gold

It has been suggested that unstable peroxides of gold are formed in the electrolysis of acid or alkaline solutions using gold electrodes (262, 263),

but no solid has been isolated that has been shown to contain a peroxy group.

XXI. The Actinides

A. THORIUM

Thorium forms several peroxides, but only one is well defined; all are of course derived from the +4 state. Neutral or weakly acid solutions of thorium salts and H_2O_2 yield gelatinous precipitates on standing or on heating (86, 96, 119, 205, 291, 408, 489, 585, 586); similar compounds have been obtained by the action of ozone or perdisulfate ion on solutions of thorium salts (408). The solids have been described by various formulas, such as $\text{Th}(\text{O})_2 \cdot 3\text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ (119), $\text{Th}(\text{O})(\text{O}_2) \cdot 4\text{H}_2\text{O}$ (492), or $\text{Th}(\text{OH})_3(\text{O}_2\text{H})$ (155), but the most detailed studies of these compounds that have so far appeared (205, 291) indicate them to be of variable composition, the maximum peroxide content being 1.75 moles per gram-atom of thorium (205); they also contain water and anions (nitrate, sulfate, or chloride, depending on the anions present in solution). Solids with the highest peroxide content were obtained from solutions allowed to stand overnight or heated for long periods to about 40° , but samples prepared under conditions that seemed almost identical were found to differ widely in composition. From nitrate solutions, the product after washing contained about half a gram-ion of nitrate per gram-atom of thorium (205), though it seems possible that the freshly precipitated material may contain one nitrate per thorium atom (86); the chloride content of the chloride derivatives was found to be between 0.5 and 1. Dialysis of a colloidal sample of the chloride for 56 days, however, reduced the chloride content to 0.03 gram-ion per gram-atom of thorium, while the ratio of peroxide to thorium remained as high as 1.45:1 (86). The water content of the nitrates varied between 1 and 4 moles per gram-atom of thorium (205).

The addition of ammonia to a solution containing H_2O_2 and thorium also gives a gelatinous precipitate, but in this material the ratio of peroxide to thorium is close to 1:1 (205).

All of these compounds, particularly those rich in peroxide oxygen, lose peroxide slowly at room temperature, and decomposition is apparently rapid at 130° (155); the chlorides are particularly unstable. The X-ray patterns of material precipitated from acid nitrate solutions contained only a few broad lines, which could be interpreted in terms of a two-dimensional hexagonal structure (592); it has been suggested that the hexagonal layers are made up of peroxide groups and thorium atoms in ratio 3:1, with anions, hydroxyl ions, or water molecules between the layers (205, 592). Little is known of the chemical properties of these materials; the solid

precipitated from hot neutral nitrate solutions is said to be soluble in cold dilute hydrochloric acid (155), while no iodine is liberated in the Riesenfeld test (492).

Although solids like the ill-defined peroxide nitrate and chloride are precipitated from thorium solutions containing sulfate ion at low acidity, solutions that are at least 0.3 *M* in sulfuric acid give a much more granular precipitate on heating (205, 206, 291). This substance has the formula $\text{Th}(\text{O}_2)\cdot\text{SO}_4\cdot 3\text{H}_2\text{O}$; the water molecules are tenaciously held, and the compound itself is remarkably stable thermally. Its powder photograph consists of a large number of sharp lines, in contrast to that of the other derivatives, indicating that the solid has a well-defined structure.

B. PROTACTINIUM

The action of H_2O_2 on weakly acidic solutions of protactinium compounds precipitates a solid that appears to be a peroxide (188, 189, 521). The speed of precipitation, which is slow, is increased by increasing the concentration of H_2O_2 or by decreasing the acidity; the peroxide seems to be rather less soluble than the analogous compounds of thorium, uranium, neptunium, or plutonium.

C. URANIUM

As with molybdenum and tungsten, the peroxide chemistry of uranium is confined to the +6 oxidation state; in view of the small potential for the +6/+5 change (0.063 volt), this is not surprising. The best characterized peroxy derivative is the tetroxide, $\text{UO}_4\cdot n\text{H}_2\text{O}$ (where *n* is 2 or 4); many peroxyuranates are known, in which the ratio of peroxide to uranium is 3:1, 5:2, 2:1, 3:2, 1:1, and 1:2 and, in addition to these, series of mixed peroxyoxalates and -carbonates have been described. In general, the peroxide content increases with pH; acids decompose the compounds to uranium(VI) salts and oxygen, while the triperoxyuranate ion is stable at pH 12–16.

1. Uranium Tetroxide

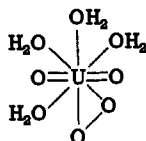
Uranium tetroxide, characterized by Fairley (135), is formed by the action of H_2O_2 on a uranyl salt at pH ~ 2 (8, 111, 121, 135, 178, 207, 250, 367, 461, 471, 582). The compound, which has been shown by reaction with potassium permanganate to contain one peroxy group per uranium atom, is precipitated as a hydrate; Fairley (135) claimed to have obtained a small amount of the anhydrous tetroxide by the action of H_2O_2 on uranyl acetate in the presence of a large excess of sulfuric acid, but attempts to repeat his experiment have failed. Two definite hydrates are known. The air-dried material usually contains four molecules of water of crystallization, but a

dihydrate is obtained if the compound is dried at 90° (69, 121, 135, 308, 459, 461, 475). Several series of experiments have shown that the dihydrate is formed without loss of peroxide oxygen (104, 121, 281, 459, 461, 475, 510) despite suggestions to the contrary (231). There is an apparent conflict of evidence as to the effect of further heating (69, 179, 308, 459, 476); some of the contradictions may arise from differences in experimental conditions, and some from the slowness with which thermal equilibrium is reached, though it seems that one set of results (231) is inconsistent with the rest. On heating in an atmosphere of O_2 to temperatures between 100° and 130° , an intermediate peroxide of formula U_2O_7 or $[U_2(O)_5(O_2)]$ has been obtained (69, 75), though this may be hydrated (459); no such intermediate was detected in the course of thermal decomposition under vacuum (179). It is clear that dehydration of the dihydrate is accompanied by loss of peroxide oxygen, since the ultimate product of decomposition at temperatures greater than 130° is uranium trioxide. The rate of decomposition, as measured by oxygen evolution, follows first order kinetics (69); the heat of the reaction



has been measured indirectly (407).

Because two molecules of water of crystallization are constitutional and cannot be removed without loss of peroxide oxygen, it has been suggested that the peroxide is present as H_2O_2 of crystallization (120, 231). Studies of the thermal decomposition of samples containing O^{18} , however (75, 179), show that the dihydrate contains three types of oxygen atom, present in atomic ratio 1:1:1, a state of affairs most simply explained if the compound has the structure $[U(O)_2(O_2) \cdot 2H_2O]$. The broad line NMR spectrum is consistent with this formulation (413), though it seems that the sample studied contained a different molecular species as well, perhaps $[U(O)_2(OH)(O_2H) \cdot H_2O]$ or $[U(O)(OH)_2(O_2) \cdot H_2O]$; there may be proton migration through the crystal. The presence of the hydroxylated form would also account for the observation that three of the oxygen atoms exchange O^{18} with enriched water at room temperature, though it is not entirely obvious why the fourth of the nonperoxy oxygen atoms did not exchange as well (315). To use an analogy developed by Russian workers (93, 190), the tetrahydrate may well have a structure like that of the triacetatouranyl anion (593) with a planar arrangement of peroxy and water oxygen atoms around the uranium atom and in the plane perpendicular to the axis of the uranyl group:

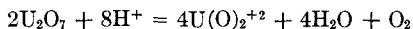


Two other structures have been proposed. A dimeric formulation is given by Russian workers (190, 287), while the compound has several times been described as uranyl triperoxyuranate, $[\text{U}(\text{O})_2]_2[\text{U}(\text{O})_2(\text{O}_2)_3]$ (135, 543, 544). This last suggestion is based partly on a description of the reaction with alkali that is not consistent with later work (196) and partly on analysis of the infrared spectrum. The spectroscopic evidence by no means establishes the presence of uranyl ions in the solid, and in view of the hydrolysis of the $[\text{U}(\text{O})_2(\text{O}_2)_3]^{-4}$ ion at low pH it seems unlikely that this ion is present in the tetroxide.

Both hydrates are yellow compounds which are stable for long periods at room temperature, though the dihydrate is apparently thermodynamically unstable with respect to the trioxide at room temperature (308). The infrared spectra (69, 120, 543, 544) and X-ray powder photographs (459) have been described; both hydrates have body-centered lattices. The corrected paramagnetic susceptibility, χ_M , of 111×10^{-6} cgs units, is temperature-independent (540) as would be expected for a derivative of uranium(VI) (93). The chemical properties have been relatively little studied. The compound is a powerful oxidizing agent, and with strong acids it gives H_2O_2 . With sodium hydroxide it has been said to form a mixture of uranate and triperoxyuranate (543, 544); more recent work, however, (196) suggests that the reaction is more complicated, and depends on the concentration of the alkali used. Between pH 8 and 14, sparingly soluble salts of the anions $[\text{U}_2(\text{O})_5(\text{O}_2)_2\text{H}]^-$ or $[\text{U}_2(\text{O})_5(\text{O}_2)_2]^-$ are formed; with 10 *M* potassium hydroxide, the monoperoxyuranate $\text{K}_2[\text{U}(\text{O})_3(\text{O}_2) \cdot 4\text{H}_2\text{O}]$ is precipitated (114), while with strong sodium hydroxide a soluble colored species is formed, whose ultraviolet spectrum is not the same as that of the triperoxyuranate anion (196).

2. U_2O_7

This compound, which contains one peroxy group to two uranium atoms, has been obtained as an intermediate product of the thermal decomposition of the tetroxide in an atmosphere of oxygen (69, 296), though it appears that the proportion of the compound formed at 195° is greatest at a partial pressure of oxygen gas of less than 15 mm (75), an observation hard to reconcile with other descriptions of the thermal decomposition (179). The solid obtained by Boggs and El-Chehabi is orange and hygroscopic (69), while another report describes the compound as hydrated (459); it reacts with water or dilute acids to give O_2 , treatment with dilute sulfuric acid, for example, giving 94% of the O_2 calculated from the equation



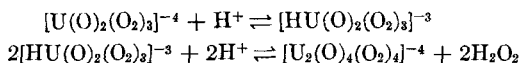
The remaining 6% could be accounted for in terms of its solubility in the solution (69). The compound decomposed slowly at temperatures greater

than 150° to give uranium trioxide (69), though another report claims that decomposition occurs at temperatures greater than 195° (75). It may have been this compound that was obtained by heating uranium(VI) derivatives in oxygen (77, 272); one of these products (77), which oxidized halide ion, also reacted with water to give O₂. The product obtained by heating the tetroxide did not decompose potassium permanganate solution (69).

3. 3:1 Peroxy Species

Salts of formulas $M_4^1UO_8 \cdot nH_2O$ are obtained by the action of hydrogen peroxide on uranates at pH > 12 (93, 190, 354, 462); the cations include Na⁺, K⁺, Li⁺, NH₄⁺, Ba⁺², and the guanidinium ion. The compounds are orange-red, and have been shown spectrophotometrically (93, 190) and by reaction with permanganate solution (354, 462) to contain three peroxy groups per uranium atom. Since the sodium salt can be dehydrated at 100° without loss of peroxide oxygen (31) while the guanidinium salt is obtained without water of crystallization from aqueous solution (462), the anion should probably be represented as $[U(O)_2(O_2)_3]^{-4}$; the six peroxy oxygen atoms may well lie in the plane containing the uranium atom and perpendicular to the axis of the UO₂ group. The potassium salt of formula K₄H₄UO₁₆, obtained from solutions of pH 11 that are rich in H₂O₂ (190), is probably best represented as K₄[U(O)₂(O₂)₄]·4H₂O₂; it reacts with concentrated potassium hydroxide solution to give the 3:1 derivative.

These salts are relatively stable thermally, as is apparent from the conditions used to dehydrate the sodium salt (31) [whose X-ray power photograph has been recorded (190)]. The solubilities of the 3:1 potassium salt (197) and of the much less soluble 7:1 potassium salt (197) (see above) and 3:1 sodium salt (426) have been measured at 0°; the pH of the solution of the sodium salt was 11.6, and the solubility dropped with increasing pH. Though it has been claimed on the basis of potentiometric studies that two molecules of H₂O₂ are formed by hydrolysis when the sodium salt dissolves in water (31), spectrophotometric studies (199, 200) have shown that when the pH > 12 the ion $[U(O)_2(O_2)_3]^{-4}$ is present even in solutions as dilute as 10⁻⁴ M; a cryoscopic determination using the potassium chlorate/water eutectic (in which it was established spectrophotometrically that the anion did not decompose) indicated that the sodium salt gave five particles on dissolving, which is consistent with the presence of the triperoxyuranate ion in solution. On the addition of acid, hydrolysis occurs; apparently the first step is the addition of a proton to the anion, which then loses H₂O₂ and gives a dimeric species (191, 199, 200, 426):



In alkaline solutions, the decomposition products are very complicated and depend on the conditions (190, 193, 194, 195, 412, 427, 429). In solutions that are very dilute in uranium ($\sim 10^{-4} M$), the initial product of decomposition is a mononuclear monoperoxy anion, $[\text{U}(\text{O})_2(\text{O}_2)(\text{OH})_2]^{-2}$, which in turn decomposes to give an anion containing no peroxy oxygen (190, 193). The decomposition of solutions 0.5–1.0 M in uranium gives a range of products which contain varying ratios of peroxide to uranium and differ in the extent to which they are polymerized (190, 193, 194, 195, 412, 429). The kinetics of the decomposition have also been studied (201, 428). The addition of uranyl ion to solutions of triperoxyuranates leads to a drop in pH, with the formation of peroxyuranyl anions containing less than 3 moles of peroxide per uranium atom (544).

The chemical properties of the triperoxyurate ion have been little studied. The salts react quantitatively with acid permanganate (354, 462); the electrolytic reduction at a platinum cathode in dilute solutions apparently involves formation of a 1:1 (peroxide:uranium) peroxyurate, and the electrolytic deposit contains uranium(IV) as well as uranium(VI) (192, 201). The 7:1 potassium salt $\text{K}_4[\text{U}(\text{O})_2(\text{O}_2)_3] \cdot 4\text{H}_2\text{O}_2$ gave 14 electron equivalents of iodine per mole with acid potassium iodide solution, but with buffered potassium iodide in the modified Riesenfeld test only two equivalents were produced (492).

4. 5:2 Peroxy Species

It is by no means clear that any compounds of this group have been isolated. Zahn (594) prepared salts to which he gave formulas $\text{M}_3^{\text{I}}\text{UO}_7 \cdot n\text{H}_2\text{O}$, and in which the peroxide:uranium ratio was 5:2; Rosenheim and Daehr (462), however, on repeating his work obtained compounds in which the peroxide:uranium ratio was 2:1, and which they formulated as $\text{M}_2^{\text{I}}\text{U}_2\text{O}_{13} \cdot n\text{H}_2\text{O}$. One Russian review (93) seems to accept Zahn's work, while another (190) appears to agree with Rosenheim and Daehr. The evidence for the formation of the dimeric 2:1 species is strong, and is discussed in the next section; nonetheless, it is not possible to dismiss Zahn's results without more thorough reinvestigation. It has been suggested that the anion $[\text{U}_2(\text{O})_4(\text{O}_2)_5]^{-6}$ is an intermediate in the alkaline hydrolysis of the triperoxyurate ion (190).

5. 2:1 Peroxy Species

Orange-red compounds of formulas $\text{M}_2^{\text{I}}\text{UO}_6 \cdot n\text{H}_2\text{O}$, $\text{M}_6^{\text{I}}\text{U}_2\text{O}_{13} \cdot n\text{H}_2\text{O}$, and $\text{M}_8^{\text{I}}\text{U}_4\text{O}_{24} \cdot n\text{H}_2\text{O}$, in all of which the peroxide:uranium ratio has been shown to be 2:1, have been obtained from solutions containing alkali, H_2O_2 , and uranium(VI) in moderately high concentrations (190, 194, 195, 412, 462);

these species are also formed in the hydrolysis of triperoxyuranates, but it is not clear how the different 2:1 anions are related to one another. Cryoscopic measurements, in which the ion formulated as UO_6^{2-} was synthesized *in situ* by the action of the calculated amount of nitric acid on the triperoxyuranate ion, indicate that this species is largely dimerized in aqueous solution (191); there does not seem to be direct evidence for writing the ion $\text{U}_4\text{O}_{24}^{8-}$ as a tetramer rather than a dimer, and it seems possible that all these compounds contain dimeric anions, though it has been claimed (190) that monomers are also formed, at least in solution.

Although the disodium salt " $\text{Na}_2\text{UO}_6 \cdot n\text{H}_2\text{O}$ " has been precipitated by the action of alcohol on an aqueous solution at 90° (544), these compounds are not particularly stable thermally (190, 195, 462); the salts $\text{M}_6\text{U}_2\text{O}_{13} \cdot n\text{H}_2\text{O}$ are rather more stable, but " Na_2UO_6 " loses oxygen "rapidly and completely" when dry at 100° , and " $\text{K}_2\text{UO}_6 \cdot n\text{H}_2\text{O}$ " decomposes in a day or so in air (195). The potassium salt " $\text{K}_2\text{UO}_6 \cdot n\text{H}_2\text{O}$ " is not very soluble in water, and hydrolyzes in aqueous solution to a monoperoxy species (190). The X-ray powder photographs of some of these salts have been described (190, 195, 298). Chemically, they are strong oxidizing agents and give chlorine with hydrochloric acid, though reaction with potassium iodide may not be quantitative (462).

6. 3:2 Peroxy Species

Here again two series of salts have been described. Rosenheim and Daehr (462) made sodium, potassium, and ammonium salts of one series by treating the appropriate hydroxide with uranyl nitrate and H_2O_2 , the alkali being less concentrated than that used in making the peroxide-richer species. Reaction with potassium permanganate established the peroxide:uranium ratio, and on the basis of analysis the salts were described as $\text{M}_2\text{U}_2\text{O}_{10} \cdot n\text{H}_2\text{O}$. The sodium salt (in this case described as a monomer, NaUO_5) was made by adding alcohol to a solution of sodium diuranate in H_2O_2 (544) and has also been obtained, with other products, by heating a solution of sodium triperoxyuranate in 2 *M* sodium hydroxide (412). Little is known of these compounds, save that they have moderate thermal stability, they react quantitatively with permanganate solution, and all their peroxide oxygen is active to potassium iodide (462).

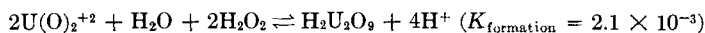
A different series of compounds, sometimes described as $\text{M}_8[\text{U}_4\text{O}_{22}]$ (194, 412), has been considered by Gurevich (190) to contain the ion $[\text{U}_2(\text{O})(\text{O}_2)_3]^{-4}$. The sodium and potassium salts have been obtained as decomposition products of triperoxyuranates (412) and their X-ray powder photographs have been described (190, 194, 298). The sodium salt, whose color varies from one sample to another from brown to red, is thermally very stable; it may be dried at 100° , is not decomposed by hot water in which

its solubility is very low, and has been kept without decomposition for a year at room temperature (190).

7. 1:1 Peroxy Species

The 1:1 peroxyuranates that have been described are of four types. Compounds of formula $M^I\text{HU}_2\text{O}_9 \cdot n\text{H}_2\text{O}$, $M_2^I\text{U}_2\text{O}_9 \cdot n\text{H}_2\text{O}$, and $M_2\text{UO}_5 \cdot n\text{H}_2\text{O}$ have been obtained by the action of uranyl nitrate on alkaline H_2O_2 (114, 196) and as decomposition products of alkaline solutions of triperoxyuranates (194, 195); the potassium salt $\text{KHUO}_5 \cdot 2\text{H}_2\text{O}$ has also been obtained, by treating uranium tetroxide hydrate with carbonate-free potassium hydroxide solution⁸ (114). All these compounds have been shown by reaction with potassium permanganate to contain one peroxy group per uranium atom, but it is not entirely clear how they are related to one another.

Spectrophotometric evidence, coupled with studies of pH, makes it plain that species containing one peroxy group to each uranium atom are formed in solution (198, 200, 544); the effect of adding H_2O_2 to uranyl nitrate solution upon the pH and ultraviolet absorption of the system has been interpreted in terms of the formation of diperoxydiuranic acid:



This species is stable in solution at pH 3–6. If this is correct, then the salts of formulas $M^I\text{UO}_5 \cdot n\text{H}_2\text{O}$ should probably be described as $M_2^I\text{U}_2\text{O}_9 \cdot (2n + 1)\text{H}_2\text{O}$, while those of formulas $M_2^I\text{UO}_5$ are presumably derived from this system by further removal of protons. There is not enough evidence to decide whether monomeric as well as dimeric species have been prepared. Since in any case all the salts are hydrated, it is likely that coordination at uranium is higher than is implied by the above formulas (190).

These salts are relatively stable, though the potassium derivatives $\text{KHUO}_5 \cdot n\text{H}_2\text{O}$ and $\text{K}_2\text{UO}_5 \cdot n\text{H}_2\text{O}$ decompose on heating, giving O_2 and uranate or diuranate (114). The X-ray powder photographs of $\text{KHUO}_5 \cdot 2\text{H}_2\text{O}$, $\text{K}_2\text{UO}_5 \cdot 3\text{H}_2\text{O}$ (114), $\text{K}_2\text{U}_2\text{O}_9 \cdot 5\text{H}_2\text{O}$, $\text{KHU}_2\text{O}_9 \cdot 6\text{H}_2\text{O}$, $\text{NaHU}_2\text{O}_9 \cdot 7\text{H}_2\text{O}$, and $\text{Na}_2\text{U}_2\text{O}_9 \cdot 7\text{H}_2\text{O}$ have been recorded [data for the last four compounds are given in reference (190)]. The sodium salt $\text{Na}_2\text{U}_2\text{O}_9 \cdot 7\text{H}_2\text{O}$ is apparently insoluble in water, and dissolves only to a very small extent in *N* alkali at 100° (190).

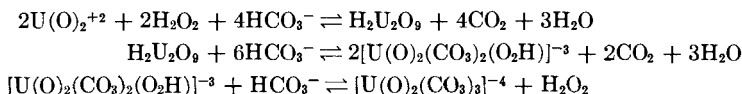
Besides these salts, there are other reports of 1:1 peroxides. The salts Na_2UO_5 , K_2UO_5 , and BaUO_5 were obtained by fusing uranyl chloride, UO_2Cl_2 , with the appropriate hydroxide in air (381); the products were orange-red solids which evolved O_2 when heated, leaving uranates, and

⁸ The (1:1) anion $\text{U}_4\text{O}_{13}^{-6}$, detected spectrophotometrically (200), should perhaps be regarded as $\text{H}_2[\text{U}_4\text{O}_{20}]$, i.e., $\text{H}_2[\text{U}_4(\text{O})_{12}(\text{O}_2)_4]^{-6}$ or $\text{H}[\text{U}_2(\text{O})_6(\text{O}_2)_2]^{-3}$.

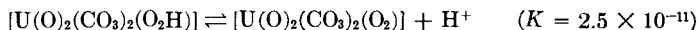
whose other properties were said to correspond with those of the peroxy-uranates made by Fairley (135). The published analytical information, however, is extremely meager; the preparative reaction is so unexpected, in view of the thermal instability of other peroxyuranates, that a reinvestigation of these results would be valuable. There is also evidence that a 1:1 peroxy species is formed in the electrolytic reduction of peroxy-uranates (201).

8. Complex Peroxyuranates

a. Carbonates. The effect of carbonate and bicarbonate ions on the ultraviolet absorption of peroxyuranates has been noted (9, 495, 496), but it has not always been appreciated that peroxycarbonatouranates are formed. Spectrophotometric and cryoscopic studies indicate that in the presence of bicarbonate the reaction between uranyl ion and H_2O_2 leads first to the formation of diperoxydiuranic acid, which then combines with bicarbonate to form a monomeric monoperoxy-monocarbonatouranate anion:

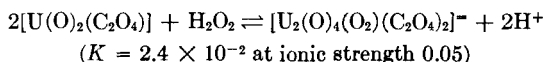


It should be noted that there is no evidence for locating the proton on the peroxy group. Addition of alcohol to a solution of uranyl nitrate, potassium bicarbonate, and H_2O_2 in molar proportions 1:7:1 precipitates a solid that was identified by analysis as the potassium salt $\text{K}_3[\text{U}(\text{O})_2(\text{CO}_3)_2(\text{O}_2\text{H})]$, possibly contaminated with potassium bicarbonate (288). When carbonate is taken instead of bicarbonate, spectrophotometric evidence indicates that at higher pH the proton is removed from the peroxyanion (190, 290)



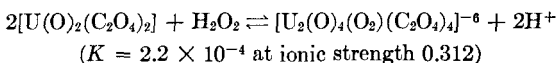
(see also 337). Cryoscopic measurements, using the potassium nitrate/water eutectic, were consistent with the formation of a monoperoxydicarbonato anion (290). The monocarbonate derivative $(\text{NH}_4)_2[\text{U}(\text{O})_2(\text{CO}_3)(\text{O}_2)] \cdot 2\text{H}_2\text{O}$ was prepared by the addition of alcohol to a solution containing carbonate, uranate, and ammonium ions (346), but (as with the rest of these complexes) little is known about its chemical properties.

b. Oxalates. It has been shown spectrophotometrically that a peroxy-oxalatouranate anion is formed when H_2O_2 is added to a solution of uranyl oxalate (289):



The change in pH in the titration of a solution of uranyl perchlorate, H_2O_2 , and sodium oxalate against sodium hydroxide affords further evidence for the formation of this ion in solution (93). A solid of composition $(\text{NH}_4)_2[\text{U}_2(\text{O})_4(\text{O}_2)(\text{C}_2\text{O}_4)_2]$ was precipitated by the addition of H_2O_2 to a saturated solution of ammonium uranyl oxalate (or a concentrated solution of ammonium and uranyl oxalates in appropriate proportions) (289, 346); the analysis, though not exact, supports the proposed formula quite closely.

In the presence of excess oxalate ion, the formation of a peroxy dioxalato species was detected spectrophotometrically:



By adding H_2O_2 to a solution saturated in both uranyl and ammonium oxalates, a yellow solid of composition $(\text{NH}_4)_6[\text{U}_2(\text{O})_4(\text{O}_2)(\text{C}_2\text{O}_4)_4] \cdot 7\text{H}_2\text{O}$ was obtained (346); when H_2O_2 was added to a solution containing less ammonium oxalate, no precipitate was formed but alcohol precipitated a different hydrate of the same anion, $(\text{NH}_4)_6[\text{U}_2(\text{O})_4(\text{O}_2)(\text{C}_2\text{O}_4)_4] \cdot 3\text{H}_2\text{O}$ (346).

A third ammonium peroxyoxalate, formulated as $(\text{NH}_4)[\text{U}(\text{O})_2(\text{O}_2)(\text{C}_2\text{O}_4)] \cdot n\text{H}_2\text{O}$, has been obtained by adding 30% H_2O_2 to a 14% solution of ammonium uranyl oxalate (289) while a fourth, described as $(\text{NH}_4)_2[\text{U}_2(\text{O})_4(\text{O}_2)_2(\text{C}_2\text{O}_4)] \cdot n\text{H}_2\text{O}$, has been mentioned in a Russian review (93); it is not clear whether the last two compounds are really different (289).

c. Carboxylic Acids. The addition of dilute H_2O_2 to a solution of uranyl nitrate and ammonium acetate leads to the precipitation of yellow crystals which are soluble in ammonium acetate solution but which decompose slowly to give uranium tetroxide hydrate, and analyzed to the composition $(\text{NH}_4)_2\text{UO}_4 \cdot \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_4$ or $(\text{NH}_4)_2[\text{U}_2(\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_4(\text{O}_2)]$ (346). (The formula given by Mazzucchelli and Bimbi at first sight seems to show only one ammonium ion, but this does not agree with the calculated percentage of ammonia in the table they give.) A similar sodium peroxyvaleratouranate was obtained, contaminated with sodium valerate. The action of H_2O_2 on a solution of barium and uranyl acetates precipitated the yellow salt $\text{Ba}[\text{U}(\text{O})_2(\text{C}_2\text{H}_3\text{O}_2)(\text{O}_2)] \cdot 6\text{H}_2\text{O}$. A crude sample of a sodium peroxyphthalatouranate was precipitated by the addition of alcohol to a solution of uranyl nitrate, sodium phthalate, and H_2O_2 ; it contained uranium and peroxide in the ratio 1:1 (346).

A spectrophotometric study (105) of the effect of H_2O_2 on a solution of uranyl nitrate containing salicylic acid showed that the only complex formed at pH's 9 and 10.3 contained peroxide and uranium in the ratio 1:1. It is not clear whether the species was a simple peroxyuranate or a peroxy-salicylatouranate; the latter is the more likely, since no sign was

detected of the triperoxyuranate anion that might have been formed at the higher pH, and salicylate ion interferes with the spectrophotometric determination of uranium with H_2O_2 (458). Finally, it is possible to use sodium tartrate instead of sodium carbonate in the spectrophotometric determination of uranium with H_2O_2 at high pH, implying that there may be tartrato complexes analogous to the carbonato complexes (458).

d. Pyrophosphate. An orange solid was obtained by the action of H_2O_2 on a solution containing uranyl, sodium, and pyrophosphate ions (346); it analyzed according to the formula $\text{Na}_4[\text{U}_2(\text{O})_4(\text{O}_2)_2(\text{P}_2\text{O}_7)] \cdot 18\text{H}_2\text{O}$. Phosphate ion interferes in the spectrophotometric determination of uranium using carbonate and peroxide, which also indicates complex formation (458).

e. Fluoride. The action of H_2O_2 on sodium uranyl fluoride, $\text{Na}[\text{U}(\text{O})_2\text{F}_5] \cdot n\text{H}_2\text{O}$, gave a yellow solution which on heating to 60–70° deposited yellow crystals of formula $\text{Na}[\text{U}(\text{O})_2(\text{O}_2)\text{F}(\text{OH}_2)] \cdot 4\text{H}_2\text{O}$; four molecules of water of crystallization were lost at 100°. Treatment of a solution of the potassium salt $\text{K}_3\text{U}(\text{O})_2\text{F}_5$ with H_2O_2 gave similarly a yellow solid which had the composition $\text{K}_4\text{U}_4(\text{O}_2)_4(\text{O})_7\text{F}_6 \cdot 4\text{H}_2\text{O}$, a formula very difficult to rationalize (316). Uranium tetroxide, however, is only sparingly soluble in many fluoride solutions (113).

f. Sulfate. The interference of sulfate ion in the spectrophotometric determination of uranium with carbonate and H_2O_2 may indicate the formation of a peroxyulphato complex (458).

3. Relationships between Compounds

At first sight the formulas of the peroxyuranates and their complex derivatives present a bewildering and unrelated complexity. Recently, however, it has been suggested (93, 190) that their structures may be rationalized if it is assumed that the peroxy group acts as a bidentate ligand, and that in general the uranyl ion is six-coordinated, the remaining coordination positions being occupied by water molecules. This fits in with what is known about the coordination of complex uranyl compounds, and explains the formation of mixed peroxycarbonato, -oxalato, and -acetato anions. The formulas, based on these schemes, look a little cumbersome; they are set out in Table IV, with the formulas by which the various compounds have been best known in the past, and the rough pH range over which the species are stable. There is no evidence at present to show whether the binuclear species are linked by oxo or peroxy bridges.

It is clear that high pH favors the formation of monomers that are rich in peroxide, but that these may be persuaded to condense in the course of thermal decomposition in solution. Figures 8 and 9 give some idea of the ways in which these peroxy compounds may be converted into one another; they are based on data in reference (190).

TABLE IV
STRUCTURAL FORMULAS SUGGESTED FOR SOME PEROXYURANIUM COMPOUNDS

pH stable	O ₂ /U	Usual formula	Rationalized formula ^a
12.5	3:1	M ₄ ^I UO ₈ ·nH ₂ O	M ₄ [U(O) ₂ (O ₂) ₃]·nH ₂ O
10.7–12	3:1	[HUO ₈] ^{−3}	[U(O) ₂ (O ₂) ₃ H] ^{−3}
—	5:2	M ₃ ^I UO ₇ ·nH ₂ O	M ₆ [U ₂ (O) ₄ (O ₂) ₅ (OH ₂) ₂](2n − 2)H ₂ O
14.0	2:1	M ₆ ^I U ₂ O ₁₃ ·nH ₂ O	M ₆ [U ₂ (O) ₄ (O ₂) ₄ (OH) ₂ (OH ₂) ₂](n − 3)H ₂ O
10.7–12	2:1	M ₂ ^I UO ₆ ·nH ₂ O	M ₄ [U ₂ (O) ₄ (O ₂) ₄ (OH ₂) ₄](2n − 4)H ₂ O
14.0	2:1	M ₈ ^I U ₄ O ₂₄ ·nH ₂ O	M ₄ [U ₂ (O) ₄ (O ₂) ₃ (O ₂ H)(OH)(OH ₂) ₄]($\frac{n}{2} - 5$)H ₂ O
14.0	3:2	M ₈ ^I U ₄ O ₂₂ ·nH ₂ O	M ₄ [U ₂ (O) ₄ (O ₂) ₃ (OH) ₂ (OH ₂) ₄]($\frac{n}{2} - 5$)H ₂ O
~10.5	3:2	M ₂ ^I U ₂ O ₁₀ ·nH ₂ O	M ₂ [U ₂ (O) ₄ (O ₂) ₃ (OH ₂) ₆](n − 6)H ₂ O
14.0	1:1	M ₆ ^I U ₄ O ₁₉ ·nH ₂ O	M ₃ [U ₂ (O) ₄ (O ₂) ₂ (OH) ₃ (OH ₂) ₅]($\frac{n - 13}{2}$)H ₂ O
13.0–14.0	1:1	M ₂ ^I UO ₅ ·nH ₂ O	M ₄ [U ₂ (O) ₄ (O ₂) ₂ (OH) ₄ (OH ₂) ₄](2n − 6)H ₂ O
13–14	1:1	M ₂ U ₂ O ₉ ·nH ₂ O	M ₂ [U ₂ (O) ₄ (O ₂) ₂ (OH) ₂ (OH ₂) ₆](n − 7)H ₂ O
~8	1:1	MHU ₂ O ₉ ·nH ₂ O	M[U ₂ (O) ₄ (O ₂) ₂ (OH)(OH ₂) ₇](n − 7)H ₂ O
6	1:1	H ₂ U ₂ O ₉ ·nH ₂ O	[U ₂ (O) ₄ (O ₂) ₂ (OH ₂) ₈](n − 7)H ₂ O
—	1:1	UO ₄ ·4H ₂ O	[U(O) ₂ (O ₂)(OH ₂) ₄]
—	1:1	K ₃ HU(CO ₃) ₂ O ₄	K ₃ [U(O) ₂ (CO ₃) ₂ (O ₂)H]
—	1:1	BaU(C ₂ H ₃ O ₂) ₂ O ₄	Ba[U(O) ₂ (C ₂ H ₃ O ₂) ₂ (O ₂)]
—	1:1	NaUO ₄ F·5H ₂ O	Na[U(O) ₂ (O ₂)(OH ₂) ₃ F]·2H ₂ O
—	1:2	(NH ₄) ₆ U ₂ (C ₂ O ₄) ₄ O ₆ ·7H ₂ O	(NH ₄) ₆ [U ₂ (O) ₄ (C ₂ O ₄)(O ₂)(OH ₂) ₂]·5H ₂ O

^a The rationalized formulas assume that the uranyl ion is six-coordinated, and in some cases the degree of polymerization has not been determined experimentally.

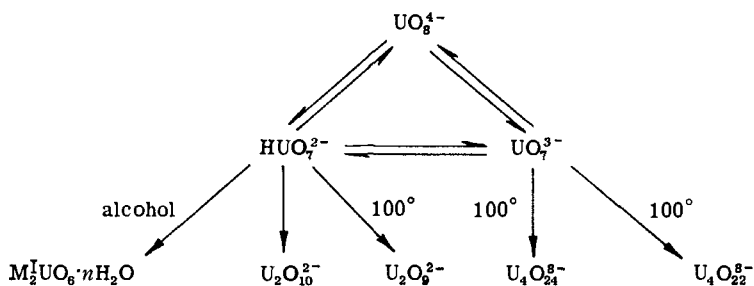


FIG. 8. Relationships between peroxyuranium species in aqueous solution, at $[U] \leq 10^{-4} M$ (190). The simple formulas used may be converted to "rationalized" formulas by using Table IV.

When the peroxy group is considered with other bidentate ligands to uranium(VI), the displacement reactions in which, for instance, peroxy-carbonatouranates are formed from H_2O_2 and uranium carbonates show that the bonding between the peroxy group and the uranium atom must be relatively strong.

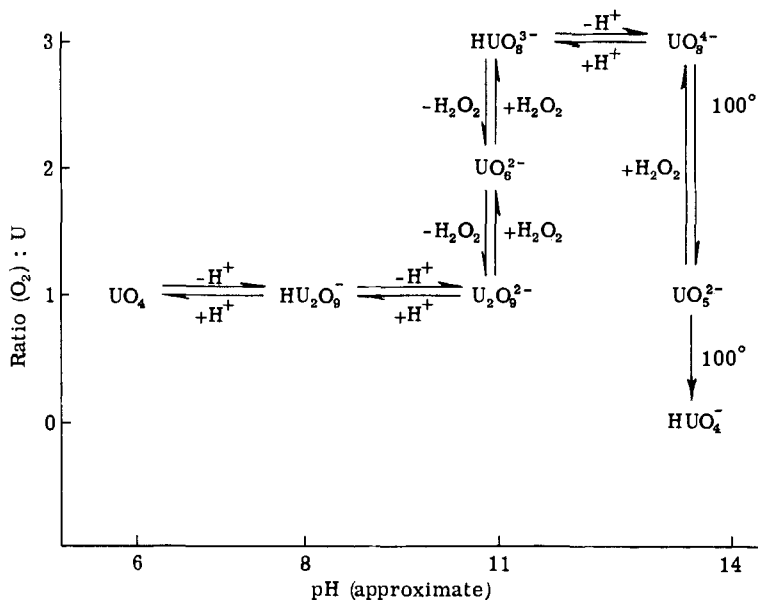
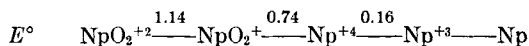


FIG. 9. Relationships between peroxyuranium species in aqueous solution, at $0.1 \leq [U] \leq 1.0 M$ (190). The simple formulas used may be converted to "rationalized" formulas by using Table IV.

D. NEPTUNIUM

The oxidation potentials for neptunium ions in solution (274) are summarized below. They indicate that the +6 state is less stable with respect to the lower states than for plutonium or uranium, but that complex oxidation-reduction reactions might be expected with H_2O_2 .

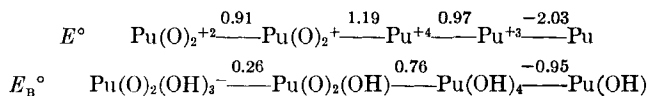


In 0.5 *M* nitric acid it seems that neptunium (VI) is rapidly reduced by H_2O_2 to the +5 state, but that there is little further reduction over a period of 24 hours at room temperature (300). Neptunium(IV) is slowly oxidized to the +5 state by O_2 in 1 *M* sulfuric acid (323), but in general the details of the interaction between neptunium and H_2O_2 have not been extensively studied.

The addition of H_2O_2 to a solution of neptunium(IV) hydroxide in nitric acid leads to the slow precipitation of a grayish purple solid that has been formulated as $\text{NpO}_4 \cdot 2\text{H}_2\text{O}$ (300, 323), presumably by what may be an unfortunate analogy with uranium. As with plutonium, there are two forms: the compound precipitated from 1.0 *M* nitric acid has a face-centered cubic lattice with $a = 17 \text{ \AA}$, and contains 2.9 moles of peroxide oxygen to each two neptunium atoms; the substance precipitated from 3.0 *M* nitric acid has a hexagonal lattice, and contains 3.0 moles of peroxide oxygen to each two neptunium atoms. There was no sign of the formation of soluble complexes like the brown plutonium compounds (118).

E. PLUTONIUM

The complicated oxidation-reduction relationships in the solution chemistry of plutonium have their effect on reactions between H_2O_2 and solutions of plutonium compounds. The oxidation potentials (273) are summarized below:

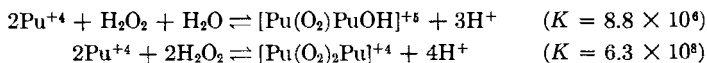


In acid solution, plutonium(VI) is reduced to plutonium(V) by H_2O_2 , but further reduction to plutonium(IV) is slow. Plutonium(IV) is reduced to plutonium(III) in certain acids, but plutonium(III) is slowly oxidized by air or by H_2O_2 in dilute solution to plutonium(IV) (99, 100). There is, however, a marked change in ultraviolet absorption when H_2O_2 is added to a solution containing $\text{Pu}(\text{III})$ (98).

Dilute solutions of plutonium(IV) form soluble brown peroxy complexes on the addition of H_2O_2 ; green solids are precipitated if the solution is more concentrated. The solid derivatives, which are rather ill-defined, are in many ways like the peroxides of thorium. No peroxides of plutonium derived from any oxidation state other than the +4 state have been isolated.

1. Soluble Peroxides

When dilute solutions of plutonium(IV) are treated with H_2O_2 , they first turn brown and then red; no O_2 is evolved, and it was concluded that the plutonium remained in the same oxidation state (97, 98, 100). Spectrophotometric studies indicate that both brown and red species are binuclear, the brown containing one peroxy group, and the red two, to each two plutonium atoms. These results were corroborated by EMF measurements; the effect on the system of altering the pH suggested that the brown species contained an OH group. The equilibrium constants for the two equations below were determined spectrophotometrically:



2. Insoluble Peroxides

Careful analysis of the solids precipitated from acid solutions of plutonium(IV) compounds by the addition of H_2O_2 confirmed the presence of plutonium(IV) (291), but also showed that the composition of the precipitate depends to some extent on the conditions of precipitation (204, 291, 304, 305). The peroxide oxygen content, determined either gas-volumetrically, or by reaction with iodide, is usually very close to 3 O_2 groups to each two atoms of plutonium (204, 227, 228, 291, 304, 305); in wet precipitates the ratio has been found to be closer to 3.3:2, but in most of the dried materials it was a little less than 3 (204, 304). The highest ratio, 4.56:1, was obtained from a precipitate formed in a solution containing sulfate and nitrate ions, and which had been digested for some hours at 50–70°. Besides peroxide oxygen, however, the solids always contain water, nonperoxidic oxygen, and anions. Precipitates from sulfate solutions, for example, contain between 0.24 and 0.38 gram-ion of sulfate to each gram-atom of plutonium (304, 305); even precipitates formed in nitrate solutions contained small amounts of sulfate, which was traced to contamination in the H_2O_2 used (204). The nitrate content of precipitates formed from nitrate solutions is proportionally less (204); chlorides have also been obtained (204, 304).

All of these materials were hydrated, and could be kept for a matter of days at room temperature without extensive decomposition, though the

chloride-containing materials were the least stable. Drying for short periods gave products with less than 5 molecules of water of crystallization, without substantially affecting the peroxide content, but prolonged drying reduced the ratio of peroxide:plutonium to less than 1:1, while there was some evidence that in the 3:2 materials two of the peroxy groups might be more tightly bound than the third (204). X-ray studies show that the materials form two distinct types of lattice—a hexagonal layer lattice, analogous to one form of thorium peroxide, and a face-centered cubic phase with lattice constant $a = 16.46 \text{ \AA}$ (304). Which phase is precipitated depends on the acid and on its concentration (304, 305); the hexagonal phase is precipitated from sulfuric acid more concentrated than $2 M$, from hydrochloric acid more concentrated than $3.6 M$, and from some concentrations of perchloric acid, while $0.4 M$ sulfuric acid, for example, gives the face-centered cubic phase (305). The hexagonal phase contains a higher proportion of sulfate than the cubic if both are precipitated from sulfuric acid solutions (304, 305), while it appears that the cubic phase can tolerate a peroxide:plutonium ratio as low as 1.1:1 without a change of lattice. It has been suggested (204, 369) that the hexagonal form consists of layers of peroxide groups and plutonium atoms, while the other groups—anions, water molecules—are held between the layers; this would explain the variable composition, and would account for the high peroxide content of digested precipitates, which would be supposed to contain interlayer peroxide as well as the peroxide of the layers themselves. The infrared spectrum of the hexagonal form contains bands at 2953 and 861 cm^{-1} ; in material prepared from D_2O solutions, these shifted to 2120 and 879 cm^{-1} , from which the presence of hydroperoxide $-O_2H$ groups in the substance was deduced, the higher frequency being assigned to the OH or OD stretching mode and the lower to the OO stretching vibration. In the spectrum of the cubic form, the higher-frequency band was not observed; a band at 834 cm^{-1} , which was assigned to the OO stretching mode, was not shifted in material prepared from D_2O . On this basis it was suggested that the cubic form should be represented as $Pu_2(O)(O_2)_3$ (304).

Chemically, little is known of these materials. They are partly reduced in aqueous hydrochloric acid by prolonged boiling; they decompose when heated, and react with hydrogen halides at temperatures greater than 100° to give halides of plutonium (216, 227).

XXII. Catalytic Decomposition of H_2O_2

The mechanisms by which derivatives of transition metals act as homogeneous catalysts in the decomposition of H_2O_2 are generally supposed to involve the formation of unstable peroxy derivatives. Kinetic studies have often been used to deduce the formulas of active intermediates, and

in some cases further study has led to the isolation of solid derivatives that have formulas corresponding with those of the suggested intermediates (59, 68). Unfortunately, however, those species that are active in catalysis are likely to be unstable enough to be difficult to handle as solids. Recent studies of the catalytic decomposition of H_2O_2 by chromium(VI), for example, suggest that the active intermediate is a 1:1 peroxychromate(VI), and that a more stable diperoxychromate(VI) species is formed at the same time (144, 202); when the instability of the diperoxychromium(VI) compounds is recalled, it seems unlikely that the proposed monoperoxy derivatives would be particularly stable at room temperature. Conversely, the relative inactivity of molybdate (376) or tungstate (282) ions as catalysts is presumably associated with the relatively greater stability of their peroxy derivatives.

In some cases, notably for chromium(VI), the kinetic curves are very complex (144, 202, 282, 518, 520), and their interpretation is correspondingly difficult. Several types of intermediate have been suggested for this system, but it is not easy to assess the certainty with which the species can be identified, or to decide how far it is possible on the basis of any one scheme to exclude the formation of other species. The situation is further complicated by the marked effects of promoting ions (54, 376, 416, 502), which are in some cases very difficult to explain in chemical terms. In general, it seems that the most active transition metals are those that have more than one oxidation state of rather similar stability—notably iron, chromium, or vanadium; the topic was extensively reviewed by Baxendale (27) in 1952, and reference may be made to papers dealing with the effects of compounds of vanadium (237), niobium (237), chromium (59, 202, 517, 518, 520), molybdenum (519), tungsten (282), manganese (148, 149), iron (202, 310), ruthenium (122), osmium (152), cobalt (56), nickel (264), copper (380), and plutonium (127).

XXIII. Analytical Applications

H_2O_2 has been used in analysis as a precipitant for uranium (458) (a reaction which is also of technical importance), but by far the most important application of the properties of transition metal peroxides to analytical chemistry lies in their color reactions. The usefulness of these in qualitative analysis needs no stressing here; some of the elements that may be determined spectrophotometrically using the absorption bands of their peroxy derivatives are given in Table V.

H_2O_2 has also been used in the separation of transition metal ions by paper chromatography (307) or electrophoresis (307).

It should perhaps be pointed out that peroxy species do not necessarily show the color reactions of the normal (i.e., oxy) ions, and that therefore

TABLE V
EXAMPLES OF THE USE OF H_2O_2 IN THE SPECTROPHOTOMETRIC
DETERMINATION OF TRANSITION ELEMENTS

Element	Wavelength ($\text{m}\mu$)	Acidity, etc.	Reference
Ce	370–380	pH 8.7, in presence citrate	(539)
Ti	405–410	1.5–3 <i>N</i> H_2SO_4 , HCl, or HClO_4	(156)
V	450	0.6–6 <i>N</i> acid	(564, 584)
	290	10–20% acid	(534)
Nb	365 ^a	96% H_2SO_4	(382)
Ta	287	96% H_2SO_4	(382)
Cr	565	Extracted from acid solution with ethyl acetate ^b	(170)
Mo	330	20% HClO_4	(533; see also 154)
Re	390	96% H_2SO_4	(382)
Fe	520	pH 9–12; with EDTA	(451)
Co	(460) ^c	HCO_3^-	(535)
	260	HCO_3^-	(535)
U	370–400	pH 2; in presence of OH^- , CO_3^{2-} , SO_4^{2-} (pH 4–5) ^d	(458)

^a This band shifts to shorter wavelengths in more dilute acid; $\lambda_{\text{max}} = 320 \text{ m}\mu$ in 30% H_2SO_4 .

^b Method impaired by the instability of the complex.

^c

^d The lower pH range has been used with an acetate buffer, but is less satisfactory.

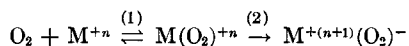
the precipitation reactions of such species as molybdate or tungstate are markedly affected by H_2O_2 (136).

XXIV. Oxygen Carriers

The properties of naturally occurring (334) and synthetic (558) O_2 carriers have recently been reviewed, while much interesting information about these substances and the related enzyme catalysts for biological oxidations involving O_2 is to be found in a collection of articles published in 1963 (213). A transition metal seems to be present in almost all naturally occurring O_2 carriers; the metals found in biological systems are iron or copper, but simple cobalt (326) and iridium (551) O_2 carriers have been synthesized, there is a suggestion that the rhenium complex anion $[\text{Cl}_5\text{ReOReCl}_5]^{-4}$ may combine reversibly with O_2 (259), and there is a less well-established claim for nickel dimethylglyoxime (498). It now appears that manganese(II) phthalocyanine does not show O_2 -carrying properties (129). In most of these systems, up to one mole of O_2 is taken up to each atom of transition metal present, but some derivatives of iron, cobalt, and copper are known in which the fully oxygenated form contains one molecule

of O₂ to each two atoms of the transition metal. No structure of an oxygenated species has yet been determined, though one has been proposed for the oxygenated form of the cobalt(II)-histidine complex (472); it has been variously suggested that the O₂ molecule in oxyhemoglobin lies with its axis perpendicular (390), at 60° (389), or parallel (180) to the plane of the protoporphyrin ring. The last arrangement is most in keeping with the structures of transition metal peroxides that have been determined, though the structure proposed for the cobalt(II)-histidine complex is more like the 60° model.

The list of O₂-carrying transition metals is an interesting one, for of the metals in it only cobalt forms a well-defined and well-known series of peroxides; the peroxides of the earlier transition metals—titanium, vanadium, and chromium—are much better known, but so far no O₂-carrying compounds of these elements have been described. Another interesting feature is that all the O₂-carrying complexes contain the metal in a relatively low oxidation state; since in hemocyanine the copper atoms are apparently in the +1(*d*¹⁰) state (160, 375), there seems to be no great significance in the number of *d* electrons in the metal. What is probably much more important is the ease with which electron transfer occurs from the metal to the O₂ ligand. In the reversible combination between O₂ and a complex of an oxidizable metal, there is the possibility of a redox reaction:



If a molecule is to be an efficient O₂ carrier, step 2 must be prevented. This is clearly the function of the globin in hemoglobin, though the way in which this is achieved is not clear; it has been suggested that the environment of low dielectric constant hinders the charge separation that is involved in the redox reaction (560). In the iridium derivative [Ir(Ph₃P)₂Cl(O₂)CO], the electron-acceptor properties of the carbonyl and phosphine systems presumably stabilize the lower state of iridium, and so make possible the reversible dissociation to O₂ and iridium(I), though the oxygenated complex has been described as containing iridium(III) (551). The redox step 2 is of great importance in the operation of the oxygenase enzymes; many of these contain transition metals, and may operate through the intermediate formation of unstable peroxy or oxygenated complexes (159, 340).

XXV. Summary and Conclusions

Several different types of peroxide have been described in this review. The solid hydrated peroxides of elements such as copper(II), praseodymium(III), or cerium(IV) may well contain O₂²⁻ ions (though there is no

crystallographic evidence to support this view); the only roughly stoichiometric peroxides of thorium and plutonium represent a slightly different class of compound, but may still be essentially ionic. The peroxides of transition metals either in complexes or in high oxidation states (or in both), however, contain peroxide linked to the metal by directed bonds, and are closely related to the oxygenated O_2 -carrying complexes. The characteristic and interesting properties of transition metal complexes are largely associated with compounds of the last two classes (see Table VI).

TABLE VI
DIFFERENT TYPES OF PEROXIDE FORMED BY THE TRANSITION ELEMENTS^a

Type	Elements forming peroxides of this type ^b
Solid, "ionic"	Sc, rare earths, Ti, Zr, Hf, ?Fe, ?Co, ?Ni, Cu
Solid, "non-stoichiometric"	Th, ?Pa, Np, Pu
Complex	Ce, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Co, ??Ni, ?Cu, ?Th, U, Pu
Oxygen-carrying systems	??Re, Fe, Co, Ir, ?Ni, Cu

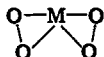
^a See Section XXIV.

^b Question mark means doubtful.

Most of the known transition metal peroxides have been obtained by the action of H_2O_2 on some derivative of the metal; in aqueous solution, the proportion of peroxide in the product increases with increasing pH, though this may not be true in solvents other than water. Peroxides of rhenium and cobalt, and of course the oxygenated O_2 -carrying species containing iron, iridium, or copper, have been made from O_2 instead of H_2O_2 ; there is evidence that peroxy derivatives of uranium have been obtained by heating compounds of uranium(VI) in air, while peroxides are often postulated as unstable intermediates in the oxidation by air of such species as chromium(II). Most peroxy compounds in which the metal is in a high oxidation state are unstable thermodynamically with respect to decomposition into O_2 and a metal oxide or derivative at room temperature; the formation of a peroxide from O_2 involves formal reduction of the oxygen, and it seems likely that reaction with O_2 to form a peroxide occurs either when lattice energies are favorable (as, presumably, with uranium), or when a low-oxidation state species is involved. In the latter case, though redox reactions frequently occur with formation of an oxidized metal derivative, electron transfer may be inhibited if the lower state of the metal is stabilized by other ligands; reversible dissociation may then lead to oxygen-carrying properties.

In all the peroxy complexes of transition metals whose structures have so far been described (save for the diamagnetic cobalt cation

$[(\text{H}_3\text{N})_5\text{Co}(\text{O}_2)\cdot\text{Co}(\text{NH}_3)_5]^{+4}$, D_{4h}^{1+} , details of whose structure are not yet available), the peroxy group is "laterally" coordinated to the metal, that is, with $\text{M}-\text{O}-\text{O}$ angles of the order of 90° or less. The arrangement shown below, with one $\text{O}-\text{M}-\text{O}$ angle close to 180° , is found in all the peroxides of chromium and tungsten whose structures are known:



Despite this, the peroxy group seems to behave as a monodentate ligand; it replaces single-atom groups such as O^{2-} , or would give the metal an improbable coordination number (7 for cobalt in P_a^1 , 8 for chromium in $[\text{Cr}(\text{O}_2)_4]^{-3}$) if regarded as a bidentate ligand. Similarly, in oxyhemoglobin the O_2 group replaces the monodentate water. The bonding in these "monodentate" systems has in some cases been described in terms of molecular orbital theory. In uranium complexes, there is a suggestion (not so far supported by X-ray evidence) that the peroxy group occupies two coordination positions, while the structure proposed for the oxygenated iridium complex $[(\text{Ph}_3\text{P})_2\text{Ir}(\text{O}_2)(\text{CO})\text{Cl}]$ also involves bidentate O_2 . It seems quite likely that the steric requirements for coordination around the uranyl ion are different from those in other transition metal complexes.

The values reported for the $\text{O}-\text{O}$ bond lengths in complex peroxides are collected in Table VII. Most of them do not differ significantly from

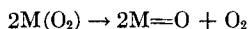
TABLE VII
VALUES FOR THE $\text{O}-\text{O}$ DISTANCES IN PEROXY COMPLEXES

Compound	$r(\text{O}-\text{O})$ (Å)	Reference
$\text{K}_2[\text{Cr}(\text{O}_2)_4]$	1.405 ± 0.039	(524)
	1.472 ± 0.025	(522a)
$\text{PyCr}(\text{O})(\text{O}_2)_2$	1.405 ± 0.02	(522)
$(\text{H}_3\text{N})_3\text{Cr}(\text{O}_2)_2$		
Orthorhombic	1.42 ± 0.03	(522b)
Monoclinic	1.31	(320)
	$1.2-1.4^a$	(522b)
$\text{K}_2[(\text{CN})_3\text{Cr}(\text{O}_2)_2]$	1.445 ± 0.016	(522c)
$\text{K}_2[(\text{O}_2)_2\text{W}(\text{O})\text{OW}(\text{O})(\text{O}_2)_2]\cdot 4\text{H}_2\text{O}$	1.50	(126)
$[(\text{H}_3\text{N})_5\text{Co}(\text{O}_2)\cdot\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$	1.45 ± 0.06	(549)

^a This range of values comes from a least-squares refinement of the experimental data from reference (320).

the 1.49 ± 0.04 of O_2^{2-} , though it is possible that in peroxychromium compounds $\text{O}-\text{O}$ distance may be a little less than this. This is consistent with the observation of infrared bands in the spectra of complex peroxides

at frequencies close to that assigned to the O—O stretching mode of H_2O_2 , though no significance should be attached to the small differences observed. Most peroxides in which no internal oxidation-reduction process is possible are thermodynamically unstable with respect to the reaction



mainly because of the high bond energy in O_2 itself. The Russian thermochemical work that undertakes to measure the hypothetical energy $E(\text{MO}=\text{O})$, and which finds it to be rather less than in H_2O_2 , should probably be reinterpreted in terms of a comparison between $E(\text{M}=\text{O})$ and $E[\text{M}=(\text{O}_2)]$, but there are many uncertainties involved. The evidence suggests that $E[\text{M}=(\text{O}_2)]$ is a little less than $E(\text{M}=\text{O})$.

As far as bonding in peroxy complexes is concerned, it is not clear what is the best way to describe the metal-peroxide interaction. Perhaps the simplest way is through a comparison of O_2^- and C_2H_4 as ligands.⁹ In the ethylene complexes, the olefin is usually considered as donating electrons from the π -bonding orbital to the metal, while the metal donates electrons from an appropriate, filled d orbital to the empty, antibonding π^* orbital of the olefin. In the peroxide ion, the π^* orbital is already filled, so that no back-bonding is possible. At the same time, there may be donation to the metal both from the π - and the π^* orbitals of the peroxy group, at least when the metal is in a high oxidation state. The effect of coordination on the O—O bond would then depend on the relative strengths of the two interactions—in other words, on whether donation was principally from π - or from π^* orbitals of the peroxy group (see Fig. 10).

For metals with many d electrons, this description is less satisfactory. At the same time, it is worth noting that the cation $[(\text{H}_3\text{N})_5\text{Co}(\text{O}_2)\cdot\text{Co}(\text{NH}_3)_5]^{+6}$ has a “ π -complex” structure; the reduced species $[(\text{H}_3\text{N})_5\text{Co}(\text{O}_2)\cdot\text{Co}(\text{NH}_3)_5]^{+4}$, on the other hand, in which the t_{2g} orbitals of the cobalt atoms are filled, has a structure for which the “ π -complex” description is clearly inappropriate.

As yet there are few generalizations that can usefully be made about the chemical properties of these compounds. The complicated relationships between the peroxides of individual elements are only beginning to be understood; it is to be hoped that as more information becomes available, something more like an over-all pattern will emerge.

Warning. Many peroxy complexes are thermodynamically unstable with respect to spontaneous decomposition at room temperature and may explode when touched or gently warmed, as we have found. The derivatives of Cr, Mo, and W are particularly treacherous, but great care should

⁹ An even closer comparison can be made of peroxide and acetylene as ligands.

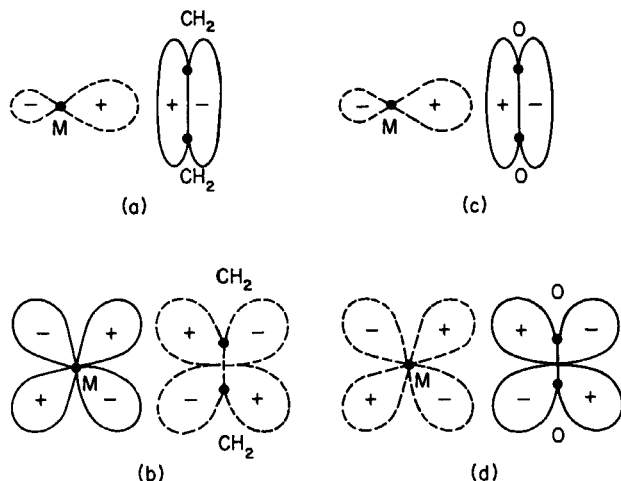


FIG. 10. Possible scheme for representing the interaction between a transition metal atom and ethylene or peroxide as ligands. (a) Donation to the metal from a π -bonding orbital of ethylene; (b) donation from the metal to a π -antibonding orbital of ethylene; (c) donation to the metal from a π -bonding orbital of peroxide; (d) donation to the metal from a π -antibonding orbital of peroxide. An orbital indicated by full lines contains an electron-pair; those indicated by broken lines are empty. For simplicity, the metal orbital interacting with the π -bonding ligand orbitals have been drawn as sp hybrids, although they will probably have d -character.

be taken when handling even very small amounts of any solid peroxy complex.

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THE DIRECT SYNTHESIS OF ORGANOSILICON COMPOUNDS

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I. Introduction

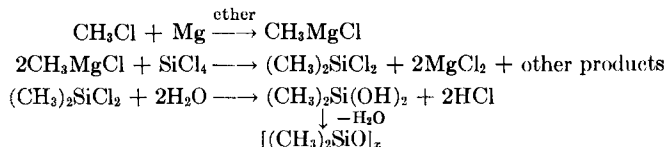
Reviewing forty years of work on organosilicon compounds (199), F. S. Kipping in 1937 thought the economic potentialities of these compounds to be slight; yet only a decade later an industry based on the organosiloxane (*silicone*) polymers had come into being. It is the purpose of this review to describe the methods for the synthesis of intermediates for this industry and their extension to organic derivatives of other elements.¹

The first methods for the preparation of organosilicon compounds utilized the halides. Elemental silicon (which is made by reduction of silica with carbon at 1500°) or ferrosilicon (35% Si) reacts readily with chlorine or chlorides; ferrosilicon and chlorine, for example, yield almost pure silicon tetrachloride at 500°, the intermediate polychlorosilanes formed being destroyed by their thermal instability and susceptibility to further chlorination at this temperature (39, 238). Hydrogen chloride reacts with silicon to yield a variety of products (SiCl_4 , SiHCl_3 , SiH_2Cl_2 , and higher chlorides); at 170–200°, 30% yields of polychlorosilanes are obtained (72, 126, 399). Halosilanes may be converted to organosilicon compounds by

¹ Other reviews of this subject have recently appeared in the Russian language (376) with 161 references and in Japanese (189) with 18 references.

several routes (see 33, 101), chief among which are: treatment with zinc, mercury, or aluminum alkyls; the action of an organic halide in the presence of a halogen acceptor such as zinc, sodium, or lithium; the action of organosodium or -lithium compounds; interaction with reactive methylene compounds; treatment with diazomethane; and the Grignard synthesis. Of these the last is probably the most flexible.

In Kipping's classic work the condensation of silanols (obtained by hydrolysis of organosilicon halides) was shown to lead to the formation of high molecular weight substances of empirical formula R_2SiO , named *silicones* because of the expectation that the reactions would lead to the silicon analogs of ketones. These substances were the prototypes of today's polysiloxane fluids, rubbers, and resins, and the term still persists; the interested reader will find information on history, production, and applications in a number of reviews (3, 18, 20, 28, 114, 118, 173, 224, 247, 249, 267, 294, 311, 334, 349, 354). The first plants for the production of silicones in the United States were based on the Grignard process, the essential reactions being:



Among the disadvantages inherent in this route were: (1) the need to handle large quantities of ether and of reagents highly sensitive to moisture, (2) interference in separation procedures by the magnesium salts which are precipitated, (3) its inapplicability to compounds containing functional groups which react with Grignard reagents, (4) the number of stages, (5) low efficiency, (6) dependence on silicon tetrachloride, which contains only 16% of silicon. Thus there arose an urgent need for a new synthesis of organosilicon compounds which could be applied to the large-scale production of silicone polymers; the outcome was E. G. Rochow's method, which forms the main subject of this article.

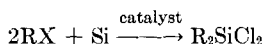
II. The Rochow Reaction

A. REACTION OF METHYL CHLORIDE WITH SILICON

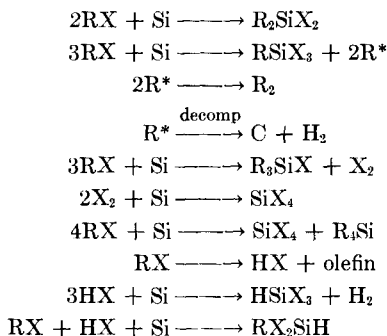
1. Products

The problem of the efficient large-scale production of compounds with silicon-carbon bonds was essentially solved by Rochow in 1940. The reaction, involving what is now known as the Direct Synthesis, was discovered

independently by Müller (264) in 1942 and by James (190) in 1944. A point of some interest is that Wöhler (72) and Combes (86) had narrowly missed making the discovery a century earlier.² Rochow's original paper (336), published at the end of World War II,³ describes the reaction of methyl chloride with elemental silicon in presence of copper metal as a catalyst at 285°. A flow system was used. In the over-all process, which is simple in concept but complex in its chemistry, the net changes may be represented by the equation



The process is, however, better represented by a series of parallel reactions, among which may be the following:



Reference is made in Section IV to the possible role of the catalyst. In practice, as with the classical methods mentioned previously, a mixture of products is always obtained. In the methyl chloride reaction under appropriate conditions the product consists of ca. 65% of dimethyldichlorosilane (b.p. 70.0°), 25% of methyltrichlorosilane (b.p. 65.7°), and 5% of trimethylchlorosilane (b.p. 57.3°). The remaining 5% is a complex mixture which includes silicon tetrachloride, trichlorosilane, methylchlorosilanes, tetramethylsilane, dimethylchlorosilane, and higher silanes. Table I lists almost thirty compounds isolated by various workers. Unfortunately the

² The technique of reaction of hydrogen chloride with silicon was well-known to both, even to the inclusion of copper powder. Rochow himself believes, "They *did* try it unsuccessfully; he himself spent over a year trying to get methyl chloride to react with silicon under the conditions of Wöhler and Combes, but to no avail. It is not as simple as that" (350).

³ The basic method has since been published and patented many times by various groups (24, 45, 56, 98, 111, 119, 123, 129, 153, 183, 184, 188, 265, 326, 337, 342, 353, 361, 472).

TABLE I
 SOME COMPOUNDS OF THE REACTION OF CH_3Cl WITH $\text{Si}-\text{Cu}$

Compound	B.P.	Reference
H_2	-252.8°	(254, 390, 397)
CH_4	-161.5°	(254, 390, 397)
C_2H_4	-104.9°	(397)
C_2H_6	-88.3°	(397)
HCl	-83.7°	(397)
CH_3Cl	-24.2°	(254, 390)
$\text{CH}_3\text{SiH}_2\text{Cl}$	8.0°	(397)
H_2SiCl_2	8.3°	(228b, 397)
$(\text{CH}_3)_4\text{Si}$	26.5°	(296, 297, 362, 363, 390, 397)
HSiCl_3	31.8°	(297, 390, 397)
$(\text{CH}_3)_2\text{SiHCl}$	36.0°	(296, 297)
$\text{CH}_3\text{SiHCl}_2$	41.0°	(228a, 297, 362, 363, 384, 385, 390, 397)
$(\text{CH}_3)_3\text{SiCl}$	57.3°	(336, 397)
CH_3CHCl_2	57.3°	(382)
$\text{ClCH}_2\text{CH}_2\text{Cl}$	57.4°	(384, 385)
SiCl_4	57.6°	(336, 382, 397)
2-Methylpentane	60.4°	(382)
3-Methylpentane	63.3°	(382)
CH_3SiCl_3	65.7°	(336, 397)
$(\text{CH}_3)_2\text{SiCl}_2$	70.0°	(336, 397)
$(\text{CH}_3)_2\text{HSiOSiH}(\text{CH}_3)_2$	70.5°	(258, 296)
$\text{CH}_3\text{C}_6\text{H}_{11}$	90.1°	(384, 385)
$(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$	100.5°	(258)
$(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_3$	113°	(258)
$\text{Cl}_3\text{SiSiCl}_2\text{CH}_3$	$134-135^\circ$	(258, 260)
$(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_2\text{Cl}$	$135.5-137^\circ$	(216, 258, 260)
$(\text{CH}_3)_2\text{ClSiSiCl}(\text{CH}_3)_2$	$146.5-148^\circ$	(219, 258, 260)
$\text{Cl}_3\text{SiSiCl}_3$	147.0°	(258, 260)
$\text{Cl}_2(\text{CH}_3)\text{SiSi}(\text{CH}_3)_2\text{Cl}$	$154.4-156.8^\circ$	(79, 216, 217, 219, 258, 260)
$\text{Cl}_2(\text{CH}_3)\text{SiSi}(\text{CH}_3)\text{Cl}_2$	$150-160^\circ$	(79, 217, 219, 260)
$\left. \begin{array}{l} [(\text{CH}_3)_n\text{SiCl}_{3-n}]_2 \\ [(\text{CH}_3)_n\text{SiCl}_{3-n}]_2\text{O} \\ [(\text{CH}_3)_n\text{SiCl}_{3-n}]_2\text{CH}_2 \end{array} \right\}$	$100-190^\circ$	$\left. \begin{array}{l} (79, 217, 219, 220a, 260) \\ (218, 219, 220a) \\ (218, 219, 220a) \end{array} \right\}$
Other inert hydrocarbons	—	(32, 385)
$\text{R}_n\text{SiCl}_{4-n} (\text{R} > \text{CH}_3)$	—	(32)
$(\text{CH}_3)_n\text{Cl}_{6-n}\text{Si}_2\text{O}$	—	(32)
$(\text{CH}_3)_n\text{Cl}_{6-n}\text{Si}_2$	—	(32, 258, 260)
$(\text{CH}_3)_n(\text{SiCH}_2\text{Si})\text{Cl}_{6-n}$	—	(32)
$(\text{CH}_3)_n(\text{SiCH}_2\text{CH}_2\text{Si})\text{Cl}_{6-n}$	—	(32)
$(\text{CH}_3)_n(\text{SiCH}_2\text{SiCH}_2\text{Si})\text{Cl}_{8-n}$	—	(32)
Higher silanes, siloxanes, and silcarbanes	—	(32)
$(\text{Cl}_3\text{Si})_2\text{CH}_2$	$178-84^\circ$	(293)

purity of the methyl chloride used is almost never stated and some of the minor constituents may arise from impurities.⁴

Many of the less volatile compounds listed in Table I have been isolated from stillpot residues collected from the continuous distillation of large quantities of product. The approximate composition of a typical residue after removal of dimethyldichlorosilane is shown in Table II.

TABLE II^a
HIGH-BOILING RESIDUES AFTER REMOVAL OF $(\text{CH}_3)_2\text{SiCl}_2$

$\text{R}_n\text{SiCl}_{4-n} (\text{R} > \text{CH}_3)$	27%	$(\text{CH}_3)_n\text{Si}_2\text{Cl}_{6-n}$	8.8%
$(\text{CH}_3)_n(\text{SiCH}_2\text{Si})\text{Cl}_{6-n}$	26.9%	$(\text{CH}_3)_n\text{Si}_2\text{OCl}_{6-n}$	6.1%
$(\text{CH}_3)_n(\text{SiCH}_2\text{CH}_2\text{Si})\text{Cl}_{6-n}$		$\text{Cl}_3\text{SiSiCl}_3$	4.4%
$(\text{CH}_3)_n(\text{SiCH}_2\text{SiCH}_2\text{Si})\text{Cl}_{6-n}$		$(\text{CH}_3)_n\text{SiCl}_{4-n}$	4.4%
Inert hydrocarbons	18.3%	Higher silanes, siloxanes, and silcarbanes	4.1%

^a Reference (32).

The high-boiling residues can be passed with (32) or without (260) hydrogen chloride over hot quartz, or heated with hydrogen chloride at high pressure to convert some of these by-products to simple methylchlorosilanes (400).

2. Laboratory Methods

The laboratory synthesis of methylchlorosilanes is described by Rochow in *Inorganic Syntheses* (348). Powdered silicon (60-mesh) is mixed with 10% by weight of finely divided metallic copper and suspended loosely on glass wool in a Pyrex tube held in a furnace. The reaction proceeds without a catalyst, but the second metal facilitates the process. An alternative preparation of the contact mass involves mixing the silicon with powdered copper chloride. When the reaction tube is heated, reduction of the copper salt occurs, silicon tetrachloride distills, and the silicon becomes coated with a highly reactive layer of copper. Additional variations on contact mass preparation are described in Subsection B.

For reactants which are gaseous at room temperature, it is convenient to carry the vapor through the system in a stream of inert gas. Liquid charges may be introduced with a large hypodermic syringe. Working on a laboratory scale, the usual arrangements are made for condensing the product and excluding moisture, and the temperature can be recorded with a protected thermocouple.⁵ A convenient working temperature is 300° with

⁴ Commercial methyl chloride may contain air, moisture, hydrogen chloride, and vinyl chloride.

⁵ For syntheses where poor yields are expected a recycling system may be preferred (176).

a methyl chloride flow rate of ca. 7 gm/hr. The reaction is exothermic and, once started, will maintain itself with less heat than is needed for its initiation. In spite of the closeness of the boiling points of the methylchlorosilanes, they may be separated with an efficient distillation assembly where high reflux rates can be maintained.

B. REACTION CONDITIONS

One of the main conditions for the satisfactory operation of the Direct Synthesis is that the temperature be kept as low as possible. About 1000 BTU is evolved per pound of methyl chlorosilanes produced and this must be dissipated as far as possible. At higher temperatures pyrolysis of organic radicals may occur to form hydrocarbons or hydrogen and carbon soot. The latter accumulates on the surface of the contact mass and lowers its activity. Worse still, the pyrolysis reaction is autocatalytic and the presence of carbon causes further decomposition of the organic groups with further decrease in the over-all ratio of organic groups to chlorine per silicon atom in the product. It is clearly desirable to maintain a temperature close to the minimum for effective reaction. The threshold temperature varies with the organic halide and appears to depend on the strength of the carbon-halogen linkage in any homologous series.

1. Contact Mass

Lowering the reaction temperature is one of the functions of the catalyst. Commercial silicon is mainly reported as reacting with methyl chloride only above 400°, though a reaction at 300° has recently been observed for pure methyl chloride and chemically purified silicon (0.07% Al, <0.01% Mg, Ca, and Ti) giving dimethyldichlorosilane in 90% yield (192), but activation of this silicon may have occurred during leaching with aqueous hydrogen halides and aqua regia. Methyl chloride itself begins to pyrolyze at 400° (459). There is clearly some uncertainty about the exact conditions for the reaction of *pure* silicon with methyl chloride but, in presence of copper, a reaction occurs at as low as 285°. Threshold and operating temperatures, as well as yields of the various products, depend on the method used to incorporate the catalyst in the contact mass,⁶ and the effectiveness of various catalyst preparations has been reported in detail (1b, 10, 44, 45, 47, 63, 90, 94a, 108, 119, 128a, 148, 160, 184, 266, 303, 331, 391a, 392a, 423a, 424, 425a, 439a, 447a,b, 449).

a. Preparation of Contact Mass. In Rochow's original paper (336) he reported three methods for the preparation of silicon-copper contact masses, which are still those preferred (113). These are:

⁶ For example, the preparation is important in the production of Si—H compounds (14, 145, 146, 263, 427).

(i) Fusion of copper and silicon in a reducing medium to form an alloy. Rapid cooling prevents segregation of the copper. The material may be either used as lumps or ground to a powder (131).

(ii) Heating a mixture of silicon and copper chloride powders packed loosely in a reaction tube at above 265°. Silicon tetrachloride distills leaving an active silicon-copper contact mass. The powders may also be pressed into pellets and fired (57).

(iii) Sintering a mixture of finely divided silicon and copper powders in a quartz tube in a stream of hydrogen at just below the melting point of copper (1050°C) (46, 47, 302). An ideal particle size is said to be 74–105 μ for silicon (131) and <44 μ for copper (132). Copper shavings or chips may be used to loosen the mass and provide better surface contact (9).

b. *Addition of Active Metals as Hydrogen Chloride Acceptors.* This often leads to a higher yield of the more highly alkylated silane (CH₃)₃SiCl from the methyl chloride reaction (176). Thus 2–25% aluminum metal incorporated in a 9:1(w/w) contact mass and sintered in hydrogen at 1000° increases the yield of (CH₃)₃SiCl from the usual 3–5% to 10–20% (55, 393, 394). Aluminum can be fused with a copper-silicon in a graphite crucible near the eutectic temperature (800–1100°) (231, 473). Surprisingly, as little as 0.05–0.01% of aluminum is said to increase the yield of more highly alkylated products (106, 176, 231). Other metals such as zinc (110, 369) or magnesium (110, 171) can also be used.

c. *Addition of a Metal Halide.* This results in enhanced reactivity with lower threshold temperatures, but there is a corresponding increase in the proportion of more highly halogenated products. For example, ferric chloride (284, 285, 287), aluminum chloride (232a, 284, 391), tin(II) chloride (172, 284), tin(IV) chloride (284), sodium chloride (391), zinc chloride (61, 441), cobalt chloride (102), zirconium chloride (289), hexachlorozirconates (289), metal fluorides (419), or mixtures of these (285) have all been claimed to increase the proportion of methyltrichlorosilane from the methyl chloride reaction.

d. *Oxide Catalysts.* Porous yet mechanically strong contact masses with high surface area and quick reactivity with alkyl halides result when various metal salts are combined with powdered silicon and the mixtures sintered in hydrogen at high temperatures (303). Cupric hydroxide (464, 465) and ammonium formate (295) have been used in this way, while the use of cupric nitrate, acetate, or formate is said to plate the silicon with copper after heating to 900° in a closed vessel (326, 330, 450). Because of its ready availability, ferrosilicon often finds application in the Direct Synthesis (9, 102, 142, 147, 326, 367). It is less satisfactory, however, and prior leaching of the contact mass with acid is sometimes used to remove part of the iron (248). Elements of Group V are claimed to activate mixtures of silicon

and copper powders (89, 90, 91, 196, 286, 288), but these elements are known to react with methyl chloride and their use would be expected to complicate further the list of products. The claim that metal oxides act catalytically, or that air-dried or "aged" silicon-copper is effective is curious in light of the probability that oxide films on silicon have to be broken before reaction with halides can take place. Nevertheless, the usefulness of compounds such as cuprous or cupric oxide has been asserted (360), as has that of aluminum oxide (170). It has been shown by X-ray diffraction that copper normally has a coating of Cu_2O (185).

e. Other Metal Catalysts. The same metal catalyst need not be effective for all organic halides and, indeed, it is found that silver is the best catalyst for the reaction of chlorobenzene with silicon (2, 359). Fifty per cent copper-silicon is also effective (359). Cobalt, nickel, zinc (91, 424), tin (172), and lead (207) have all been proposed. Alloys of pure silicon and copper are also found to be less effective than those containing the usual commercial impurities (Fe, Al, Ca, Ti, etc.) (441), and lead, antimony, bismuth (143), and copper sulfate are said to poison the catalyst. It would be of interest to know the effect of arsenic on the reactivity of silicon here as a test of the correlation between chemical and semiconductor activity.

Much effort has been devoted to finding a good catalyst for the difficult reaction of vinyl chloride in the Direct Synthesis. The original preparation (174) involved the use of copper (54, 175) but magnesium (422) and tin, formed by the reduction of stannous chloride (422), have also been suggested. More recently a careful study of the efficiency of various contact masses for this particular reaction has shown the superiority of 20% nickel-silicon alloys (404).

f. Use of Fillers. Fillers in the inert contact mass often have a favorable effect on the over-all yield of alkylated chlorosilanes (113). Twenty per cent of powdered glass (23) or, better, of Raschig rings (300) has been used, while silica, sodium silicate (440), or hydrolyzed tetraethoxysilane (36) acts as a binding agent and improves the mechanical strength of the pelleted contact mass. Such additions would be expected to give a more favorable distribution of the heat of reaction and reduce the extent of pyrolysis of organic groups.

2. Gaseous Diluents

a. Inert Gases. Addition of an inert gas to the organic halide reduces local overheating in the contact mass and so leads to less of the undesirable pyrolytic reactions (22). For example, in the reaction of methyl chloride with a 9:1(w/w) silicon-copper at 300° with nitrogen dilution, $\text{MeCl}:\text{N}_2$:2:5(v/v), the yield of dimethyldichlorosilane was reported as 86.5%. There were smaller amounts than usual of methyltrichlorosilane,

silicon tetrachloride, trichlorosilane, and other components containing silicon-hydrogen bonds, which result from pyrolysis (49, 416).

b. Addition of Hydrogen. This provides not only a diluent but also another reactant and leads to an increase in the amount of compounds with silicon-hydrogen bonds. For example, use of an equimolar mixture of hydrogen and methyl chloride at 390° increases the yield of methyldichlorosilane from 1% to 15–17% (49, 50, 417, 418). Hydrogen under pressure in static systems has a similar effect (451, 458). A possible mechanism is discussed later (see Section IV).

c. Chlorine Addition. Addition of chlorine to the organic halide would be expected to increase the amount of chlorosilanes in the product, but it also produces an extremely high activity in the contact mass. Thus a 5–35% admixture of chlorine with methyl chloride has been found to give a sevenfold increase in the total amount of product with shorter reaction times (177). A mixture of chlorine and hydrogen used with methyl chloride gives methyltrichlorosilane as the major product (ca. 70%) (292). The addition of chlorine to either methyl or ethyl chloride can also result in *in situ* formation of difunctional organic chlorides, and the organochlorosilanes expected from these reactants are found in the products (215, 293). The yield of low-boiling chlorosilanes is said to be raised, however (55, 163).

d. Hydrogen Chloride. The use of hydrogen chloride as a diluent leads to more highly chlorinated products, but the yield of silicon tetrachloride increases markedly if more than an equimolar mixture of hydrogen chloride is employed (29, 30, 31, 228a, 282, 346). Methyltrichlorosilane has also been used as an activator (145a).

C. SEPARATION OF PRODUCTS

When methyl chloride is used in the Direct Synthesis the separation of the products becomes a major problem as may be seen from the boiling points of products shown in Table I. The complexity of the problem is increased by the formation of both binary and ternary azeotropic mixtures, the most difficult of which is that formed between silicon tetrachloride and trimethylchlorosilane (b.p. 54.5°) (381, 382, 385). In addition to the construction of high efficiency distillation outfits which take into account the chemical nature of the substances being separated (e.g., their inflammability and violent reaction with moisture to produce polymeric materials and hydrogen chloride in high enough local concentration to corrode most metals), a number of physical and chemical techniques have been developed for breaking the azeotropes formed between the various components (261).

The separation of the gaseous by-products of the methyl chloride reaction is relatively easy. Unreacted methyl chloride may be recovered by

passing the exit gases over activated charcoal (474) or sandy chalk (290). Dimethyldichlorosilane and methyltrichlorosilane fortunately form no azeotropes and may be separated by efficient fractionation (26, 66, 78, 124, 225, 235). After the separation of this intermediate fraction, the problem of removing trimethylchlorosilane (b.p. 57.3°) from the low-boiling liquids must be considered. Five compounds reported as present in the product of a commercial synthesis boil in the range 57.4–63.2°. Table III lists the binary azeotropes which are known to form.

TABLE III
AZEOTROPES FOUND IN THE RANGE 57.4–63.2°

Azeotropic mixture	B.P.
SiCl ₄ , 64.8%; (CH ₃) ₃ SiCl, 35.2%	54.7°
(CH ₃) ₃ SiCl, 70%; 2-methylpentane, 30%	56.4°
(CH ₃) ₃ SiCl, 75%; 3-methylpentane, 25%	57.3°
SiCl ₄ , 63.5%; 1,1-dichloroethane, 36.5%	53.0°

This separation may be handled by the addition of a second azeotroping agent (381, 384). The following are examples:

	B.P. of azeotrope
Acetonitrile (b.p. 82°) + 92.6% (CH ₃) ₃ SiCl + 90.6% SiCl ₄	56° 49°
Acrylonitrile (b.p. 79°) + 93% (CH ₃) ₃ SiCl + 89% SiCl ₄	57° 51.2°
1,1-Dichloroethane (b.p. 57.4°) + 36.5% SiCl ₄	56.0°
Nitromethane (b.p. 101.0°) + 46.2% SiCl ₄	94.0°
Chloroform (b.p. 61.3°) + 44.0% SiCl ₄	70.0°

In addition, various chemical methods of overcoming the difficulties in the separation processes arising from the formation of azeotropes have been suggested. These include the addition of a complexing agent (179a, 281, 452) and esterification followed by regeneration (e.g. 52, 60, 64, 71, 107, 128, 150, 182, 186, 221, 232, 251a, 270, 279, 304, 304a, 377, 379, 392, 402, 460). Much of the difficulty is avoided if the conditions of synthesis are regulated so that no silicon tetrachloride is produced, then trimethylchlorosilane can be separated in a single distillation. The entire separation process may in any case be monitored by gas chromatography. Benzophenone (469) and nitrobenzene (447b) have been recommended for the stationary phase.

D. INDUSTRIAL REACTION TECHNIQUES

A number of special techniques have been proposed for the Direct Synthesis (65, 97a, 109, 110, 169, 181, 245, 278, 332, 419a, 426, 441a). Thus

for example, the use of a fluidized bed of silicon and copper powders provides a high surface area and assures an even temperature distribution. Higher pressures of methyl chloride may also be used (7, 8, 21, 43, 51, 56, 106a, 144, 227, 228, 251, 262, 333, 395, 420, 439, 442, 475). Alternatively silicon-copper powders can be suspended in paraffin oil or polysiloxanes, or in the organic reactant if the latter is a liquid such as chlorobenzene (42). Suspension in fused metal chlorides (e.g., LiCl-KCl, NaCl-AlCl₃) has also been suggested (388). No attempt will be made here to discuss in detail the more technical aspects of the processes (see ref. 36a).

III. Extension of the Direct Synthesis Reaction

A. APPLICATION OF THE DIRECT SYNTHESIS TO OTHER ELEMENTS

1. Carbon

The analog of the Direct Synthesis reaction for carbon is not known. Reaction of alkyl halides with K-graphite is entirely that expected from a potassium dispersion (140).

2. Germanium

Rochow first studied the reaction between organic halides and germanium. Methyl chloride reacts with the pure element only at temperatures in excess of 400°,⁷ but the inclusion of a copper catalyst leads to reaction at 340° (338, 339, 341). Yields of 50–55% of dimethyldichlorogermane based on the Ge taken have been obtained (389), though no trimethylchlorogermane was found (327). At 550° the mono- and dimethyl compounds are formed in equal amounts (310). The copper-catalyzed reaction of ethyl chloride at 356° gave a condensate containing diethyldichlorogermane (347), though this conclusion has been questioned (310). The analogous reaction with *n*-propyl chloride gave *n*-propyltrichlorogermane at 310–330° (357). Chlorobenzene has also been used to prepare diphenyldichlorogermane (309, 343). Allyl chloride and 2-methylallyl chloride react to give the corresponding unsaturated alkyltrichlorogermanes, but no reaction was observed with vinyl chloride (310). A full description of the methyl chloride reaction can be found in reference (389).

3. Tin

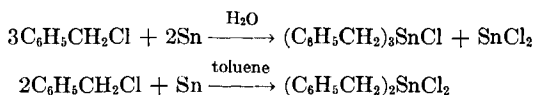
The preparation of organotin halides by Direct Synthesis has been known for over 100 years (117). Early workers heated alkyl halides with tin in sealed tubes at 130–180° for long periods (74, 76, 77, 103, 151a, 197,

⁷ Germanium reacts with chlorine at 130° (93) and so is more reactive in this way than silicon.

226). Later Rochow showed that dimethyltin dichloride could be prepared in over 50% yield by passing methyl chloride (1 gm/hr) through molten tin at 300–350° (352, 364, 410, 457). Stannous oxide was said to inhibit the synthesis of dimethyltin dichloride by producing dimethyltin which then absorbs methyl chloride to form trimethyltin chloride (364, 410). This is curious in the light of recent investigation of the reaction of methyl chloride with stannous oxide to give dimethyltin dichloride in good yield (15).

Ethyl bromide reacts with an alloy of tin, sodium, and zinc to give tetraethyltin (155, 444). This is analogous to the industrial synthesis of tetraethyllead. The standard method for obtaining alkyltin halides is, however, the reaction of alkyl halides (preferably iodides) *in situ* with tin foil and magnesium in the presence of a trace of the corresponding alcohol. Tin halides substituted with the following groups have been obtained in this way: methyl (182, 239, 243), ethyl (239), *n*-propyl (222, 241), isopropyl (241), *n*-butyl (239, 240, 244), isobutyl (241), *sec*-butyl (241), isoamyl (241), *n*-hexyl (242), cyclohexyl (241), 2-ethylcyclohexyl (241), *n*-octyl (241), *n*-decyl (241), *n*-dodecyl (241, 242), allyl (445), *n*-C₁₈H₁₇ (242), crotyl (242), and methyl vinyl carbonyl (242). A mixture of methyl and ethyl iodides gives mixed methylethyltin iodides (241). Other catalysts, such as mercuric acetate (222) or tetrahydrofuran (242, 243), are also effective. The yield of organotin halide decreases with increasing size of the alkyl group because of dehydrohalogenation of the alkyl halide (443, but see 137, 226).

A novel synthesis of di- and tribenzyltin chlorides has been reported by Japanese workers (406). Benzyl chloride reacts with tin powder in a rapidly stirred slurry in water or toluene according to the following equations (407):



In the toluene reaction a trace of water (407), tertiary amine (408), mercuric chloride (408), or dibutyl ether (156, 157) is needed, while metals are effective catalysts for the water reaction (94, 202). Methyl-substituted benzyl chlorides (406), allyl bromide (408), methylvinylcarbinyl bromide (408), crotyl bromide (408), and α -chloromethyl naphthylene (158) can also be used, but only the Wurtz condensation takes place with diphenylchloromethane, phenylmethylchloromethane, or benzal chloride (409). The synthesis does not work for silicon or arsenic (407) but does proceed in a variety of solvents (469a).

The application of the fluidized bed technique to the original synthesis

is possible if Cu_3Sn or $\text{Cu}_{31}\text{Sn}_8$ is used: both are solid at the reaction temperature (68, 411, 456). Use of γ -ray irradiation allows the synthesis of alkyltin bromides and iodides to proceed at room temperature. Neither ultraviolet radiation nor γ -rays promote reaction of alkyl chlorides below 30° (1, 1a).

4. Lead

Neither lead nor thallium reacts directly with organic halides as far as is known (356). (The commercially important synthesis of tetraethyllead from ethyl chloride and a lead-sodium alloy will not be considered here.) Direct reaction can, however, be brought about if the metals are formed *in situ* in the presence of the organic reagent, and dimethyllead diiodide (135) and trimethylthallium (134) have been synthesized by this route.

5. Other Elements

Phenylboron dibromide can be made by the action of bromine and benzene on boron dispersed with a nickel catalyst on kieselguhr (120), but the reaction probably proceeds through the intermediate formation of boron tribromide, which is found in the product. Repeated attempts to bring about reaction between methyl chloride and boron itself have failed (253).

Methyl chloride reacts with aluminum to form mono- and dimethyl-aluminum chlorides in good yield (73, 75, 125, 133, 150, 154, 165, 328, 454, 470). The method has been applied to the synthesis of methyl and ethyl aluminum chlorides, bromides and iodides, *n*-propyl and isoamyl aluminum iodides, octyl aluminum bromide, phenyl and *p*-tolyl aluminum iodides, and naphthyl aluminum bromides (229, 414). Butyl bromide also reacts with an Al—Mg alloy in ether at 70 – 100° to give $\text{Bu}_3\text{Al}\cdot 2\text{Et}_2\text{O}$ (127).

Trialkylaluminum and dialkylaluminum hydrides may also be made by the reaction of olefins and hydrogen with a clean aluminum surface, produced by grinding the metal under nitrogen (84, 471). Dehydrohalogenation reactions are always a possibility in synthesis with such active metals (88). Organohalogen compounds of other active metals such as zinc (115), cadmium (456), mercury (116, 246), and tellurium (92, 236, 447) can also be obtained by direct synthesis (70).

Although the fifth group elements have been recommended as catalysts or promoters in the Direct Synthesis of organosilanes (89, 223, 286, 288), it is only recently that the reaction of alkyl halides with these elements has been at all fully studied. Methyl chloride reacts with an 80-20 phosphorus-copper mixture to form CH_3PCl_2 in 95% yield, together with $(\text{CH}_3)_2\text{PCl}_2$. Methyl and ethyl bromides also react (233). White phosphorus gives derivatives with *m*-tolyl bromide, bromobenzene, benzyl chloride, and *n*-octyl bromide (324).

Methyl bromide and chloride also react with arsenic and antimony at 350–370° using a copper catalyst. The methyl iodide reaction begins at 280°, but yields are poor, while vinyl halides react at 450–475°. Silver is a better catalyst for the bromobenzene reaction. Bismuth does not react with methyl chloride, though it does with methyl bromide. The methyl bismuth halide undergoes extensive decomposition at the reaction temperature. For the Group V elements in general, yields are better with methyl bromide than with methyl chloride (234).

B. DETAILED CONSIDERATION OF DIRECT SYNTHESIS REACTIONS

The greater part of the foregoing description of the use of Direct Synthesis in preparing organohalides has dealt with the use of the simpler aliphatic halides and especially methyl chloride which, in the case of silicon, is the most important from the point of view of large-scale production. Much has been done with other halides, however, and also with other types of organic compounds; this is reviewed in the following pages.

1. *Aliphatic Halides*

The Direct Synthesis of organosilicon compounds has been examined with a considerable range of aliphatics. As was mentioned in Rochow's original paper (336), methylbromosilanes may be made by this route using silicon-copper, and several of the minor products have also been identified (130, 428, 432). Rochow suggested that methyl fluoride and iodide reacted similarly (229, 336, 337, 361), but methylfluoro- and methyliodosilanes were not actually isolated. Reinvestigation of the reaction of methyl iodide failed to reveal the formation of methyliodosilanes at 280–350° with copper or silver as the catalyst (194). These compounds may indeed be thermally unstable at the reaction temperature and their isolation might depend on rapid removal from the hot zone.

Reaction with ethyl chloride is very similar to that with methyl chloride and a variety of products has been isolated (5, 11, 25, 35, 89, 163, 198, 221a, 248, 336, 440a). The reaction with ethyl bromide has also been studied (196, 213, 214, 435, 436). Saturated aliphatic chlorides or bromides with up to five carbon atoms have been used in the Direct Synthesis (100, 104, 200, 236, 276, 277, 315, 322, 436), but there is a tendency for the higher alkyl bromides to decompose at the temperature of the synthesis. β -Chloropropionitrile and β -chlorovaleronitrile have also been studied and give the corresponding trichlorosilanes in 20% yield. The cyanide function does not seem to be affected (315). It is also curious that chloroacetonitrile remains unchanged when passed over silicon-copper at 450°, while 1-chloropropylene oxide reacts to give 1-trichlorosilylpropylene oxide. Ring rupture causes polymerization, however, and the pure compound could not be isolated

(372). 3-Chloropropyl methyl ether does not react at 450° (376). In general there is a decrease in yield of alkylchlorosilanes with the size of the alkyl group and a corresponding increase in the amount of olefins found in the product, probably due to hydrogen halide abstraction under the reaction conditions. Acetyl chloride does not react with silicon-copper (105).

2. Aromatic Halides

Rochow and Gilliam first described the reaction of chlorobenzene with silicon containing a silver or copper oxide catalyst (229a, 230, 335, 359). It gave a mixture of products which included

	B.P.
PhSiCl ₃	201.5° (152°/20 mm)
Ph ₂ SiCl ₂	305.2°
Ph ₃ SiCl	378.0°
PhSiHCl ₂	184°
SiCl ₄	57.6°
Ph—Ph	130°/10 mm
Ph—H	80.1°

The reaction requires a temperature about 100° higher than that for alkyl chlorides: without a catalyst it occurs at 530° and with silver or copper oxide the threshold is at 380° with an optimum at 400–420°. With bromobenzene, the composition of the condensate is: Ph₂SiBr₂, 28%; PhSiBr₃, 42%; SiBr₄, 13%. It is claimed that Ph₂SiBr₂ becomes the main product when a 1:1 copper-silicon alloy is used (429, 432). The yield of phenylchlorosilanes is raised by the addition of hydrogen and that of diphenyl is reduced (423). As in the case of the alkyl halide, reaction promoters (e.g., NaCl with Ag or AlCl₃ with Al) may be added to the contact mass (12, 68, 106, 391, 425). As would be expected, addition of hydrogen chloride gives more phenyltrichlorosilanes (346).

The reactions of polycyclic aromatic halides have been little investigated. α -Chloronaphthalene reacts at 500° with a contact mass which contains copper and silver oxide to give C₁₀H₇SiCl₃. This material is reported, however, to consist of a mixture of α - and β -naphthyltrichlorosilanes (378). 2-Chloropyridine has also been used to produce bis(2-pyridyl)-dichlorosilane (40, 67).

3. Unsaturated Hydrocarbons

The first report of the preparation of alkylenechlorosilanes (174) emphasized the difficulties that arise in this particular type of synthesis. The chlorine atom in vinyl chloride, which is attached to one of the doubly bonded carbon atoms, is known to be relatively unreactive compared with

that in alkyl chlorides. In fact, the vinyl halides show a reduced reactivity in the Direct Synthesis rather like that found in chlorobenzene, where reaction takes place only at higher temperatures and with low efficiency. In allyl chloride, on the other hand, chlorine is attached to the carbon atom adjacent to the double bond and reactivity is enhanced. Compounds with the halogen further removed from the double bond lose this special reactivity.

Allyl chloride reacts with silicon-copper at 250°. Reaction is highly exothermic and this may lead to pyrolysis of the starting material unless the heat is dissipated. Special reactions have been designed (109) and both dilution with an inert gas and the use of a filler in the contact mass have been employed (178, 181, 211). With a contact mass containing 10% of copper, the condensate contains some 40% of low-boiling products (e.g. SiCl_4 and SiHCl_3) and the remainder is a mixture of allylchlorosilane from which the following have been isolated

	B.P.
$\text{CH}_2=\text{CHCH}_2\text{SiHCl}_2$	97°
$\text{CH}_2=\text{CHCH}_2\text{SiCl}_3$	117.5°
$(\text{CH}_2=\text{CHCH}_2)_2\text{SiCl}_2$	82–84°/50 mm

Only insignificant quantities of difunctional allylchlorosilanes are produced (175) and there are no saturated products (54). Reaction with methyl-substituted allyl chlorides seems to be similar in all respects (259, 313).

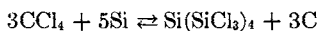
In contrast to the above, vinyl chloride reacts only sluggishly: comparatively high temperatures are necessary and yields are low. At least ten products have been isolated (13, 43, 53, 404). With a contact mass containing 20% of copper operating at 350–400°, $\text{CH}_2=\text{CHSiCl}_3$ is formed in 20% yield with 9% of $(\text{CH}_2=\text{CH})_2\text{SiCl}_2$ (402). Other variants are the use of an alloy with 24% of tin, which is said to favor the production of $\text{CH}_2=\text{CHSiHCl}_2$ (422), and more recently the use of alloys of silicon with nickel. This has been shown to be effective in retarding the pyrolysis of vinyl chloride and in promoting the formation of divinylchlorosilanes. Even so, the best yields of the latter are 10% (402, 402a).

The reaction of 1,3-dichlorobutene-2, a compound with both vinyl and allylic chlorine, resulted in a mixture of (3-chlorobutene-2)trichlorosilane with some $\text{Cl}_3\text{SiCH}_2\text{CH}=\text{C}(\text{CH}_3)\text{SiCl}_3$ (373). The allylic chlorine appears to react preferentially and, to a major extent at least, to the exclusion of the vinyl chlorine. Chloroprene polymerized at 420–450° over Si—Cu even when diluted with nitrogen, and no compounds with carbon-silicon bonds were identified (370). No attempt has yet been made to investigate the synthesis of γ - and δ -alkenyl halosilanes.

4. Polyfunctional Organic Halides

The use of reactants with more than one site for reaction is an obvious extension of the Direct Synthesis that has been fairly widely explored. It opens the possibility of synthesizing new types of organosilicon compounds with one or more carbon atoms interposed between two silicon atoms. The reactivity of methylene chloride, the simplest of the difunctional chlorides, was examined soon after the discovery of the methyl chloride reaction. The copper-catalyzed reaction sets in at about 300° and was studied with nitrogen dilution of the gas stream. The products are shown in Table IV, together with the products from CH_3CHCl_2 at 300° (281, 314) and $(\text{CH}_3)_2\text{CCl}_2$ at 280° (281, 314). Recycling was used to improve yields. 1,1-Dichloro-2-methylpropane, $(\text{CH}_3)_2\text{CHCHCl}_2$, is converted to $(\text{CH}_3)_2\text{C}=\text{CHCl}$ under the conditions of the Direct Synthesis and the products are those expected from this substituted vinyl chloride (314). *Sym*-dichloroethylene (either *cis* or *trans*) was inert even at 500°C (257a).

The products from chloroform (300°) and carbon tetrachloride are also given in Table IV. An early publication reported that no silicon-carbon bonds resulted from the uncatalyzed reaction of carbon tetrachloride with silicon at 300°: hexachlorodisilane and tetrachloroethylene were said to be the only products (38). Later work (48, 306, 359) showed the formation of SiCl_4 in high yield and 1% of tetrachloroethylene. Carbon was deposited (403). This confused situation has been resolved to some extent by careful reinvestigation of the reaction with nitrogen as a diluent (268, 269). A range of interesting compounds was identified (Table IV). The yield of bis(trichlorosilyl)acetylene increased with temperature while that of *sym*-bis(trichlorosilyl)dichloroethylene decreased. There was clear evidence for the existence of the equilibrium



The reaction of various other tetrachlorides with a sintered silicon-copper alloy has also been examined and the order of decreasing ease of exchange established is: $\text{CCl}_4 > \text{SnCl}_4 > \text{GeCl}_4 > \text{SiCl}_4$ (203, 204). Titanium tetrachloride was found not to react.

The products from a range of additional dichloro compounds shown in Table IV will not be commented on in detail. The conditions of the synthesis lead to dehydrohalogenation of 1,2-dichloroalkanes, and the products from substituted vinyl chloride are observed (314). The reaction of 1,4-dichlorobutane is of special interest because of the formation of the two cyclic compounds shown (281, 323). Reference has been made to the

TABLE IV
 PRODUCTS FROM POLYFUNCTIONAL ORGANIC CHLORIDES WITH Si

Organic chloride	Products	Reference
CH_2Cl_2		
at 300°	HSiCl_3	(19, 121, 164)
at 350°	SiCl_4	(19, 121, 164)
at 400°	CH_3SiCl_3	(121, 122)
	$(\text{CH}_3)_2\text{SiCl}_2$	(121, 122)
	$(\text{Cl}_3\text{Si})_2\text{CH}_2$	(121, 122, 430)
	$\text{Cl}_3\text{SiCH}_2\text{SiHCl}_2$	(122, 307, 434a)
	$\text{Cl}_2\text{HSiCH}_2\text{SiHCl}_2$	(431, 434a)
	$(\text{Cl}_2\text{SiCH}_2)_3$	(122, 307, 434, 434a)
	$(\text{Cl}_2\text{SiCH}_2)_n$	(122, 307)
	$\text{Cl}_3\text{SiCH}_2\text{SiCl}_2\text{CH}_2\text{SiCl}_3$	(121)
	$(\text{Cl}_2\text{HSi})_2\text{CH}_2$	(430, 431, 433, 434)
	Unsaturated hydrocarbons	(430, 431, 433, 434)
CH_3CHCl_2		
at 300°	SiCl_4	(281, 316)
	$\text{H}_2\text{C}=\text{CHSiHCl}_2$ (6.4%)	(281, 316)
	$\text{H}_2\text{C}=\text{CHSiCl}_3$ (16%)	(281, 316)
	$\text{Cl}_3\text{HSiCH}(\text{CH}_3)\text{SiHCl}_2$ (6.5%)	(281, 316)
	$\text{Cl}_2\text{HSiCH}(\text{CH}_3)\text{SiCl}_3$ (18.5%)	(281, 316)
	$(\text{Cl}_3\text{Si})_2\text{CHCH}_3$ (18.5%)	(281, 316)
$(\text{CH}_3)_2\text{CCl}_2$		
at 280°	SiCl_4	(281, 316)
	$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{SiHCl}_2$ (7.6%)	(281, 316)
	$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{SiCl}_3$ (10.1%)	(281, 316)
	$(\text{Cl}_3\text{Si})_2\text{C}(\text{CH}_3)_2$ (8.5%)	(281, 316)
	$(\text{Cl}_2\text{HSi})_2\text{C}(\text{CH}_3)_2$ (14%)	(281, 316)
	$\text{Cl}_2\text{HSiC}(\text{CH}_3)_2\text{SiCl}_3$ (11.5%)	(281, 316)
CHCl_3		
at 300°	C_2Cl_4	(272)
	HSiCl_3	(272)
	SiCl_4	(272)
	Si_2Cl_6	(272)
	$(\text{Cl}_3\text{Si})_3\text{CH}$	(272)
	$\text{Cl}_3\text{SiCH}(\text{SiHCl}_2)_2$	(272)
	$(\text{Cl}_3\text{Si})_2\text{CHSiHCl}_2$	(272)
	$(\text{Cl}_3\text{Si})_2\text{CH}_2$	(272)
	$\text{Cl}_3\text{SiCH}_2\text{SiHCl}_2$	(272)
CCl_4		
at $260\text{--}300^\circ$	SiCl_4	(48, 305, 306, 359)
at $210^\circ, 310^\circ, 410^\circ$	$\text{Cl}_2\text{C}=\text{CCl}_2$	(38, 48, 305, 306)
	Carbon	(403)
	Si_2Cl_6	(38)
	$(\text{Cl}_3\text{Si})_4\text{C}$	(268, 269)
	$(\text{Cl}_3\text{Si})_4\text{Si}$	(268, 269)

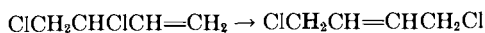
TABLE IV (Continued)

Organic chloride	Products	Reference
	$(\text{Cl}_2\text{C}=\text{CCl})_4\text{Si}$	(268, 269)
	$\text{Cl}_3\text{SiCCl}=\text{CCl}_2$	(268, 269)
	$\text{Cl}_2\text{SiCCl}=\text{CClSiCl}_3$	(268, 269)
	$\text{Cl}_3\text{SiC}\equiv\text{CSiCl}_3$	(268, 269)
	$(\text{Cl}_3\text{Si})_2\text{C}=\text{C}(\text{SiCl}_3)_2$	(268, 269)
Other tetrachlorides		
	SiCl_4	(203, 204)
$\text{ClCH}_2\text{CH}_2\text{Cl}$ at 370–380°	HSiCl_3	(305)
	SiCl_4	(305)
	$\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{SiCl}_3$	(305, 434a)
$\text{ClCH}_2\text{CHClCH}_3$ at 300°	HSiCl_3 (24.6%)	(281, 314)
	SiCl_4 (21.7%)	(281, 314)
	$\text{CH}_2=\text{CHCH}_2\text{SiCl}_3$ (7.2%)	(281, 314)
	$\text{Cl}_3\text{SiCH}_2\text{CH}(\text{CH}_3)\text{SiHCl}_2$ (23%)	(281, 314)
	$\text{Cl}_3\text{SiCH}_2\text{CH}(\text{CH}_3)\text{SiCl}_3$ (14%)	(281, 314)
$\text{ClCH}_2\text{CCl}(\text{CH}_3)_2$ at 300°	HSiCl_3 (8.7%)	(281, 314)
	SiCl_4 (36%)	(281, 314)
	$(\text{CH}_3)_2\text{C}=\text{CHCl}$ (6.8%)	(281, 314)
	$\text{Cl}_3\text{SiCH}_2\text{C}(\text{CH}_3)_2=\text{CH}_2$ (14.7%)	(281, 314)
$\text{Cl}(\text{CH}_2)_4\text{Cl}$ at 300°	HSiCl_3	(104, 281, 323)
	SiCl_4	(104, 281, 323)
	$\text{ClCH}_2\text{CH}_2\text{CH}=\text{CH}_2$	(281, 323)
	$\text{Cl}_3\text{Si}(\text{CH}_2)_4\text{SiCl}_3$ (6.1%)	(281, 323)
	$\text{Cl}_3\text{Si}(\text{CH}_2)_4\text{SiHCl}_2$ (5.7%)	(281, 323)
	$\text{Cl}_2\text{HSiCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ (5%)	(281, 323)
	CH_2-CH_2	
	SiCl_2 (30%)	(281, 323)
	$ \begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{Cl}_2\text{Si} \quad \text{SiCl}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}_2 \end{array} $	(104)
$\text{CH}_2=\text{CCl}_2$ at 450°	$\text{H}_2\text{C}=\text{C}(\text{SiCl}_3)_2$	(314)
$\text{CH}_2=\text{CClCH}_2\text{Cl}$ at 275–290°	$\text{H}_2\text{C}=\text{C}(\text{SiCl}_3)_2$	(281, 317, 319)
	$\text{H}_2\text{C}=\text{C}(\text{SiCl}_3)\text{SiHCl}_2$	(281, 317, 319)
	$\text{H}_2\text{C}=\text{C}(\text{Cl})\text{CH}_2\text{SiCl}_3$	(281, 317, 319)

TABLE IV (Continued)

Organic chloride	Products	Reference
ClCH=CHCH ₂ Cl at 370-380°	H ₂ C=C(CH ₃)SiCl ₃	(281, 317, 319)
	H ₂ C=CHCH ₂ SiCl ₃	(281, 317, 319)
	HSiCl ₃	(281, 317, 319)
	SiCl ₄	(281, 317, 319)
	H ₂ C=CHCH ₂ SiCl ₃	(281, 317, 319)
H ₂ C=CHCH(Cl)CH ₂ Cl at 330°	CH ₃ CH=CHSiCl ₃	(281, 317, 319)
	ClCH ₂ CH=CHCH ₂ Cl	(281, 312)
	Cl ₃ SiCH ₂ CH=CHCH ₂ SiCl ₃	(281, 312)
	CH—CH ₂	
	SiCl ₂ (15.6%)	(281, 312)
ClCH ₂ CH=C(Cl)CH ₃ at 250°	CH—CH ₂	
	at 275-290°	
	Cl ₂ HSiCH ₂ CH=C(Cl)CH ₃ (6%)	(281, 373)
	Cl ₃ SiCH ₂ CH=C(Cl)CH ₃ (9%)	(281, 373)
	Cl ₃ SiCH ₂ CH=C(SiCl ₃)CH ₃ (5.5%)	(281, 373)
(ClCH ₂) ₂ C=CH ₂ at 275-290°	Cl ₃ SiCH ₂ CH=C(SiHCl ₂)CH ₃ (3%)	(281, 373)
	HSiCl ₃	(281, 373)
	SiCl ₄	(281, 373)
	HSiCl ₃ (9.5%)	(281, 314)
	SiCl ₄ (11.3%)	(281, 314)
ClCH ₂ CH=CHCH ₂ Cl	(Cl ₃ SiCH ₂) ₂ C=CH ₂ (7.5%)	(281, 314)
	Cl ₃ SiCH ₂ C(CH ₃)=CH ₂ (11.5%)	(281, 314)
	Cl ₂ HSiCH ₂ C(CH ₃)=CH ₂	(281, 314)
	HSiCl ₃ (10%)	(281, 314)
	SiCl ₄ (16.7%)	(281, 314)
ClCH ₂ CH=CHCH ₂ Cl	Si ₂ Cl ₆ (6%)	(281, 314)
	Cl ₃ SiCH ₂ CH=CHCHSiCl ₃ (7.3%)	(281, 314)
	Cl ₂ Si(CH ₂ CH=CHCH ₂ Cl) (6%)	(281, 314)

behavior of compounds with chlorine atoms belonging to an allylic and a vinylic system. With 1,2-dichlorobutene-3, where both allylic and aliphatic chlorines are present, the reaction conditions are such that the allylic rearrangement occurs:



The 1,4-dichlorobutene-2 thus formed reacts at 300° to give 15.6% of the unsaturated silacyclopentene and 9% of the linear Cl₃SiCH₂CH=CHCH₂-SiCl₃ (311, 373).

5. Reactants Containing Silicon

The use of organosilicon compounds in the Direct Synthesis opens up a number of interesting possibilities. With the series of α -, β -, and γ -chloroalkyltrichlorosilanes the following possibilities are evident:

- (a) Reaction to produce the normal product, i.e., replacement of the alkyl chlorine by a trichlorosilane group.
- (b) Dehalogenation to give a dimer of the starting material.
- (c) Dehydrohalogenation and the formation of alkenyltrichlorosilanes and hydrogen chloride.
- (d) Reaction of hydrogen chloride produced in (c) to form SiHCl_3 .
- (e) Reaction of SiHCl_3 produced in (d) with the olefin from (c) to give a variety of products.
- (f) Rearrangement of the starting material under the conditions of the synthesis.

It is not surprising, therefore, that the products of reactions of this type are complex, as is evident from Table V.

Reasonable yields of the "normal product," where two or more trichlorosilyl groups have been introduced into the alkyl chain, are obtained with α - and β -chlorosubstituted alkylchlorosilanes. Even here, however, many of the possible side reactions mentioned above actually take place and the yields nowhere exceed 50%. Lengthening the alkyl chain increases the yield of compounds formed as a result of dehydrochlorination. In the case of γ -chloroalkyltrichlorosilanes, dehydrochlorination becomes the predominant reaction, and these compounds react more readily with silicon-copper, perhaps because of the activating effect of the hydrogen chloride which is constantly being produced.

Many of the compounds isolated would be difficult to obtain by other means. In addition, with use of ferrosilicon in place of silicon-copper, the reaction provides a good route to alkenylchlorosilanes. For example, β -chloroethyltrichlorosilane reacts with ferrosilicon at 400° in a nitrogen stream to give vinyltrichlorosilane in over 40% yield, along with some $\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{SiCl}_3$, formed in all probability by addition of HSiCl_3 to $\text{CH}_2=\text{CHSiCl}_3$. The use of α -, β -, and γ -chloropropyltrichlorosilanes is reported to result only in dehydrochlorination with ferrosilicon at 400 – 500° . It would be interesting in all cases to know the effect of heating with copper metal alone.

6. Perfluoroalkyl Halides

Reaction of CF_3Cl , $\text{C}_2\text{F}_5\text{Cl}$, and $\text{C}_4\text{F}_7\text{Cl}$ with silicon-copper at 500 – 1000° gave only F_3SiCl and F_2SiCl_2 : there was a marked increase in weight

TABLE V
 DIRECT SYNTHESIS WITH SI-CONTAINING STARTING MATERIALS

Type	Halide	%	Products	References
α	$\text{Cl}_3\text{SiCH}_2\text{Cl}$ 300–400°	2	SiCl_4	(317, 319, 371)
		10	MeSiCl_3	(317, 319, 371)
		30	Starting material	(317, 319, 371)
		30	Normal product	(317, 319, 371)
		8, 5	$\text{Cl}_2\text{Si}(\text{CH}_2\text{SiCl}_3)_2$	(317, 319, 371)
		—	HSiCl_3	(274)
α	$\text{Cl}_2\text{MeSiCH}_2\text{Cl}$ 360–370°	—	$\text{CH}_2=\text{CHSiCl}_3$	(274)
		2	SiCl_4	(317, 319, 371)
		21	Me_2SiCl_2	(317, 319, 371)
		17	Starting material	(317, 319, 371)
		28.7	Normal product	(317, 319, 371)
		16.7	$\text{Cl}_2\text{Si}(\text{CH}_2\text{SiMeCl}_2)_2$	(317, 319, 371)
α	$\text{Cl}_3\text{SiCH}(\text{Me})\text{Cl}$ 360–70°	3.3	SiCl_4	(317, 319, 371)
		28.3	EtSiCl_3	(317, 319, 371)
		—	$\text{CH}_2=\text{CHSiCl}_3$	(317, 319, 371)
		5	Starting material	(317, 319, 371)
		25	Normal product	(317, 319, 371)
		5	$\text{Cl}_3\text{SiCH}(\text{Me})\text{SiHCl}_2$	(317, 319, 371)
		8.3	$[\text{Cl}_3\text{SiCH}(\text{Me})]_2$	(317, 319, 371)
		6.6	$\text{Cl}_2\text{Si}(\text{CH}(\text{Me})\text{SiCl}_3)_2$	(317, 319, 371)
		—	HSiCl_3	(273)
		39.5	$\text{CH}_2=\text{CHSiCl}_3$	(372)
	400°	—	HCl	(271)
	(Fe—Si)	—	MeSiCl_3	(271)
	300–	—	C_2H_4	(271)
	500°	—	$\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{SiCl}_3$	(271)
	(Fe—Si)	—	$\text{Cl}_2\text{Si}(\text{CH}_2\text{CH}_2\text{SiCl}_3)_2$	(271)
		—	$(\text{Cl}_3\text{SiCH}_2\text{CH}_2)_2$	(271)
α	$\text{EtCl}_2\text{SiCH}(\text{Me})\text{Cl}$ 370–380°	1	SiCl_4	(374)
		8	$\text{CH}_2=\text{CHSiCl}_3$	(374)
		10	$\text{ClH}_2=\text{CHSiCl}_2\text{Et}$	(374)
		5	EtSiCl_3	(374)
		15	Et_2SiCl_2	(374)
		11	Normal product	(374)
		7.5	$\text{EtCl}_2\text{SiCH}(\text{Me})\text{SiHCl}_2$	(374)
		7.5	$[\text{EtCl}_2\text{SiCH}(\text{Me})]_2\text{SiCl}_2$	(374)
α -di	$\text{Cl}_3\text{SiCHCl}_2$ 360–370°	41	$\text{SiCl}_4 + \text{MeSiCl}_3 + \text{ClCH}_2\text{SiCl}_3$	(317, 319)
		22.4	$\text{ClH}_2(\text{SiCl}_3)_2$	(317, 319)
		13	Normal product	(317, 319)
α -di	$\text{Cl}_2\text{MeSiCHCl}_2$ 360–370°	49	SiCl_4	(317, 319)
		25.6	MeSiCl_3	(317, 319)
		4.2	Starting material	(317, 319)
		14	Normal product	(317, 319)
		10.5	$\text{Cl}_2\text{MeSiCH}_2\text{SiCl}_3$	(317, 319)
di- α -di	$(\text{Cl}_3\text{Si})_2\text{CCl}_2^a$ 360–370°	18.2	SiCl_4	(270c, 317, 319)
		—	Si_2Cl_6	(270c)
		—	$(\text{Cl}_3\text{Si})_3\text{CH}$	(270c)
		—	$(\text{Cl}_3\text{Si})_3\text{CCl}$	(270c)
		—	$(\text{Cl}_3\text{Si})_4\text{C}$	(270c)
		11.4	$(\text{Cl}_3\text{Si})_2\text{C}=\text{C}(\text{SiCl}_3)_2$	(269, 317, 319)
		—	$(\text{Cl}_3\text{Si})_2\text{C}=\text{C}=\text{C}(\text{SiCl}_3)_2$	(269, 270c)

TABLE V (Continued)

Type	Halide	%	Products	References
di- α	(Cl ₃ Si) ₂ CHCl 360–370°	6.3 16.7 29.8 10.4	SiCl ₄ CH ₂ (SiCl ₃) ₂ Normal product [(Cl ₃ Si) ₂ CH] ₂	(317, 319) (317, 319) (317, 319) (317, 319)
tri- α	(Cl ₃ Si) ₃ CCl 400°/5mm		SiCl ₄ (Cl ₃ Si) ₃ CH (Cl ₃ Si) ₄ C	(270c) (270c) (270b)
				(270c)
β	Cl ₃ SiCH ₂ CH ₂ Cl 370–400°	Trace 3 8.3 5 43.3 3.3 10 3.3	HSiCl ₃ SiCl ₄ EtSiCl ₃ CH ₂ =CHSiCl ₃ Normal product Cl ₃ SiCH ₂ CH ₂ SiHCl ₂ SiCl ₂ [CH ₂ CH ₂ SiCl ₃] ₂ Starting material	(371) (317, 319) (317, 319) (317, 319) (317, 319) (317, 319) (317, 319)
	(Fe—Si) 400°	42.2	CH ₂ =CHSiCl ₃	(273)
	(Fe—Si) 300–500°	—	MeSiCl ₃	(271)
		—	C ₂ H ₄	(271)
		—	(Cl ₃ SiCH ₂ CH ₂) ₂	(271)
β	(Fe—Si) 100 hr Cl ₂ MeSiCH ₂ CH ₂ Cl	78.5	Cl ₃ SiCH=CH ₂	(275)
	(Fe—Si) 450°	47.6	CH ₂ =CHSiMeCl ₂	(273)
β	Cl ₂ MeSiCH(Me)CH ₂ Cl	— 3.2 5.2 58	HSiCl ₃ + SiCl ₄ + MeSiHCl ₂ + MeSiCl ₃ Normal product Cl ₂ MeSiCH(Me)CH ₂ SiHCl ₂ Cl ₂ MeSi(C ₂ H ₅) isomers	(320) (320) (320) (320)
β	Cl ₃ SiCH ₂ CH(Me)Cl (Fe—Si) 150°	— 7.6 89	No normal product Cl ₃ SiCH=CH·CH ₃ Cl ₃ SiCH ₂ CH=CH ₂ Cl ₃ SiCH ₂ CH ₂ CH ₃	(274) (275) (275) (275)
β	Cl ₃ SiCH ₂ CH(CH ₂ CH ₃)Cl (Fe—Si) 145°	— — 35.5 7.3	Cl ₃ SiCH ₂ CH=CHCH ₃ No normal product Starting material Residue	(274) (274) (274) (274)
β	Cl ₃ FtSiCH ₂ CH ₂ Cl 370–380°	1 5 6 10 17 13 6 5 37	SiCl ₄ EtSiCl ₃ Et ₂ SiCl ₂ CH ₂ =CHSiCl ₃ CH ₂ =CHSiEtCl ₂ Normal product Cl ₂ EtSiCH ₂ CH ₂ SiHCl ₂ Cl ₂ Si[Cl ₂ EtSiCH ₂ CH ₂] ₂ Losses and unresolved mixtures	(374) (374) (374) (374) (374) (374) (374) (374) (374)
β -di	Cl ₃ SiCH ₂ CHCl ₂ 360–370°	37 9.1	HSiCl ₃ + SiCl ₄ + CH ₂ =CHSiCl ₃ Cl ₃ SiCH=CHCl	(317, 319) (317, 319)

TABLE V (Continued)

Type	Halide	%	Products	References
α -tri	Cl_3SiCl_3 210–220°	2.7	$\text{Cl}_3\text{SiC}(\text{Cl})=\text{CCl}_2$	(269)
	$\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$ (Fe—Si) 400–450°	—	HSiCl_3	(274)
		—	SiCl_4	(274)
		—	$\text{Cl}_3\text{SiCH}_2\text{CH}=\text{CH}_2$	(274)
		—	$\text{Cl}_3\text{SiCH}=\text{CHCH}_3$	(274)
		—	No normal product	(274)
		—	Residue	(274)
	$\text{Cl}_2\text{MeSiCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ 370–380°	—	$\text{SiCl}_4 + \text{MeSiHCl}_2 + \text{MeSiCl}_3$	(320)
		—	Dimer	(321)
		23.5	$\left\{ \begin{array}{l} \text{MeCl}_3\text{SiCH}_2\text{CH}=\text{CH}_2 \\ \text{MeCl}_3\text{SiCH}=\text{CHCH}_3 \end{array} \right.$	(321) (321)
		14.1	Normal product	(321)
		7.1	$\text{MeCl}_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SiHCl}_2$	(321)
		3.5	$[\text{MeCl}_2\text{Si}(\text{CH}_3)_2]_2\text{SiCl}_2$	(321)
	$\text{Cl}_2\text{EtSiCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ 370–380°	5.8	EtSiCl_3	(321)
		25.9	$\left\{ \begin{array}{l} \text{Cl}_2\text{EtSiCH}_2\text{CH}=\text{CH}_2 \\ \text{Cl}_2\text{EtSiCH}=\text{CHCH}_3 \end{array} \right.$	(321) (321)
		17	Normal product	(321)
		14.4	$\text{Cl}_2\text{EtSiCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiHCl}_2$	(321)
	$\text{Cl}_2\text{MeSiCH}_2\text{CH}(\text{Me})\text{CH}_2\text{CH}_2\text{Cl}$	1	HSiCl_3	(320)
		7.6	MeSiHCl_2	(321)
	270–280°	5.6	SiCl_4	(321)
	370–380°	6	MeSiCl_3	(321)
	470–480°	58	$\text{MeCl}_2\text{Si}(\text{C}_4\text{H}_7)$ isomers	(321)
		5.2	$\text{MeCl}_2\text{SiCH}_2\text{CH}(\text{Me})\text{CH}_2\text{SiHCl}_2$	(321)
		3.2	Normal product	(321)
	$\text{Cl}_2\text{EtSiCH}_2\text{CH}(\text{Me})\text{CH}_2\text{CH}_2\text{Cl}$	3.3	HSiCl_3	(320)
		1.2	SiCl_4	(320)
		12	EtSiCl_3	(320)
		49.4	$\text{EtCl}_2\text{Si}(\text{C}_4\text{H}_9)$ isomers	(320)
	370–380°	10	Normal product	(321)
		9.1	$\text{Cl}_2\text{EtSiCH}_2\text{CH}(\text{Me})\text{CH}_2\text{SiHCl}_2$	(321)
	$\text{Cl}_3\text{SiCH}(\text{Cl})\text{CH}_2\text{CH}_3$ (Fe—Si) 170°	0.6	$\text{SiCl}_4 + \text{SiHCl}_3$	(274)
		54.5	$\left\{ \begin{array}{l} \text{Cl}_3\text{SiCH}=\text{CHCH}_3 \\ \text{Cl}_3\text{SiCH}_2\text{CH}=\text{CH}_2 \end{array} \right.$	(274) (274)
		22	Starting product	(274)
		10.2	Residue	(274)
	$\text{Cl}_3\text{Si}(\text{CH}_2)_4\text{Cl}$	92	Crotyl trichlorosilane	(275)

* This starting material rearranges over copper metal alone to form SiCl_4 , $\text{Cl}_3\text{SiC}\equiv\text{CSiCl}_3$, $(\text{Cl}_3\text{Si})_2\text{C}=\text{C}(\text{SiCl}_3)_2$, and $(\text{Cl}_3\text{Si})_2\text{C}=\text{C}=\text{C}(\text{SiCl}_3)_2$ (270c).

of the contact mass, attributed to the formation of carbon (190). Later, however, patents were filed (257, 301) claiming the production of CF_3SiF_3 from the reaction of CF_3Br with a silicon-copper contact mass at 400°. With more rapid flow, $\text{CF}_3\text{SiF}_2\text{Br}$ was also said to be formed (405). These reactions, if confirmed, would be of considerable interest; it is now known that chlorotrifluoroethylene and *unsym*-trichlorotrifluoroethane react with a

moving bed of Si—Cu to form compounds containing silicon-carbon linkages (270a), and the field is one which could be extended considerably.

C. REACTION OF ETHERS

The large-scale direct preparation of organoalkoxysilanes by Direct Synthesis with ethers would be an attractive route to the production of silicones, since the alkoxy groups are readily hydrolyzed but without the formation of troublesome hydrogen chloride and much more controllably than with chlorosilanes. This question was examined some time ago (62, 345, 368) and the conclusion reached that ethers required the admixture of hydrogen halide or an alkyl halide if they were to react with catalyzed silicon. Reaction under such conditions could be explained in terms of a splitting of the ether and subsequent normal reactions of the alkyl halide. It was later claimed that ethers did react without any addition (463), but a reinvestigation of the problem (476, 477) has shown that no C—Si bonds are produced up to temperatures at which the ether pyrolyzes.

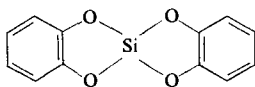
D. REACTION OF ALCOHOLS AND PHENOLS

Rochow (340) investigated the reaction of methanol with silicon-copper at 250° and obtained fair yields of tetramethyloxysilane, together with hydrogen. Analogous reactions have been observed with ethanol (51, 59, 345, 352) and phenol (210, 476, 477), and magnesium and calcium silicides have also been used (58, 152, 415).

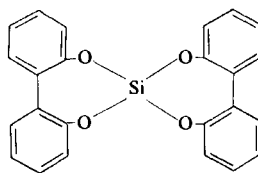
The analogous reactions with methyl mercaptan and thiophenol lead to formation of silicon sulfides in the contact mass. Extraction of the contact mass with benzene, in which the silicon sulfides are insoluble, gave material containing silicon, and it is highly probable that it resulted from thermal breakdown of the desired products (478, 479).

1. Reaction with Difunctional Alcohols and Phenols

These reactions may be studied in an autoclave with a high pressure of hydrogen, using silicon-copper formed by sintering the powders in hydrogen. Catechol reacts under such conditions at 265° to form an almost quantitative yield of the compound I, which can be sublimed from the contact mass *in vacuo* at 236°:



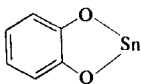
(I)



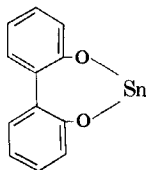
(II)

Reaction with 2,2'-dihydroxydiphenyl occurs at 230° to yield compound II. The usefulness of other polyfunctional aromatic hydroxy compounds in the Direct Synthesis is limited by their thermal stability. An interesting exception to this generalization is β -naphthol which, although thermally stable in the required temperature range, does not react with silicon-copper as phenol does (478, 479). Aliphatic diols (e.g., ethylene glycol) are also thermally unstable at temperatures where they might otherwise be useful in the Direct Synthesis.⁸

Catechol reacts smoothly at 150° with a mixture of tin and copper powders to give a good yield of *o*-phenylenedioxytin(II) (compound III). 2,2'-Dihydroxydiphenyl gives compound IV and hydrogen.⁹



(III)



(IV)

The reaction of catechol with a mixture of lead and copper powders appears to result in a reaction analogous to the above; the product decomposes, however, to lead oxide and benzene on attempted sublimation (478, 480).

IV. Reaction Mechanisms

The Direct Synthesis has, to a very large extent, been studied with the object of preparing new and useful compounds, and it is probably reasonable to question if some of the claims made in the patent literature, which has been extensively quoted in the earlier sections, are in fact scientifically accurate. The whole subject is, indeed, confused when considered from the point of view of possible reaction mechanisms. Nevertheless remarkable progress has been made in elucidating some of the steps by which the simpler reactions proceed.

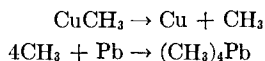
Hurd and Rochow (179) were the first to offer an explanation of the peculiar activity of copper in facilitating the reaction of methyl chloride

⁸ In light of the above, it is curious to find it reported that aromatic silicon ortho esters decompose under heat and hydrogen pressures to give phenol and elementary silicon (94). Not only phenol but methyl phenyl ether (which undergoes hydrogenolysis in the presence of finely divided metals to give phenol) produces tetraphenoxysilane from silicon under high hydrogen pressures (476, 477).

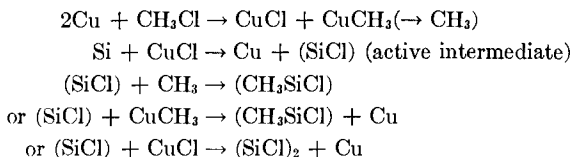
⁹ These compounds can also be obtained in analogous reaction of stannous oxide (481).

with silicon. They found that if a crystal of silicon was imbedded in copper and heated to 350° in a stream of methyl chloride, both silicon and copper were removed from the point at which they were in contact or in close proximity. When copper was heated alone at 250° in a stream of methyl chloride, its surface became coated with a film of copper(I) chloride but, simultaneously, copper metal was transported and deposited downstream. The reaction $2\text{Cu} + \text{CH}_3\text{Cl} \rightarrow \text{CuCH}_3 + \text{CuCl}$ was proposed, the carry-over of copper being attributed to the breakdown of methyl copper, to liberate the metal and free methyl radicals (87, 136).

This view was supported by a further experiment in which a lead mirror was deposited downstream from a small quantity of finely divided copper at 250°. When methyl chloride was passed the lead mirror gradually disappeared, as it is known to do when attacked by free methyl radicals:



Hurd and Rochow also established that pure silicon was not attacked at 250–400° by free methyl radicals formed by the pyrolysis of tetramethyllead, nor were SiCl_4 and Si_2Cl_6 .¹⁰ The reaction scheme proposed as being consistent with these observations is given below.



These reactions would then continue to give the observed mixture of methylchlorosilanes. The chief function of the metal catalyst is to make the halogen of the organic halide readily available for reaction with the silicon. It also makes the organic group more available by transporting and effectively prolonging the life of the radicals in the form of the metal alkyl. The copper also probably catalyzes the dehydrohalogenation of the alkyl halides (4).

The authors suggest that a similar mechanism may be operative when other metals replace copper. For example, in the synthesis of phenylchlorosilanes from chlorobenzene with a silver catalyst (359), silver chloride is readily reduced by silicon at the temperature employed and chlorobenzene is known to react with silver at 400° to give AgCl (138, 139, 179). The silver is thus able to produce the active intermediate SiCl and also phenyl radicals. It seems reasonable to suppose that other metals could also act in this

¹⁰ The possibility of methyl copper acting on silicon halides in the manner of a Grignard reagent as had been proposed (16, 17) was also ruled out.

way, though it would be very useful, and probably not difficult, to provide additional experimental evidence in support of this view.

An alternative mechanism proposed by Klebanskii and Fikhtengol'ts (200) and independently by Trambouze (437) rejects Hurd and Rochow's multistage radical scheme in favor of a mechanism involving changes in the Si-Cu system.

X-ray studies have shown the formation of a new Si-Cu intermetallic phase during the reaction of methyl chloride with the contact mass¹¹ (6, 167, 180, 209, 413, 438). The new intermetallic phase is depleted as the synthesis continues¹² (Cu lines become stronger). It is postulated that alkyl halides are chemisorbed onto the intermetallic compound and that, as a result, the C-Cl bond is deformed and polarized by the ionic charges in the lattice. This surface phenomenon is said to lower the stability of the C-Cl bond and facilitate transfer of groups to silicon. It is pointed out that reaction of cuprous chloride with silicon occurs only above 260°, while the Direct Synthesis may proceed at temperatures as low as 115°. ¹³ The transfer of chlorine from copper to silicon must, therefore, take place at the surface of the intermetallic lattice.

Some support for this viewpoint may come from the relationship between the ease of reaction of alkyl halides with Si-Cu and their dipole moments (Table VI).

TABLE VI
DIPOLE MOMENTS AND INITIAL REACTION TEMPERATURES OF ALKYL HALIDES^a

Halide	Reaction temperature	Dipole moment (D)
MeCl	290°	1.92
EtCl	195°	2.05
<i>i</i> -PrCl	115°	2.15
<i>t</i> -BuCl	122°	2.13

^a Reference (200).

The same sort of relationship is exhibited by methyl chloride, chlorobenzene, and vinyl chloride or by methyl chloride, allyl chloride, and 2,4-dichlorobutene-2. An explanation in these terms is not particularly

¹¹ Germanium forms similar compounds with copper (280).

¹² The kinetics for the decomposition of this phase with ethyl chloride have been studied, but the rate is closely dependent on the presence of structural imperfections in the alloy (193, 194, 210, 220, 228b).

¹³ The reaction of silicon with copper(I) chloride is exothermic and autocatalytic (205). It is doubtful that 115° represents an initiation temperature and so would be quite possible to achieve, once the initial passivity of the silicon is overcome.

convincing as one would expect the C—Cl bond energy to be a more significant parameter for such comparisons. It should also be pointed out that the temperature of initial reaction is itself a rather ill-defined criterion since it certainly depends on the extent to which the solid surface is covered with an oxide film. A kinetic study of the oxidation of silicon at high temperatures shows the process to be severely diffusion-controlled by the layer of vitreous oxide (69). Just as aluminum is much more susceptible to attack by chlorine and chlorides than by oxygen or oxidizing agents despite the high heat of formation of alumina, so silicon is much more readily attacked by halogens and halides. Such attack probably involves a mechanism much more drastic than diffusion of the halide through the oxide film, reaction with silicon, and outward diffusion of products. These reactions take place at a rate so high as to suggest breaching of the oxide film. In this connection it is interesting to note that silicon itself, when freshly pulverized in presence of the reactant, has an abnormally high reactivity and will react both with chlorine (208) and with carbon tetrachloride (149) at room temperature.¹⁴

Other work has helped to clarify the situation. Thus the reaction of *n*-propyl chloride with germanium copper at 310–330° provides evidence for the need of some kind of transport agent (357). *n*-Propyl chloride undergoes rearrangement to the isopropyl isomer at 280°, yet the reaction product is *n*-propyltrichlorogermane. It is also known that silicon subchlorides (161, 358) react with methyl chloride at 300° to give the same distribution of products as with elementary silicon (159, 291). Partially chlorinated silicon atoms on the surface of a silicon crystal are also known to retain the halogen very tenaciously, even in a stream of hydrogen. For example, an organic ether, which is normally unreactive to Si—Cu, reacts readily with a silicon-copper contact mass previously treated with hydrogen chloride at 500° and subsequently flushed for long periods with hydrogen at the same temperature. Organochlorosilanes are produced and reaction continues as long as the chlorine lasts (476, 477). Copper metal is transported in flow systems during reaction, and some copper may even be found in the product (166, 206); but although red deposits are observed in the pyrolysis of ethers over silicon-copper, no reaction with silicon takes place presumably because of the absence of an active silicon intermediate (476, 477). The inhibiting effect of nitric oxide on the Direct Synthesis has also been studied (396) and is found to rise sharply with temperature. This may be interpreted as meaning that it reacts preferentially with methyl radicals in the gas

¹⁴ Apparently these are examples of the mechanochemical Russell effect observed when crystals are cleaved to give fresh surfaces (211). The method is also effective with aluminum (207a).

phase but that, at elevated temperatures, those participating directly in the synthesis are affected.¹⁵

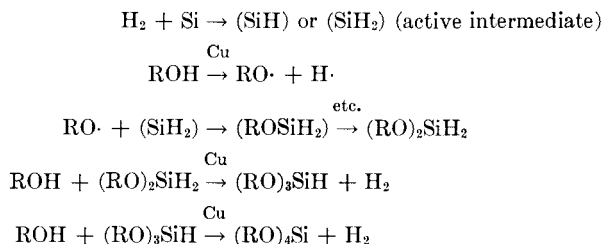
The above evidence is in no sense conclusively in favor of one or another of the views put forward on the reaction mechanism of the Direct Synthesis, though the elegant experiments made by Hurd and Rochow seem, on the whole, to provide the most satisfying basis for discussion (4, 17, 34, 37, 143a, 201, 298, 358, 365, 366, 398, 446). The engaging possibility that the active intermediate these workers describe is actually the silicon analog of dichlorocarbene cannot be ruled out. In addition the novel proposal has been put forward that the process is one of electrochemical corrosion of silicon with cathodic control (and thanks to the small thickness of the layer of adsorbed organic electrolyte and its high resistance—ohmic control as well), based on experiments with pure silicon in a heated electrolytic cell (298, 448). Unfortunately this suggestion has not been further pursued (299). The fact that the Direct Synthesis may be operated with alcohols and phenols calls for further discussion, since the Hurd and Rochow mechanism is not necessarily valid and there is no clear evidence of the part played by the copper catalyst.

One simple mechanism for the reaction of alcohols and phenols would be to regard them as reacting in the same way as an acid with a metal, hydrogen being set free and the carbon-oxygen bond remaining intact. Indeed, the action of alcohols on active metals is a case in point (412). Another lead comes from the observation that, during sintering of a silicon-copper contact mass in hydrogen over long periods, some copper is transported in the gas stream. It is known that unstable volatile copper hydride may form under such conditions (453). Silicon is also known to exhibit an abnormal volatility in hydrogen at high temperatures, which is thought to be associated with the formation of an unstable volatile silicon subhydride (27, 40, 386). Examination of the infrared spectrum of silicon powder that has been heated in hydrogen at 1000° shows a sharp peak at 2178 cm^{-1} , close to the Si—H stretching frequency at 2187 cm^{-1} observed with monosilane.¹⁶ These observations indicate that reaction of both silicon and copper with hydrogen to form a reactive intermediate may be significant in the synthesis (478, 479). The reaction of methanol with monosilane, which is strongly catalyzed by metallic copper, yields tetramethoxysilane and hydrogen and shows an increase in rate after the introduction of the

¹⁵ Nitric oxide would, of course, also be expected to inhibit Direct Synthesis by the chemisorption mechanism by tying up active sites on the surface (but the steep rise of inhibition with temperature would be difficult to justify by an activation energy argument).

¹⁶ That this absorption may be due to a defect state in the solid cannot be entirely eliminated (162).

first methoxy group (96, 308, 421). It has been recently shown that trimethoxy- and dimethoxysilane may be isolated from the products of the reaction of methanol with Si—Cu—Zn (95). Something of the relative tendency for formation of silicon subhydrides versus silicon subhalides may be judged from the reaction of hydrogen chloride with silicon, where the major product is trichlorosilane, HSiCl_3 . The following scheme suggests itself:



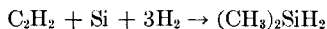
This mechanism is useful in explaining other observations such as the formation of Si—H components when hydrogen is mixed with methyl chloride passed over silicon-copper, or when methyltrichlorosilane is heated in hydrogen over silicon-copper. Another relevant reaction is that of cyanogen chloride with silicon-copper sintered in hydrogen. This gives hydrogen cyanide, cyanogen, and silicon tetrachloride, whereas only cyanogen and silicon tetrachloride are formed when sintering in hydrogen is omitted (478). A silicon subhydride would be destroyed as the result of hydrogen abstraction by organic free radicals formed in the pyrolysis of starting materials. This may account for the fact that 2,2', 1,1'-dinaphthyl decomposes under the conditions of the synthesis to give β -naphthol in good yield, but the β -naphthol does not then react as do other alcohols and phenols under similar conditions (478). Also phenol itself, which has been formed *in situ* during the pyrolysis of anisole at 600° over silicon-copper, does not combine with the silicon, whereas it otherwise reacts normally under the same conditions to give tetraphenoxysilane (355). It is also quite possible that copper functions in these reactions by forming a volatile unstable alkoxy compound, though there is no direct evidence of this.

V. Other Direct Syntheses

There are almost certainly other reactions related to that used in making alkyl- and arylchlorosilanes, which remain to be discovered in the future (see e.g., 354). Foremost among these is the direct reaction of elements such as silicon with hydrocarbons, with or without the addition of hydrogen, to form compounds such as alkyl silicon hydrides (19, 81, 83, 141, 252, 462). In fact, it has been claimed that when hydrocarbon gases

are passed over silicon carbide at 1500° and the exit gases are rapidly quenched, alkyl silanes are produced (82). Such a reaction, if it could be brought about at lower temperatures by a suitable catalyst, would be of the greatest interest. Patents have also been granted for processes involving the dilution of alkyl halides in the Direct Synthesis with methane or benzene. It is said, for example, that addition of methane to ethyl chloride leads to methylethylchlorosilane, but there appears to be doubts about these reactions as some workers have failed to isolate the products claimed (143, 188, 260, 464-467).

The reaction



has a high driving force (−78.7 kcal) but hydrogenation of the acetylene occurs preferentially. Hydrocarbons have been used in Direct Synthesis by intermediate formation of organic halides with hydrogen chloride or chlorine. For example, natural gas (presumably containing considerable methane, petroleum gases (containing ethylene) (237), or even waste gases from the Direct Synthesis itself (235, 329), if passed with chlorine at 400–850° over a silicon-copper contact mass form methylchlorosilanes (112, 252). Methane with hydrogen chloride at 350° is reported to give $\text{CH}_3\text{SiHCl}_2$ in 38.8% yield along with the usual products (264), and organochlorosilanes result if a mixture of olefins with hydrogen chloride is bubbled through a suspension of Si—Cu in paraffin oil (387). Aromatic hydrocarbons also find a use here, as in the reaction of hydrogen chloride with benzene over Si—Cu at 600–850°, which gives PhSiCl_3 (254, 462). When the reaction is carried out in presence of chlorobenzene it can be run at 475–550° (85). Aromatic hydrocarbons have also been utilized in Direct Synthesis reactions in the presence of compounds containing silicon-chlorine bonds (e.g., SiCl_4 , PhSiCl_3 , MeSiCl_3) to produce phenylchlorosilanes (99). Here, however, the main reaction is between the silicon-halogen linkages and the aromatic hydrocarbon, and this is catalyzed directly by Lewis acids (255, 325). A single-step route to organofluorosilanes utilizes calcium fluoride, coal, sand, sodium chloride, and an organic halide at 800° (168).

VI. Conclusion

In his book *Organosilicon Compounds*, (101). Professor C. Eaborn states, "The present widespread interest in organosilicon chemistry stems very largely . . . from the commercial importance of silicones, which were first studied as potentially valuable polymers in the late 1930's. . . . The most important single step in these researches was Rochow's discovery, published in 1945, of the Direct Synthesis of organochlorosilanes. . . . Without this process for the all-important methylchlorosilanes, from which

the methylsilicones are obtained by hydrolysis, it is certain that the growth of the silicone industry would have been slower [and] the fundamental studies of organosilicon chemistry which it stimulated would also have been delayed."

In the two decades since its discovery, a vast amount of research effort has been concentrated on Rochow's Direct Synthesis method itself. The future possibilities, however, both for the utilization of elemental silicon as a raw material and for the expansion of the usefulness of the Direct Synthesis as a synthetic method are very great indeed.

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THE MÖSSBAUER EFFECT AND ITS APPLICATION IN CHEMISTRY

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I. Introduction

It has long been believed that the physical behavior of the atomic nucleus is independent of the state of chemical bonding of the atom to which it belongs. That this is not so is shown particularly clearly by the phenomenon of nuclear magnetic resonance (NMR). In 1949, Knight found that the conditions for the nuclear magnetic resonance of the phosphorus nucleus in different phosphorus compounds depended on the way in which the phosphorus atom was bonded (29). The same phenomenon was later observed for other isotopes. The differences in behavior, though small, were large enough to form a new type of spectroscopy, nuclear magnetic resonance spectroscopy, which today is among the most important physical aids to chemistry.

In this article another resonance phenomenon of the atomic nucleus, namely, the Mössbauer effect, and its significance for chemistry will be discussed. In this effect, as in nuclear magnetic resonance, the chemical bonding of the atom in question again plays a part.

II. The Mössbauer Effect

The effect discovered by Mössbauer (33, 34, 35) and named after him is concerned with the resonance fluorescence of the so-called recoilless γ -radiation of the atomic nucleus.

A. THEORY OF RESONANCE FLUORESCENCE

Fluorescence phenomena have been known for a long time. An atom or molecule can be excited by absorption of a sufficiently energy-rich light

quantum $h\nu$, i.e., it can be raised to a higher quantum state (a higher shell). When the atom or molecule reverts from the excited state to the ground state, the absorbed energy is re-emitted as light quanta. If this reversion to the ground state takes place via several quantum states, the energy of the separate light quanta emitted is smaller than that of the incident light quanta. If, however, the atom or molecule is transformed into only the first excited state by the incident quantum, the process of reversion can lead only to the emission of quanta with a single energy, which is equal to that of the quantum absorbed. This special case of fluorescence is termed resonance fluorescence.

A very clear picture of the energy processes involved in resonance fluorescence has been given by Frauenfelder (14). Suppose a free atomic or nuclear system of mass m has two energy levels A and B , differing in energy by E_r , as shown in Fig. 1. When the system passes from B to A a

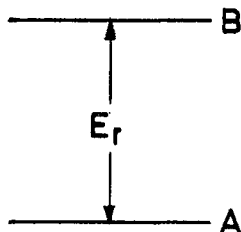


FIG. 1. Energy levels of an atomic or nuclear system: ground state A , first excited state B .

photon with energy E_γ is emitted. It follows from the momentum principle that the momentum p of the photon and the momentum of the atom undergoing recoil, P , must be equal in amount and opposite. If c denotes the velocity of light, the momentum p of the photon is given by Eq. (1):

$$p = \frac{E_\gamma}{c} \quad (1)$$

The recoil energy of the atomic or nuclear system, R , is then

$$R = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{P^2}{2m} = \frac{E_\gamma^2}{2mc^2} \quad (2)$$

It is assumed that the energy of the photons is negligibly small compared with the rest energy mc^2 of the radiating system, i.e., that the recoil system need not be treated relativistically.

From the law of the conservation of energy, the transition energy E_r

by which the two energy levels A and B are separated must be equal to the sum of the energy of the photon and the recoil energy R , i.e.,

$$E_r = E_\gamma + R \quad (3)$$

Bearing in mind that the recoil energy R is small compared with E_γ , E_γ in Eq. (2) may be replaced by E_r , so that we have

$$R \cong \frac{E_r^2}{2mc^2} \quad (4)$$

If it is assumed that an atom or atomic nucleus is in an excited state B (Fig. 1) and reverts to the ground state A with emission of a photon, the photon may be absorbed when it encounters another atom of the same element and raise it to the excited state. The second atom subsequently reverts to the ground state and emits a photon of the same energy. The processes of absorption and secondary emission are independent of one another.

Considering the energy of the photons emitted by many excited atoms, it is found that they do not all have exactly the same energy. This is a consequence of the Heisenberg uncertainty principle, according to which the product of the uncertainty of the time τ and the uncertainty of the energy Γ is of the order of magnitude of \hbar , where $2\pi\hbar = h$, and h is Planck's constant. If τ is the mean life of a state, the uncertainty of the energy Γ is given by

$$\Gamma = \frac{\hbar}{\tau}$$

When τ is very large, i.e., the state is very stable, the energy of the state is sharp. On the other hand if τ is very small, the energy of the state in question is very uncertain, i.e., it cannot be exactly measured. This implies that, for example, the energy of the stable ground state A of an atom is sharp whereas that of the excited state is not sharp. A characteristic energy distribution for the state B is shown in Fig. 2a. The photons emitted in the transition from B to A accordingly show an analogous energy distribution: the emitted line has a "natural width." Its maximum corresponds to an energy of $E_r - R$ (Fig. 2b).

When a photon with energy E_γ and momentum p impinges on another atom of the same element which is at rest, the whole momentum is transferred to it. It undergoes a recoil and the recoil energy R is again given by Eq. (4). This energy must be made available by the photon. In order to raise the atom in question from state A to a state B , the photon must have

the energy $E_r + R$ if the energy difference between the levels is E_r . A resonance phenomenon will then be observed only if at least some of the photons have a sufficiently high energy to reach the energy level B and simultaneously provide energy R for the recoil system. Resonance fluores-

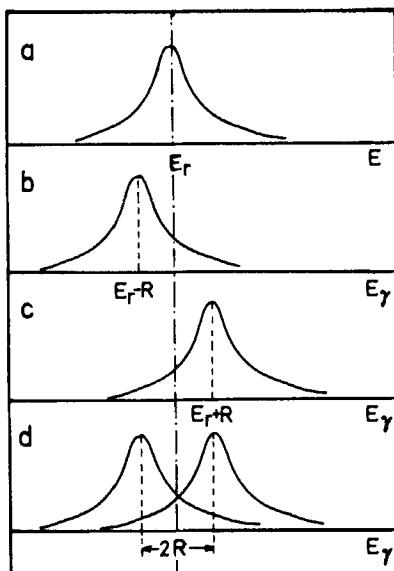


FIG. 2. Energy distribution in resonance fluorescence: (a) energy distribution of the excited state B , (b) energy distribution for the photon emitted in the transition $B \rightarrow A$, (c) energy spectrum for the excitation of the state B and providing the energy R , (d) overlapping of (b) and (c) (14).

cence will thus occur only if the energy distribution curve for the excitation process (Fig. 2c) and that for the photons available (Fig. 2b) overlap. For this to be the case the line width must be approximately as big, or bigger, than $2R$, i.e.,

$$\Gamma \geq 2R$$

Whereas this condition is always satisfied for optical transitions, where transition energies are of the order of 1 eV, it is not in general the case for nuclear transitions with transition energies of the order of 1 keV up to 1 MeV and more.

So far it has been assumed that the radiating and absorbing systems are at rest whereas, in fact, both are in thermal motion. This causes a further broadening of the emission and absorption lines. This broadening

$$D = 2 \sqrt{\frac{P_i^2 R}{2m}} \quad (6)$$

where P_i is the initial momentum of the radiating atom.

The Doppler broadening for optical radiation is very much greater than the recoil energy R . The overlapping of the emission and absorption lines shown in Fig. 2d occurs to a marked extent.

An experimental arrangement for observing resonance fluorescence is shown schematically in Fig. 3. It consists of a source of radiation Q, the

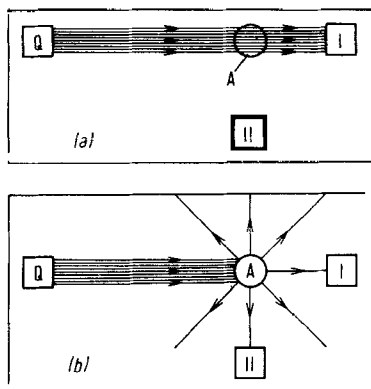


FIG. 3. Schematic representation of resonance fluorescence: (a) no resonance, (b) resonance; Q, radiation source; A, absorber; I and II, radiation detectors.

absorber A, and two detectors I and II. The detectors, which serve to determine radiation intensities, are so placed that one is in the path of the radiation and the other at right angles to it. If the energy of the light quanta emitted from the radiation source does not correspond to that of the first excited state of the atom shell of absorber A, in the sense of what has been said above, no resonance fluorescence will occur. Detector I placed in the path of the beam will then indicate the full intensity passing from the radiation source into the solid angle of the detector, while detector II will receive no radiation (Fig. 3a). If, on the other hand, the energy of the light quanta from Q corresponds to the excitation energy of the first excited state, resonance will occur. The absorber will emit an isotropic radiation which will be observed with detector II (Fig. 3b). The incidence of resonance will be shown by a decrease in the radiation intensity registered by

detector I, and a simultaneous indication of a certain radiation intensity reaching Detector II.

Atoms of the same sort as those which make up the absorber and which are in the requisite excited state will serve as a light source capable of emitting light quanta with the precisely defined energy that is necessary for the excitation of resonance fluorescence. When they revert to the ground state the quanta of the correct energy will be emitted.

B. NUCLEAR RESONANCE FLUORESCENCE

All that has been said in the previous section about the conditions for the appearance of fluorescence in the atom is valid in principle for nuclear resonance fluorescence. An atomic nucleus is excited to a suitable energy by irradiation with γ -rays. The γ -radiation emitted from a nucleus in an excited state, like the light coming from the shell, is electromagnetic radiation, so that it should again be possible to observe resonance fluorescence. In general, however, the γ -quanta, because of their substantially higher energy, impart a considerable recoil to the nucleus in the emission process. As a result a considerable part of the excitation energy of the nucleus is lost as recoil energy, and the γ -quantum emitted is consequently too low in energy to excite a nucleus of the absorber.¹ An analogous recoil loss also occurs, as described above, in the absorption process. This recoil loss may be compensated for by imparting to the nucleus prior to the emission of the γ -quantum a velocity in the direction of the absorber, and so securing a Doppler shift of the emitted γ -quantum which corresponds exactly to the expected energy loss. A Doppler shift of $2R$ requires a velocity of E_r/mc . If such a Doppler shift can be attained in any way, nuclear resonance fluorescence can be observed, i.e., a measurable value for the effective cross section (see p. 440) may be obtained. Several methods of obtaining such a Doppler shift have been described. Thus, for example, a Doppler shift of the quantum energy may be secured by mechanical movement of the nucleus, using an ultracentrifuge (for literature, see ref. 35). Such an experiment was first made in 1950 by Moon (36, 37). He attached a Au^{198} source to the tip of a fast-moving rotor. γ -Quanta emitted tangentially acquired additional energy which was sufficient to compensate for the recoil

¹ The recoil energy for a 14.4-kev γ -quantum which is emitted by an excited iron atom of mass 57 amounts to 1.9×10^{-3} ev from Eqs. (2) or (4), i.e., the γ -quantum ($E = 14,400$ ev) from an excited Fe^{57} atom has an energy smaller by this amount than the energy difference, E_r , corresponding to the two levels *A* and *B*. In general, the recoil energy of a free nucleus of mass number M is given by Eq. (7), where E denotes the γ -ray energy:

$$R \text{ (ev)} \simeq \frac{5.37 \cdot 10^{-4} E^2 \text{ (kev)}}{M} \quad (7)$$

loss. An improved overlap of the absorption and emission lines can be obtained by producing a Doppler broadening by means of an increase in temperature (for literature, see ref. 35). Finally, earlier emission and absorption processes, such as a β decay preceding the γ transition or the capture of a particle can bring about a Doppler broadening or a Doppler shift of the quantum energy (for literature, see ref. 35).

The effects produced by such methods are, however, very small since only a minute fraction of the atoms will have exactly the right velocity. This is even more true as the relative line width is generally much smaller than for the lines in optical spectra. In the latter case the energy of the quanta emitted from the radiation source is often within the line width, even if it is reduced by such small energy losses due to recoil, i.e., it still suffices to excite the orbital electron of the absorbing atom. In contrast to this, the finite line width of the γ lines of nuclei is much smaller.

In the Mössbauer effect, the recoil loss is not compensated but avoided altogether. Thus if the emitting atom is incorporated firmly in a suitable crystal lattice, the recoil momentum is taken up by the whole crystal and practically no energy loss occurs provided lattice vibrations are not excited during emission. The resonance criterion is thus satisfied directly for these recoil-free quanta and, in principle, experiments analogous to those for optical resonance fluorescence may be carried out, as shown diagrammatically in Fig. 3a. Resonance can be destroyed if a velocity is given to the radiation source relative to the absorber: this produces a change in energy of the γ -quanta (Doppler shift). If the first energy level of the atomic nucleus of the absorber is shifted for some reason to higher or lower values, so that the energy needed for excitation is somewhat smaller or greater than the energy of the γ -quantum from the radiation source, source and absorber must be set in motion relative to one another for resonance to occur. The requisite velocities are very small. If resonance absorption is observed, i.e., is picked up by detector I in Fig. 3b, the characteristic intensity distribution shown in Fig. 4 will be obtained for the recorded radiation as a function of the velocity of the absorber relative to the radiation source.

The classical experiments on optical and conventional nuclear resonance fluorescence were in general scattering experiments. The true Mössbauer effect, on the other hand, usually involves a study of transmission of γ -rays. The intensity of these transmitted rays is much greater than that of the scattered radiation, and this simplifies the measurement as well as making it more accurate. For nuclei with high conversion coefficients α (see p. 444) the intensity of the scattered radiation is further reduced, since only a fraction $1/(1 + \alpha)$ of the absorbed γ -radiation is re-emitted.

Not all atoms incorporated in a lattice are able to emit the type of recoil-free γ -quanta under discussion, for lattice vibrations are excited to

some extent and some of the energy of the quantum is lost as vibrational energy in this case. The magnitude of the Mössbauer effect thus depends on the proportion of recoil-free quanta to the total intensity, the so-called

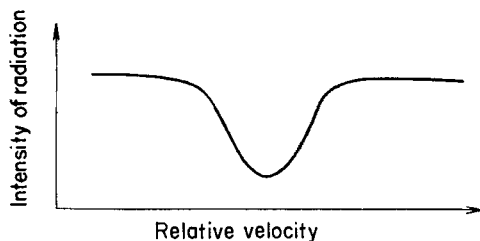


FIG. 4. Intensity of radiation received by detector I as a function of the relative velocity of the radiation source and absorber.

Debye-Waller factor. The effect is greater the smaller the probability of exciting lattice vibrations; i.e., the smaller the γ -quantum energy, the lower the temperature of the crystal and the firmer the bonding of the atom in the lattice.

If it is assumed that there is only one absorbency or scattering level and that the width of the level is determined only by the decay process, the effective cross section² for the absorption and scattering process with thin absorbers is given by Eqs. (8) and (9):

$$\sigma_{\text{absorbing}} = \sigma_0 \frac{\Gamma_\gamma \Gamma}{4(E - E_r)^2 + \Gamma^2} \quad (8)$$

$$\sigma_{\text{scattering}} = \sigma_0 \frac{\Gamma_\gamma^2}{4(E - E_r)^2 + \Gamma^2} \quad (9)$$

where E is the energy of the γ -ray, Γ the total width of the absorption line, Γ_γ its γ -ray width, and σ_0 the maximum resonance cross section. The last magnitude is given by Eq. (10)

$$\sigma_0 = \frac{2I_B + 1}{2I_A + 1} \cdot 2\pi\lambda^2 \quad (10)$$

where $2\pi\lambda^2$ is the wavelength, I_A the spin of the ground state, and I_B the spin of the excited state. The maximum cross section σ_0 would be observed if the incident γ -rays had energy E_r with a small line width relative to Γ and

² The yield of a nuclear process in atomic physics is often expressed in terms of the effective cross section of the nucleus concerned. It depends on the kinetic energy of the exciting particle or, in our case, on the energy of the γ -quantum. The effective cross section denotes the area which the nucleus must possess if each particle collision or each γ -quantum is to lead to a nuclear transformation or to nuclear excitation. Effective cross sections are often expressed in units of 10^{-24} cm². This unit is called 1 barn.

if the conversion coefficient were zero. With the above provisos the energy distributions of the absorption and scattering cross sections have a Lorentz shape, as shown in Fig. 2.

Mössbauer discovered the effect with Ir^{191} nuclei, the quantum energy of which is 129 kev. The radiation source was Os^{191} . This decays according to the scheme shown in Fig. 5, with a half-life of 16 days with emission of β -rays, into the second excited state of Ir^{191} . This passes over with emission

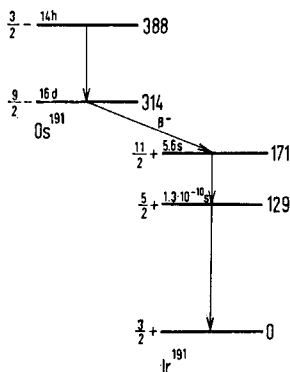


FIG. 5. Decay scheme for $\text{Os}^{191} \rightarrow \text{Ir}^{191}$.

of a 42-kev γ -quantum into the first excited state, which interests us here. This has a life of 1.4×10^{-10} sec. The ground state is reached by the emission of the 129 kev γ -quantum. Ground state Ir^{191} nuclei in the absorber are excited by these γ -quanta and then revert to the ground state with emission of the fluorescent radiation.

In transmission measurements the γ -quanta arising from the fluorescence radiation are generally ignored. For very exact studies, however, it is necessary to take into account this secondary radiation, which depends on the conversion coefficient and the solid acceptance angle of the photomultiplier detector.

Another measurement made by Mössbauer must also be mentioned, namely, the observation of the temperature effect (33). In this case both the source and the absorber were at rest, the latter at a fixed temperature of 88°K and the former at temperatures which could be varied from 88°K to room temperature. He measured the transmission of 129-kev γ -quanta through the absorber as a function of the source temperature. His results are shown graphically in Fig. 6 in terms of the effective absorption cross section. The rise in effective cross section with decreasing temperature (which is quite the reverse of the behavior with gaseous sources and absorbers) was interpreted as due to an increase in the probability of recoil-free emission by the nucleus in the source with decreasing temperature.

TABLE I
PHYSICAL DATA ON ATOMIC NUCLEI^{a,b}

Nucleus	Natural abundance (%)	E (kev)	$T_{1/2}$ (sec)	Q	α (e/γ)	R (10^{-2} ev)	σ'_0 (10^{-19} cm ²)	Effect
Fe ⁵⁷	2.17	14.4	$1.0 \cdot 10^{-7}$	$3.2 \cdot 10^{12}$	9.5	0.19	23	X
Ni ⁶¹	1.25	71	$5.2 \cdot 10^{-9}$	$8.1 \cdot 10^{11}$	K 0.11	4.4	6.6	X
Zn ⁶⁷	4.11	93	$9.4 \cdot 10^{-6}$	$1.9 \cdot 10^{15}$	K 0.63	6.9	1.2	X
Ge ⁷³	7.67	13.5	$4 \cdot 10^{-6}$	$1.1 \cdot 10^{14}$	3600	0.13	0.022	—
Kr ⁸³	11.55	9.3	$1.5 \cdot 10^{-7}$	$3.1 \cdot 10^{13}$	10	0.055	21.0	X
Ru ⁹⁹	12.7	89	—	—	—	4.3	1.0	—
Ru ¹⁰¹	17.0	127	$1.4 \cdot 10^{-9}$	$3.9 \cdot 10^{11}$	K 0.4	8.5	0.97	—
Ag ¹⁰⁷	51.35	93	44.3	$9.0 \cdot 10^{21}$	16	4.3	0.67	—
Ag ¹⁰⁹	48.65	88	39.2	$7.6 \cdot 10^{21}$	14	3.8	0.85	—
Sn ¹¹⁷	7.57	161	—	—	K 0.13	12.0	1.7	—
Sn ¹¹⁹	8.58	24	$1.9 \cdot 10^{-8}$	$1.0 \cdot 10^{12}$	7.3	0.26	10.0	X
Sb ¹²³	42.75	161	$6 \cdot 10^{-10}$	$2.1 \cdot 10^{11}$	—	11.0	0.71	—
Te ¹²³	0.87	159	$1.9 \cdot 10^{-10}$	$6.6 \cdot 10^{10}$	K 0.17	11.0	1.7	—
Tc ¹²⁵	6.99	35	$1.6 \cdot 10^{-9}$	$1.2 \cdot 10^{11}$	K 12	0.52	3.1	X
I ¹²⁷	100	59	—	—	K 2.7	1.5	2.5	—
I ¹²⁹	unstable	26.8	$1.85 \cdot 10^{-8}$	$1.1 \cdot 10^{12}$	5	0.30	25.6	X
Xe ¹²⁹	26.44	40	$7 \cdot 10^{-10}$	$6.2 \cdot 10^{10}$	K 7.5	0.67	30.0	X
Xe ¹³¹	21.18	80	$4.8 \cdot 10^{-10}$	$8.4 \cdot 10^{10}$	K 1.73	2.6	0.70	—
Cs ¹³³	100	81	$6.0 \cdot 10^{-9}$	$1.1 \cdot 10^{12}$	K 1.5	2.7	1.1	—
La ¹³⁷	unstable	10	$8.9 \cdot 10^{-8}$	$2.0 \cdot 10^{12}$	140	0.039	1.3	—
La ¹³⁹	99.9	163	$1.5 \cdot 10^{-9}$	$5.4 \cdot 10^{11}$	K 0.22	10.0	0.56	—
Nd ¹⁴⁵	8.29	67	$3.3 \cdot 10^{-8}$	$4.8 \cdot 10^{12}$	K 3.3	1.7	0.63	—
	—	72	$<1 \cdot 10^{-9}$	—	K 3.3	1.9	0.82	—
Sm ¹⁴⁹	13.8	22	$>2.8 \cdot 10^{-9}$	—	—	0.17	—	X
Sm ¹⁵²	26.63	122	$1.4 \cdot 10^{-9}$	$3.7 \cdot 10^{11}$	K 0.7	5.3	4.8	—
Eu ¹⁵¹	47.77	22	$9.5 \cdot 10^{-9}$	$4.5 \cdot 10^{11}$	L 12	0.17	5.2	—
Eu ¹⁵³	52.23	84	—	—	—	2.5	4.6	—
	—	97	$<1 \cdot 10^{-9}$	—	K 0.3	3.3	2.0	—
	—	103	$3.4 \cdot 10^{-9}$	$7.7 \cdot 10^{11}$	K 1.2	3.7	0.70	—
Gd ¹⁵⁴	2.15	123	$1.2 \cdot 10^{-9}$	$3.2 \cdot 10^{11}$	1.5	5.3	3.2	—
Gd ¹⁵⁵	14.7	60	—	—	—	1.2	10.0	—
	—	87	—	—	K 0.4	2.6	2.3	X
	—	105	—	—	—	3.8	3.3	—
Gd ¹⁵⁶	20.47	89	$2 \cdot 10^{-9}$	$3.9 \cdot 10^{11}$	K 1.0	2.7	7.7	—
Gd ¹⁶⁰	21.9	75	—	—	—	1.9	22.0	—
Tb ¹⁵⁹	100	58	$3.5 \cdot 10^{-11}$	$4.5 \cdot 10^9$	K 6.	1.1	1.5	—
	—	137	$5.4 \cdot 10^{-11}$	$1.6 \cdot 10^{10}$	—	6.3	2.6	—
Dy ¹⁶⁰	2.294	87	$1.8 \cdot 10^{-9}$	$3.4 \cdot 10^{11}$	K 1.5	2.6	6.4	—
Dy ¹⁶¹	18.88	25.7	$2.8 \cdot 10^{-8}$	$1.6 \cdot 10^{12}$	—	0.22	37.0	X
	—	49	—	—	—	0.8	6.8	—
	—	74.5	$3 \cdot 10^{-9}$	$4.9 \cdot 10^{11}$	K 0.46	1.8	2.0	X
Dy ¹⁶²	25.53	81	$3.2 \cdot 10^{-9}$	$5.7 \cdot 10^{11}$	—	2.2	19	—
Dy ¹⁶³	24.97	75	—	—	—	1.8	5.8	—
Dy ¹⁶⁴	28.18	73	$3.5 \cdot 10^{-9}$	$5.6 \cdot 10^{11}$	K 2.7	1.7	6.2	—
Hf ¹⁶⁵	100	95	$3.3 \cdot 10^{-11}$	$6.9 \cdot 10^9$	K 1.77	2.9	1.2	—
Er ¹⁶⁴	1.56	91	$1.4 \cdot 10^{-9}$	$2.8 \cdot 10^{11}$	K 1.9	2.7	5.1	—
Er ¹⁶⁶	33.4	80	$1.8 \cdot 10^{-9}$	$3.2 \cdot 10^{11}$	K 1.7	2.1	7.1	X

TABLE I (Continued)

Nucleus	Natural abundance (%)	E (kev)	$T_{1/2}$ (sec)	Q	α (e/γ)	R (10^{-2} ev)	σ'_0 (10^{-19} cm ²)	Effect
Er ¹⁶⁸	27.07	79.8	$1.84 \cdot 10^{-9}$	$3.2 \cdot 10^{11}$	K 2.1	2.0	6.2	—
Tm ¹⁶⁹	100	108.4	$4 \cdot 10^{-9}$	$7.4 \cdot 10^{10}$	—	0.022	700	X
	—	118	$5 \cdot 10^{-11}$	$1.3 \cdot 10^{10}$	K 0.7	4.4	3.1	—
Yb ¹⁷⁰	3.03	84.2	$1.57 \cdot 10^{-9}$	$2.9 \cdot 10^{11}$	K 1.6	2.2	6.6	X
Yb ¹⁷¹	14.31	66.7	$< 5 \cdot 10^{-7}$	—	—	1.4	11.0	—
Yb ¹⁷²	21.82	78.7	—	—	—	1.9	20.0	—
Yb ¹⁷³	16.13	78.7	—	—	—	1.9	5.2	—
Yb ¹⁷⁴	31.84	76.5	—	—	—	1.8	21.0	—
Lu ¹⁷⁵	94.4	113.8	$8 \cdot 10^{-11}$	$2.0 \cdot 10^{10}$	K 1.6	4.0	0.90	—
Hf ¹⁷⁶	5.21	88.3	$1.35 \cdot 10^{-9}$	$2.6 \cdot 10^{11}$	K 1.32	2.4	6.7	—
Hf ¹⁷⁷	18.5	113	$4.2 \cdot 10^{-10}$	$1.0 \cdot 10^{11}$	K 0.75	3.9	1.4	X
Hf ¹⁷⁸	27.1	93.1	$1 \cdot 10^{-9}$	$2.0 \cdot 10^{11}$	—	2.6	14.0	—
Hf ¹⁸⁰	35.22	93	$1.4 \cdot 10^{-9}$	$2.9 \cdot 10^{11}$	KL 4.0	2.6	2.8	—
Ta ¹⁸¹	100	6.25	$6.8 \cdot 10^{-6}$	$9.4 \cdot 10^{13}$	44	0.012	17	—
	—	136.1	$5.7 \cdot 10^{-11}$	$1.7 \cdot 10^{10}$	K 1.5	5.5	0.66	X
W ¹⁸⁰	0.135	102	—	—	5	3.1	2.0	—
W ¹⁸²	26.4	100	$1.3 \cdot 10^{-9}$	$2.9 \cdot 10^{11}$	4.5	2.9	2.2	X
W ¹⁸³	14.4	46.5	—	—	9	0.63	2.3	X
	—	99.1	$5.2 \cdot 10^{-10}$	$1.1 \cdot 10^{11}$	3.5	2.9	1.7	X
W ¹⁸⁴	30.6	111	$1.3 \cdot 10^{-9}$	$3.2 \cdot 10^{11}$	K 0.99	3.6	5.0	—
W ¹⁸⁶	28.4	123	$1.0 \cdot 10^{-9}$	$2.7 \cdot 10^{11}$	K 0.45	4.4	5.6	—
Re ¹⁸⁵	37.07	125	—	—	K 2.4	4.5	0.61	—
Re ¹⁸⁷	62.93	134	$2 \cdot 10^{-9}$	$5.9 \cdot 10^{11}$	K 2.1	5.2	0.58	X
Os ¹⁸⁶	1.59	137	$5.1 \cdot 10^{-10}$	$1.5 \cdot 10^{11}$	K 0.45	5.4	4.5	—
Os ¹⁸⁸	13.3	155	$6.2 \cdot 10^{-10}$	$2.1 \cdot 10^{11}$	K 0.40	6.8	3.6	—
Os ¹⁸⁹	16.1	69.5	—	—	—	1.4	—	—
Os ¹⁹⁰	26.4	187	$3.5 \cdot 10^{-10}$	$1.4 \cdot 10^{11}$	K 0.2	9.9	2.9	—
Os ¹⁹²	41.0	206	$2.8 \cdot 10^{-10}$	$1.3 \cdot 10^{11}$	K 0.16	12.0	2.5	—
Ir ¹⁹¹	38.5	82.6	$3.9 \cdot 10^{-9}$	$7.1 \cdot 10^{11}$	—	1.9	1.8	—
	—	129	$1.4 \cdot 10^{-10}$	$4.0 \cdot 10^{10}$	K 2.9	4.7	0.56	X
Ir ¹⁹³	61.5	73	$6 \cdot 10^{-9}$	$9.6 \cdot 10^{11}$	—	1.5	2.3	X
	—	139	$1.0 \cdot 10^{-9}$	$3.1 \cdot 10^{11}$	K 2.2	5.4	0.59	—
Pt ¹⁹⁵	33.8	99	$1.4 \cdot 10^{-10}$	$3.0 \cdot 10^{10}$	9.0	2.7	0.50	X
	—	129	$5.5 \cdot 10^{-10}$	$1.6 \cdot 10^{11}$	—	4.6	4.4	—
Au ¹⁹⁷	100	77	$1.9 \cdot 10^{-9}$	$3.2 \cdot 10^{11}$	2.5	1.6	0.59	X
Hg ¹⁹⁹	16.84	158	$2.4 \cdot 10^{-9}$	$8.3 \cdot 10^{11}$	K 0.2	6.7	2.4	—
Hg ²⁰¹	13.22	32.1	—	—	—	0.27	24.0	—
	—	167.6	$< 2 \cdot 10^{-9}$	—	K 1.5	7.5	0.18	—

^a From Fraunfelder (14) and personal communication.

^b Q = ratio of γ -ray energy E_γ to line width $\Gamma = \hbar \ln 2/T_{1/2}$.

α = total internal conversion coefficient (K implies α_K , L implies α_L).

R = recoil energy of free nucleus in units of 10^{-2} ev.

σ'_0 = Mössbauer absorption cross section in units of 10^{-19} cm², calculated with the listed values of the conversion coefficient and assuming natural line width. In the case of an unknown conversion coefficient the cross section has been calculated by assuming $\alpha = 0$. Once α is known, the correct cross section can be found by multiplying the value in the table by $1/(1 + \alpha)$.

X = an effect has been observed.

Mössbauer was able to explain these results quantitatively by modifying a theory due to Lamb (30), which dealt with the resonance absorption of neutrons by nuclei fixed in a crystal lattice. Mössbauer applied this theory to the γ -resonance process.

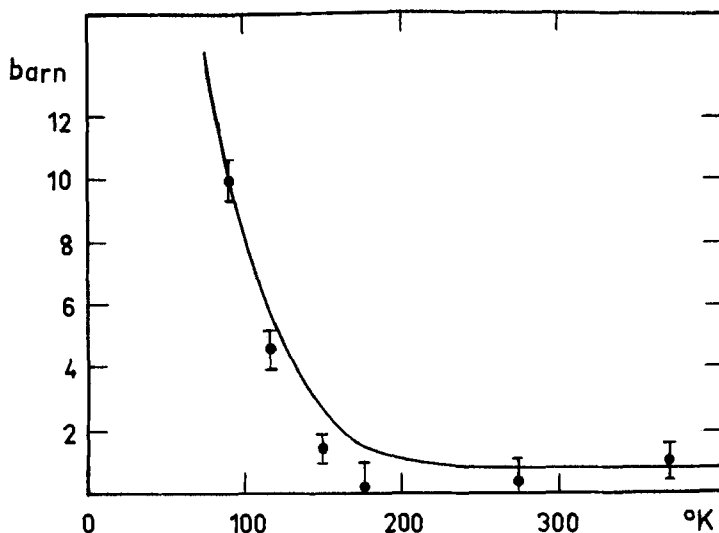
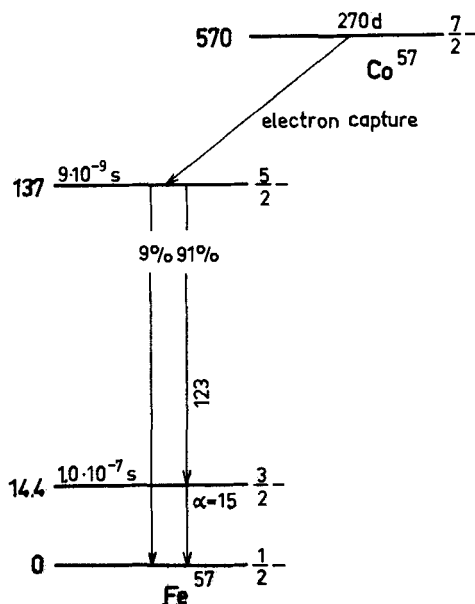


FIG. 6. Effective cross section per Ir^{191} nucleus (temperature of absorber, 88°K).

Table I shows the isotopes known at present for which the Mössbauer effect has been observed or which appear to be suitable for this purpose. It is, however, certainly correct to assume that other isotopes will be found in the future which will be useful for the type of investigation described in this article. The isotope Fe^{57} has proved to be particularly suitable for the study of effects due to the nature of the chemical bonding of the atom, which is dealt with in what follows.

Excited Fe^{57} results from the decay of Co^{57} (cf. decay scheme, Fig. 7). The energy of the quantum is 14.4 kev, the half-life of the first excited state is 1.0×10^{-7} sec, and the derived line width is 4.6×10^{-9} ev. Velocities needed for measurements of the line width are of the order of some tenths of a millimeter per second, a velocity of 0.1 mm/sec corresponding to an energy of 4.8×10^{-9} ev.

In principle such studies are possible for all nuclei with a low-energy first excited state, a sufficiently small line width, and a sufficiently small conversion coefficient α . The conversion coefficient α gives the ratio of the decays by internal conversion with resultant electron emission to one by γ -quanta. When internal conversion occurs instead of emission of a γ -quantum, the nucleus is able to return to the ground state when an electron in

FIG. 7. Decay scheme for $\text{Co}^{57} \rightarrow \text{Fe}^{57}$.

the inner shell takes up the excitation energy and leaves the atom. Such conversion is particularly large for small γ energies. With Fe^{57} the conversion coefficient for the 14.4-keV level is about 9.5. The total line width Γ and the γ -ray line width Γ_γ are related by Eq. (11)

$$\frac{\Gamma_\gamma}{\Gamma} = \frac{1}{1 + \alpha} \quad (11)$$

Finally, the nuclear spin should not be greater than $\frac{3}{2}$, as the structure of the spectrum is otherwise very complex and difficult to resolve. If the isotopes in Table I are considered from this point of view, it will be seen that Sn^{119} is very suitable, in addition to Fe^{57} . Nuclei such as Ni^{61} , Zn^{67} , Xe^{129} , Dy^{161} , Tm^{169} , Ta^{181} , Pt^{195} , and Au^{197} are also useful.

III. Applications of the Mössbauer Effect

A. PHYSICAL APPLICATIONS

One of the possible applications of the Mössbauer effect in nuclear physics is the determination of the life of an energy state from the line width of the resonance and the measurement of the magnitude of the effect as a function of various factors. The line width Γ may be determined readily

and the life of the state may then be calculated from Eq. (13). If the line width is expressed in ev, the mean life τ is given by:

$$\tau \text{ (sec)} = \frac{6.58 \times 10^{-16}}{\Gamma(\text{ev})} \quad (13)$$

or the half life, $T_{1/2}$ by:

$$T_{1/2} \text{ (sec)} = \frac{4.55 \times 10^{-16}}{\Gamma(\text{ev})} \quad (14)$$

The relationship between mean life and half life of a state is $T_{1/2} = \tau \ln 2 = 0.6931 \tau$. Thus, for example, Mössbauer found for the mean life of the 129-kev level of Ir^{191} a value of $\tau = 1.0 \times 10^{-10}$ sec, and for the 134-kev level of Re^{187} $\tau = (1.5 \pm 0.2) \times 10^{-11}$ sec.

Earlier electronic measurements had given a mean life of $\tau = 1.4 \times 10^{-7}$ sec for the excited state of Fe^{57} , corresponding by Eq. (13) to a line width Γ of 4.7×10^{-9} ev. Using the narrow lines of Fe^{57} (ratio of line width to quantum energy about $1:10^{12}$) it was further shown, for example, that the small energy shifts of γ -quanta in the gravitational field could be detected, i.e., it was shown that the γ -quanta had altered in energy by a certain amount after falling through a certain height in the earth's gravitational field (41).

Finally, it is possible to use the Mössbauer effect to measure directly the Zeeman effect, i.e., the splitting of excited states in a magnetic field, which is very small for nuclei because of their small magnetic moments (17). Thus the resonance line of Fe^{57} was split into six components (cf. Figs. 13 and 14). The very strong magnetic field needed to produce this splitting is produced by the crystal field and orbital electrons. The nuclear magnetic moments or the field strength at the nucleus could be deduced from the magnitude of the splitting.

B. CHEMICAL APPLICATIONS

The possibility of using the Mössbauer effect in chemistry arises from the observation that the position and shape of the resonance line depend on the chemical bonding of the atom to which the nucleus in question belongs in ways to be discussed fully later. Since the properties of the iron isotope Fe^{57} are particularly favorable for the precise study of the Mössbauer effect, the phenomena of isomer shift, quadrupole interaction and temperature shift, described in the following sections, were first studied in detail with this isotope. Points of chemical interest arising from the results are discussed and analogous studies with Sn^{119} are reported in Section III,B,10.

1. Methods of Measurement

The substance to be studied is used in the measurements as a resonance absorber, and its transmission is observed as a function of the relative velocity of the absorber and source. In measuring the transmission of the resonance absorber, it is important to have automatic recording of the whole velocity spectrum as well as a sufficient over-all accuracy. In this connection the method which was first used by Ruby *et al.* (46) is coming increasingly into use with various modifications. The source (or the absorber) is set into vibration by means of a loud-speaker, the instantaneous velocity being measured with a coil in a homogeneous magnetic field. The γ pulses are recorded as a function of the velocity in a multichannel analyzer. Figure 8 shows diagrammatically a typical setup for making the measurement (24).

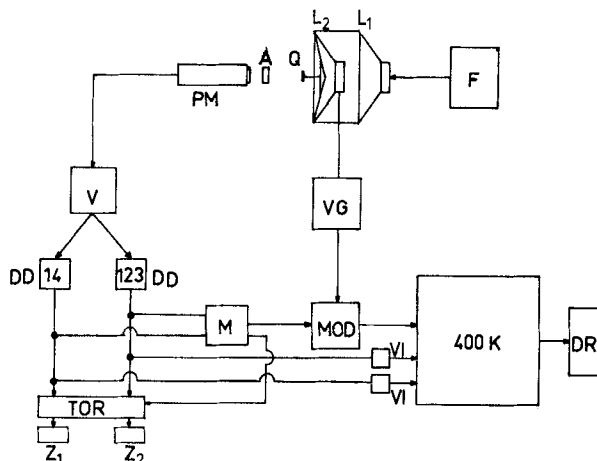


FIG. 8. Diagram of the assembly for measuring the Fe^{57} Mössbauer effect: Q, Co^{57} source; A, resonance absorber; PM, γ -detector (photomultiplier); VI, pulse amplifier; DD 14 and DD 123, differential discriminators; M, pulse-mixer system; Z_1 and Z_2 counters; F, low frequency generator; L_1 driver loud-speaker; L_2 , measurement loud-speaker; VG, direct current amplifier; MOD, modulator; 400-K, multichannel pulse-height analyzer (kicksorter); V, variable delay line; DR, recorder.

Two acoustically coupled loud-speakers, L_1 and L_2 , are used as velocity drive and for measuring the velocity. The γ -quanta emitted by the Co^{57} source after passage through the resonance absorber reach a 1-mm thick NaI(Tl) crystal and are recorded by a photomultiplier PM. The pulse leaving the detector is fed through a pulse amplifier to differential discriminators, where the pulses of the 14.4-keV and 123-keV γ -radiation are separated. The solid angle of the detector (1%) is defined by a lead diaphragm. The driver loud-speaker L_1 , which is fed by the generator F, sets

the membrane of the loud-speaker L_2 in vibration acoustically with the resonance frequency of approximately 30 cycles/sec. The Co^{57} source Q is rigidly linked with the voice coil of L_2 . The mechanical mounting of the loud-speaker used for the measurement must be very stable so as to eliminate vibrations. The voltage induced in the voice coil of the measuring loud-speaker L_2 , which is proportional to the instantaneous velocity, serves, after it has been amplified in a broad-band direct-current amplifier VG, as a means of modulating the detector output pulses, the height of the pulse thus becoming a linear function of the velocity. Figure 9 shows the principle

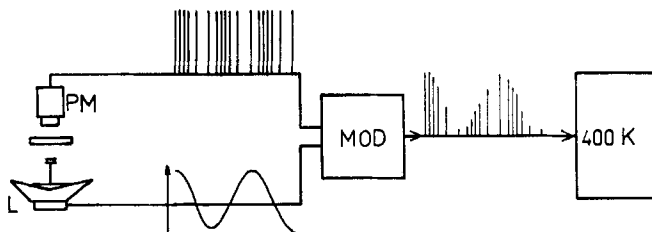


FIG. 9. Operation of modulator. Pulses from the photomultiplier PM are modulated through the velocity spectrum in the modulator MOD and then fed into the multi-channel pulse-height analyzer, 400-K. The source is mounted on the coil of loud-speaker L.

of the modulation procedure. The pulses of the photomultiplier PM are modulated in the modulator MOD by the velocity spectrum $v(t)$ and then fed to the multichannel pulse height analyzer.

The modulator MOD deals with the 14.4-kev and 123-kev pulses from the pulse mixer system M, which are fed after modulation to a 400-channel pulse-height analyzer. The record of the intensity of the 14.4-kev radiation is stored in the first half and that of the 123-kev radiation in the second half of the multichannel analyzer as a function of the velocity. Distribution between the two halves is secured by a gate signal from the 123-kev pulses, the delay of which is arranged so that the positions of the channels are the same for both halves. The U-form velocity distribution resulting from the sinusoidal movement is eliminated by normalization of the 14.4-kev resonance radiation with respect to the 123-kev radiation, i.e., by division of the corresponding channels of the two halves.

The test sample (absorber) is pressed into circular Plexiglas disks of 11-mm internal diameter and 0.5–1.0-mm thickness and closed on both sides with sheets of plastic material, e.g., Sellotape. In investigating solutions or substances which are liquid at room temperature, similar containers are used with walls made of 30- μ thick aluminum foil. The liquid is filled into the container through a slit in the frame, which is sealed with cement.

The thickness of the absorber is chosen so that it contains 4–30 mg Fe per cm^2 . Metallic absorbers are used with a thickness of 10–30 μ . In making measurements at various temperatures the absorber is in a thermally insulated airtight chamber which can be heated or cooled. The temperature of the chamber is measured with a thermoelement.

In addition to the usual determination of resonance in absorption it is possible, as Barloutaud (1) first showed, to carry out scattering experiments. Figures 10a and 10b show the velocity spectra of absorption and

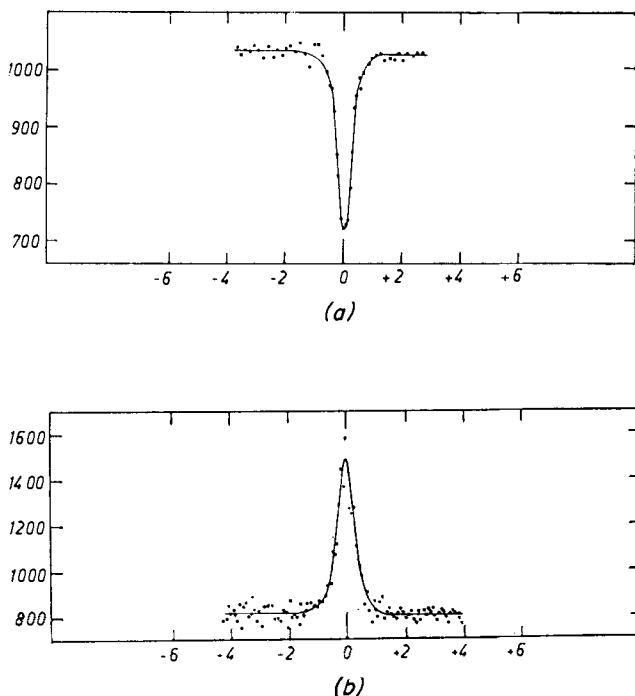


FIG. 10. Velocity spectrum of transmission and scattering measurements (24) with a Co^{67} source in Vacromium and (a) a Vacromium absorber, (b) a Vacromium scatterer. Ordinate: intensity of transmitted or scattered radiation (arbitrary units). Abscissa: relative velocity of source and absorber (mm/sec).

scattering measurements with a Co^{67} source in Vacromium G (stainless steel) and a Vacromium G absorber or scatterer. The scattering experiments allow, *inter alia*, the study of thick samples.

2. Radiation Sources

In studying the resonance of Fe^{57} nuclei, Co^{67} atoms which are incorporated into a crystal lattice are used as the source of radiation. The

Co^{57} atoms decompose according to the scheme shown in Fig. 7. Various authors have used sources in which Co^{57} is diffused into stainless steel, although approximately double the natural line width is obtained in this case. Approximately the same line width is also obtained with a Co^{57} source in copper. Particularly narrow emission lines are obtained by using platinum in place of stainless steel. The strong absorption of the radiation in the electron shell of platinum may be largely avoided by restricting the diffusion of the Co^{57} into it. The emission line from a source of Co^{57} in palladium is likewise narrow and only some 10% broader at the most than the natural line width. Absorption of the γ -radiation by palladium is also less than that by platinum. Figure 11 shows velocity spectra for $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ obtained with sources of Co^{57} in Pt, Pd, and Vacuomium G (Fe, 55; Cr, 25; Ni, 20%).

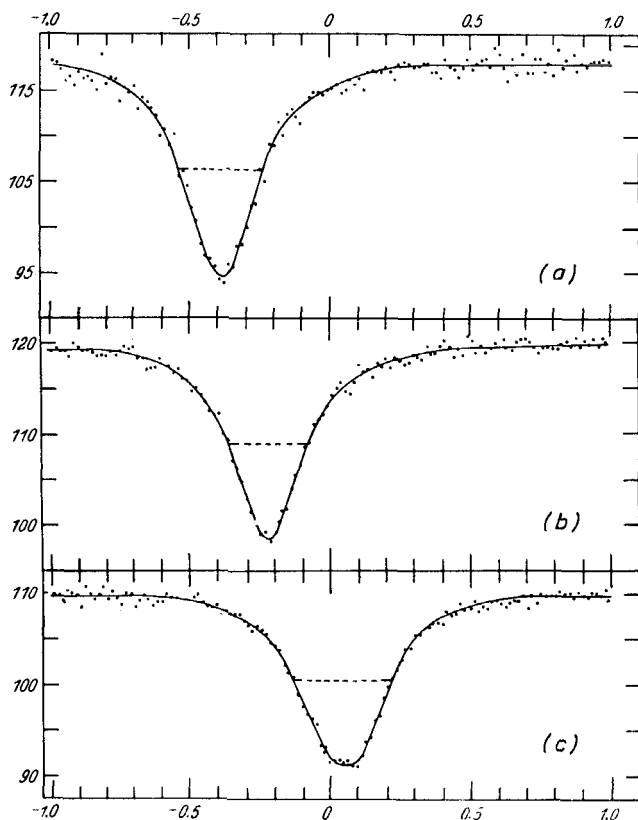


FIG. 11. Velocity spectrum of $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ with (a) Co^{57} in Pt, (b) Co^{57} in Pd, (c) Vacuomium G. Ordinate: transmission (arbitrary units). Abscissa: relative velocity of source and absorber (mm/sec).

The line shift obtained with Co^{57} in palladium is 0.165 ± 0.002 mm/sec higher than that measured with Co^{57} in platinum, while the value found with Co^{57} in Vacromium G on the radiation source is shifted by 0.432 ± 0.002 mm/sec with respect to the value measured with Co^{57} in platinum. All the shifts recorded in this article refer to a source of Co^{57} in platinum unless otherwise mentioned. Table II gives the shifts δ for other metallic

TABLE II
VALUES OF THE SHIFTS δ FOR METALLIC SOURCES AND ABSORBERS^a

Source: Co^{57} in	Shift (mm/sec) of	
	Source (+25°C)	Absorber (+25°C)
Vacromium G	0.432 ± 0.002	-0.431 ± 0.003
Fe	—	-0.351 ± 0.002
Cu	0.124 ± 0.010	-0.124 ± 0.011
Pd	0.165 ± 0.002	-0.165 ± 0.003
Pt	0	0.000 ± 0.002

^a From Kerler *et al.* (25).

sources (25°) and the corresponding shifts δ for these systems as absorbers at 25°. The latter are given for Pt, Cu, and Pd sources and the possible differences between the source and the corresponding absorber have been taken into account in assessing the probable error.

3. Isomer Shift

The influence of the nature of the chemical bonding of the iron atom shows itself in the magnitude of the so-called isomer shift, in the temperature shift described in Section III,B,4, and in the quadrupole interaction which is discussed in Section III,B,5.

If the γ -radiation from a radiating source falls on an absorber which has nuclei bonded chemically in the same way and situated in the same crystal lattice as the source, then, from what has been said, resonance will occur. This is no longer the case if the nuclei in question in the resonance absorber are in a different state of chemical bonding from those in the radiation source. In order to satisfy the condition of resonance, it then becomes necessary to impart a definite velocity to the absorber relative to the source and thus change the energy of the incident quanta until they correspond to the excitation energy of the nuclei in the absorbing substance. The velocity may be positive or negative, i.e., in many cases the absorber must be moved towards the source and in others away from it, according to whether the excitation energy of the nucleus of the absorber is larger or

smaller than the energy of the γ -quanta emitted by the source of radiation. This shift relative to the zero velocity of an arbitrarily chosen radiation source is called the line shift.

It is made up of the isomer shift³ and the temperature shift. The shift is usually expressed in terms of mm/sec or cm/sec. In order to convert data in Mc to cm/sec it is necessary to multiply by the conversion factor $h \times c/E$. E here represents the energy of the γ -quantum concerned. For the quanta from Fe^{57} , for example, $14,400 \text{ ev} = 14,400 \times 1.602 \times 10^{-12} \text{ erg}$. The conversion factor for Fe^{57} is thus 8.643×10^{-3} .

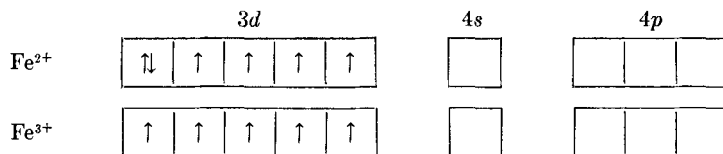
The isomer shift describes the energy difference ΔE for the same energy transition in two atomic nuclei which have different electron wave functions at the nucleus. E is given by Eq. (15):

$$\Delta E = \frac{2Z \cdot e^2}{3} (R_B^2 - R_A^2) \{ |\psi_a|^2 - |\psi_e|^2 \} \quad (15)$$

where Ze is the nuclear charge, R_B and R_A are the nuclear radii of the excited and the ground state, respectively, and ψ_a and ψ_e are the wave functions at the nuclei in the absorber and emitter, respectively. The phenomenon was first observed by Kistner and Sunyar (27) for Fe^{57} and has since been found for Sn^{119} (2), Au^{197} (48), and other nuclei.

The isomer shift is a linear function of the s electron density at the nucleus and is caused by interaction of the s electrons with the different nuclear charge distributions in the excited state and ground state. [It may be noted that only the s electrons can have a finite density at the nucleus; p , d , and f electrons, which have zero density at the nucleus can nevertheless exert an influence on the electron density at the nucleus by screening the s electrons. Calculations on this screening effect for $3d$ electrons have been made by Watson and Freeman (53), and Walker *et al.* (52) applied these calculations to iron compounds.] The isomer shift decreases linearly with increasing s electron density at the nucleus, i.e., an increasing s electron density produces a shift of the resonance line to negative velocities. In the case of Fe^{57} the magnitude of the isomer shift is determined essentially by the occupation of the $3d$ and $4s$ states, and in certain cases by external effects (e.g., by the proportion of covalent-bonding or the fields of neighboring ions). This means, for example, that the shift for Fe^{2+} ions is more positive than that for Fe^{3+} ions because in the first case the $3s$ electrons are more strongly screened by the additional $3d$ electron (8, 49, 52).

³ In the literature this quantity is also called the chemical shift. Since the latter term has come into use for the line shift occurring in nuclear magnetic resonance, the term isomer shift is preferred (isomeric nuclei are understood in nuclear physics to denote nuclei of equal charge and mass but different energy).



The high negative shift shown by metallic iron is a result of the high s electron density caused by the partial occupation of $4s$ orbitals.

Considering the values of the isomer shifts of numerous iron compounds given in Table III, it will be seen that these have characteristic values for

TABLE III
SHIFTS, QUADRUPOLE SPLITTINGS, AND THEIR TEMPERATURE
DEPENDENCE FOR IRON COMPOUNDS

Absorber	Shift (at -130°C)	$-\Delta\delta/\Delta T$ (mm/sec/ 100°C)	Quadrupole splitting (at -130°C)	$-\Delta\epsilon/\Delta T$ (mm/sec/ 100°C)
$\text{K}_4[\text{Fe}(\text{CN})_6]$	-0.333 ± 0.005	0.038	—	—
$(\text{NH}_4)_4[\text{Fe}(\text{CN})_6]$	-0.360 ± 0.005	0.028	—	—
$\text{Cu}_2[\text{Fe}(\text{CN})_6]$	-0.389 ± 0.006	0.036	—	—
$\text{Ag}_4[\text{Fe}(\text{CN})_6]$	-0.397 ± 0.006	0.047	—	—
$\text{K}_3[\text{Fe}(\text{CN})_6]$	-0.413 ± 0.003	0.039	0.373	0.06
$\text{Cu}_3[\text{Fe}(\text{CN})_6]_2$	-0.454 ± 0.007	0.034	0.760	0.18
$\text{Ag}_3[\text{Fe}(\text{CN})_6]$	-0.439 ± 0.007	0.035	0.860	0.06
$\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$	-0.560 ± 0.003	0.030	1.725	} <0.01
$\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$	-0.284 ± 0.007	0.036	0.667	
$\text{Na}_4[\text{Fe}(\text{CN})_5\text{NO}_2]$	-0.383 ± 0.007	0.038	0.855	
$\text{Na}_5[\text{Fe}(\text{CN})_5\text{SO}_3]$	-0.322 ± 0.007	0.036	0.730	
FeS_2 (pyrite)	$+0.033 \pm 0.003$	0.044	0.632	
FeS_2 (marcasite)	$+0.007 \pm 0.007$	0.051	0.531	} —
$[\text{Fe}(\text{dipyridyl})_3]\text{Cl}_2$	$+0.039 \pm 0.007$	0.034	0.350	
$\text{Fe}(\text{CO})_5$	-0.44 ± 0.003	0.05	2.532	
$\text{Fe}(\text{CO})_4\text{I}_2$	$+0.08 \pm 0.003$	—	0.74	—
$\text{Fe}_2(\text{CO})_9$	-0.192 ± 0.007	0.054	0.400	0.02
$\text{Fe}_3(\text{CO})_{12}$ (outer lines)	-0.242 ± 0.010	—	1.098	0.10
$\text{Fe}_3(\text{CO})_{12}$ (inner lines)	-0.302 ± 0.007	—	—	—
K_2FeO_4	-1.202 ± 0.005	0.041	—	—
$\text{BeFeO}_4 \cdot \text{H}_2\text{O}$	-1.195 ± 0.010	0.04	—	—
BaFeO_4	-1.159 ± 0.010	0.035	—	—
KFeS_2	-0.103 ± 0.010	—	0.504 (25°C)	—
KFeO_2	-0.116 ± 0.020	0.05	—	—
Red Roussin salt	-0.275 ± 0.007	0.040	0.667	0.03
Black Roussin salt	-0.216 ± 0.007	0.042	0.896	0.03
Fe^{2+} salts	$+0.93$ to $+1.01$	0.046 – 0.061	1.70 – 3.60	0.15 – 0.48
Fe^{3+} salts	$+0.10$ to $+0.16$	0.046 – 0.061	0 – 0.66	0 – 0.03
Fe metal	-0.264	0.056	—	—
Vacromium	-0.343	0.057	—	—

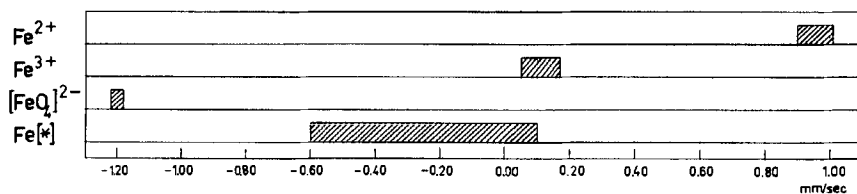


FIG. 12. Region of isomer shift for various classes of compound. Radiation source: Co^{57} in Pt at 25° . Abscissa: relative velocity of source and absorber (mm/sec).

various groups of iron compounds. Thus shifts for Fe^{2+} salts (Fig. 12) at about -120° fall in the range 0.9–1.0 mm/sec, those for Fe^{3+} salts in the range 0.1–0.2 mm/sec [$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ falls outside this range with $\delta = 0.555$ mm/sec (25°)], while complex compounds of iron vary between -0.6 and $+0.1$ mm/sec. Metallic iron itself ($\delta = -0.27$ mm/sec) falls in the last region. These ranges characteristic of the various states of bonding are discussed systematically in Section III,9.

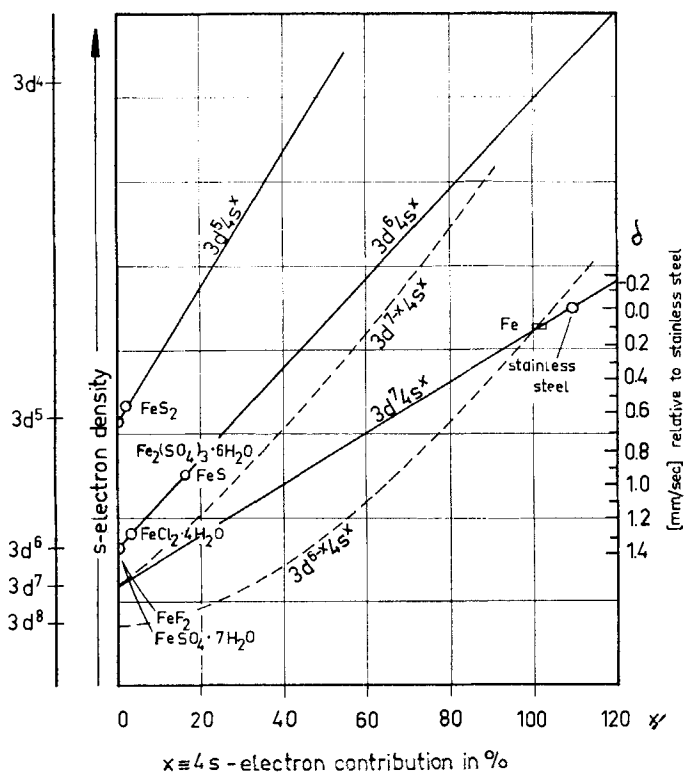


FIG. 13. Interpretation of the isomer shift. The total s electron density is represented as a function of the $4s$ character for various d electron configurations (52).

Walker and associates (52) combined the observed data, particularly for ionic compounds, with the Hartree-Fock calculations of Watson (53) on the various d configurations of iron in order to obtain a calibration of the isomer shifts in terms of the s electron density. The shift for iron in a transition metal alloy was explained by supposing that a certain proportion of a $4s$ electron is added to a $3d^7$ configuration of iron. This proportion could be determined by evaluating the $4s$ electron wave function density at the nucleus from the Fermi-Segrè-Goudsmit formula (12, 15). Figure 13 shows this postulated relationship between the isomer shift and the total s electron density, which is expressed as a function of the percentage of $4s$ character for various d electron configurations. Shifts referred to stainless steel (type 310) are shown on the right-hand scale of the diagram. Shifts for ionic Fe^{2+} and Fe^{3+} compounds may be identified with Watson's densities for $3d^6$ and $3d^5$, respectively. The straight lines in the diagram represent s electron densities for hypothetical $3d^n4s^x$ configurations, while the dotted curves show the s electron densities for $3d^{8-x}4s^x$ and $3d^{7-x}4s^x$ configurations. Experimental values for some Fe^{2+} and Fe^{3+} compounds are shown on the $3d^64s^x$ or $3d^54s^x$ lines. It is readily seen that the $4s$ orbital of iron plays an increasingly important part as the ionic character of the bond diminishes: the electrons of the ligands occupy the $4s$ orbital in increasing measure. A high $4s$ electron density is observed in metallic iron and its alloys as one would expect. It does not depend much on the host metal, showing that the iron has essentially the same configuration in all cases.

4. Temperature Shift

In interpreting minor differences in shifts, it may be noted that the observed line shift is temperature dependent, i.e., is made up of the true isomer shift and a temperature shift. The proportion of the temperature shift in terms of the total line shift is generally small in relation to the isomer shift, being of the order of 0.05 mm/sec per 100° . The temperature dependence is practically linear in the region -120° to $+80^\circ$. Figure 14 shows shifts for a range of iron compounds as a function of temperature. Most salts show the same dependence on temperature as the metal, though complex salts give smaller values.

The temperature shift expresses both the magnitude of the Debye-Waller factor and the characteristics of the vibrational spectrum (20, 41). It is proportional to the inner energy of the crystal, which reaches a saturation value with the excitation of all the lattice vibrations. The change of temperature shift with temperature is proportional to the specific heat.

The slope $-\partial\delta/\partial T$ depends only on the temperature shift if the s electron density is assumed to be independent of temperature. Whether the electron density arising from $3s$ and $4s$ electrons is actually independent

of temperature is undecided. In principle a temperature dependence seems possible if strongly dependent internal fields exist which can influence the electron distribution.

To compare δ values for various substances from the point of view of isomer shift, it is best to go to low temperatures where the temperature

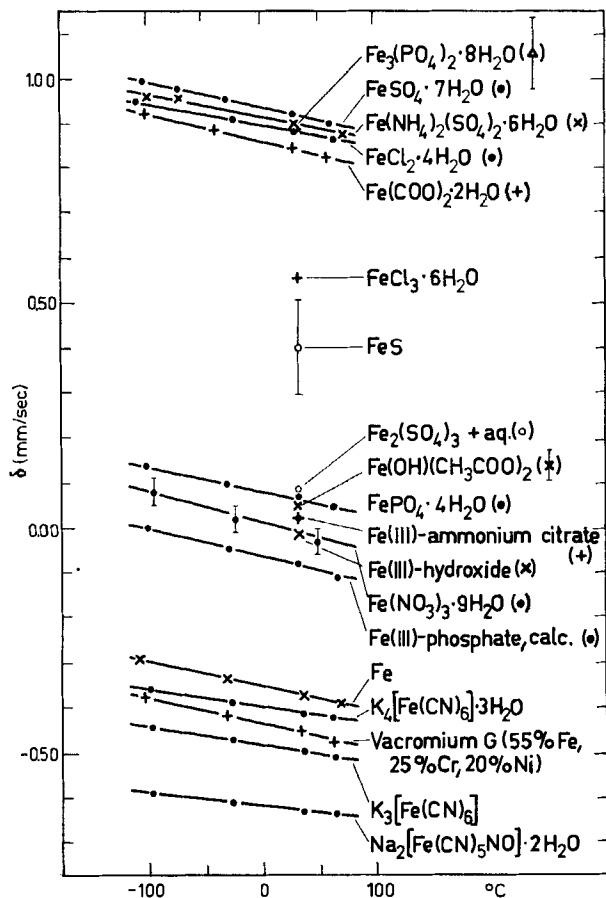


FIG. 14. Shift δ as a function of temperature. Ordinate: mm/sec. Abscissa: temperature ($^{\circ}\text{C}$) (23).

shift is at a minimum. The differences in the contribution of the temperature shift are then substantially smaller and the residual mean contribution does not interfere with interpretation, provided comparisons are made with a source giving a definite shift.

In Table III the line shifts observed at low temperatures are specified.

The corresponding shifts at higher temperatures are tabulated in detail in the original publications (13, 19, 24, 25, 26, 54).

As has been said in the previous section, the observed shift depends on the nature of the radiation source. All the values given above refer to a Co^{57} source in platinum at 25°C . To convert the shifts from mm/sec to Mc it is necessary to multiply by 11.6 (cf. p. 452).

5. Quadrupole Splitting

In many cases it is found that the resonance line emitted from the substance examined consists not of one but of two lines, even when all of the nuclei in question are in the same state of bonding. The so-called quadrupole splitting of the resonance line arises from interaction of the electrical field gradient at the nucleus with the electrical quadrupole moment of the excited Fe^{57} nucleus. The field gradient at the nucleus depends on the electronic configuration of the atom in question and on its environment. [Good reviews of quadrupole interaction are given by Cohen and Reif (5) and by Das and Hahn (7).] Consequently conclusions may be drawn from the quadrupole splitting about the nature of the chemical bonding and the crystal lattice.

Quadrupole splitting of resonance lines was first studied by Kistner and Sunyar (27) with Fe^{57} . Here the position is particularly simple, since the ground state with a spin of $\frac{1}{2}$ has no quadrupole moment and splitting of the resonance line is due only to the excited state with a spin of $\frac{3}{2}$. Values for the quadrupole splitting ϵ (distances between the two lines) for the compounds studied are given in Table III. Figure 15 shows graphically

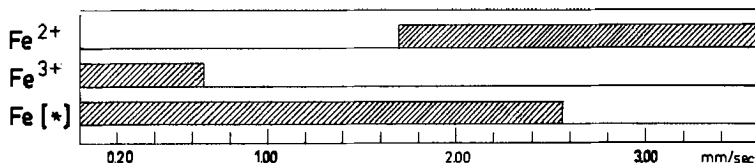


FIG. 15. Region of quadrupole splitting for various classes of compound. Abscissa: relative velocity between source and absorber (mm/sec) $\text{Fe}[*]$ iron in complexes.

the quadrupole splitting characteristic of different types of compound, and Fig. 16 gives ϵ as a function of temperature for a series of compounds.

It is seen that Fe^{3+} salts have very small splittings up to about 0.6 mm/sec (13, 24) (see, for example, Fig. 17a). Unusually large splittings are observed in silicates containing iron (cf. Section III,B,8,f). They arise principally because of the field gradients produced by the crystal lattice at the nucleus, since the Fe^{3+} ion has a spherically symmetrical charge distribution and cannot give rise to any interaction with the electrical quadrupole

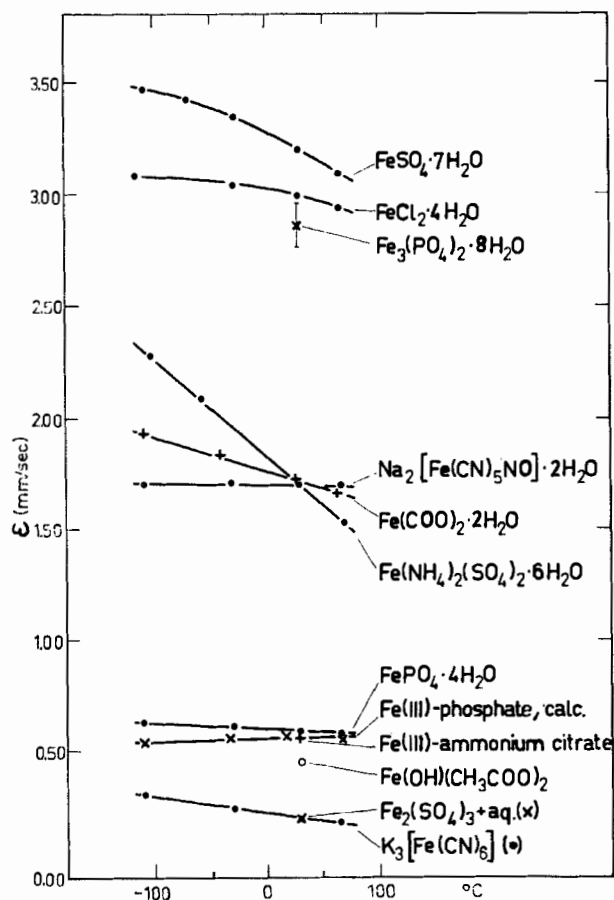


FIG. 16. Quadrupole splitting ϵ of absorption lines for various compounds as a function of temperature. Ordinate: mm/sec. Abscissa: temperature ($^{\circ}\text{C}$) (23).

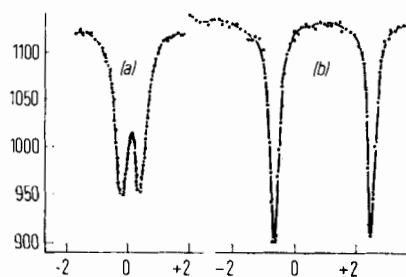


FIG. 17. Velocity spectra of (a) $\text{FePO}_4 \cdot 4\text{H}_2\text{O}$ and (b) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Ordinate: transmission (arbitrary units). Abscissa: relative velocity of source and absorber (mm/sec).

moment. Field gradients in the crystal are strengthened by a factor of about 7 by Sternheimer antishielding (50, 51) of the Fe^{3+} shell, which is a polarization effect. An interpretation due to Burns (4) is satisfactory for explaining the relatively weak temperature dependence of quadrupole splitting for Fe^{3+} salts. This is attributed to the differential homogeneous contraction of the crystal in two axis directions.

The Fe^{2+} salts show very large quadrupole splittings due to the additional d electron (8). Depending on the temperature this electron occupies different terms split in the crystal field. This leads to a relatively large temperature-dependent field gradient at the nucleus. The velocity spectrum of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is shown in Fig. 17b. Quadrupole splittings for Fe^{2+} ions generally fall in the range 1.7–3.6 mm/sec (19).

In the octahedral iron complexes which have been studied, two of the $3d$ orbitals of iron are used in forming the six hybrid orbitals and the $3d$ electrons are therefore accommodated in the remaining three $3d$ orbitals. These are fully occupied, for example, in a complex such as $[\text{Fe}(\text{CN})_6]^{4-}$, leading to a spherosymmetrical charge distribution. Consequently $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ exhibits no quadrupole splitting. In the case of $\text{K}_3[\text{Fe}(\text{CN})_6]$, where one electron is lacking to complete the filling of the remaining three $3d$ orbitals, splitting occurs, which, as in the case of Fe^{2+} , is strongly temperature dependent, (in place of an electron in addition to the half-filled shell in Fe^{2+} there is an electron hole in $[\text{Fe}(\text{CN})_6]^{3-}$). For nitrosyl prussiates, on the other hand, one finds a large splitting which is practically independent of temperature, as would be expected for a complex ion with closed shells and this particular symmetry. The observed quadrupole splittings in iron complexes fall in the range 0–2.6 mm/sec.

6. Magnetic Splitting

Atomic nuclei often have a magnetic moment which may be considered as arising from a mechanical nuclear spin. The total angular momentum of such a nucleus is given by Eq. (16):

$$|\vec{I}| = \frac{h}{2\pi} \sqrt{I(I+1)} \quad (16)$$

where h is the Planck constant ($h = 6.624 \times 10^{-27}$ erg sec), and I is the nuclear spin number. From quantum mechanics the maximum observable component of the angular momentum is a whole or a half-integral multiple of $h/2\pi$:

$$\vec{I} = I\hbar \quad (17)$$

The nuclear spin I must be a multiple of a half-integral or a whole number. The vectors of the magnetic moment of the atomic nucleus can have only

certain values in a magnetic field. The nuclear moment is able to take up $2I + 1$ orientations with respect to the field and the possible values are described by $2I + 1$ values of the magnetic quantum number m , namely

$$m = I, I - 1, I - 2, \dots, -(I - 2), -(I - 1), -I$$

Thus if the nuclear spin is $\frac{3}{2}$, for example, m may have the values $\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}$, and $-\frac{3}{2}$. For nuclei with $I = \frac{1}{2}$, the possible values for m are $+\frac{1}{2}$ and $-\frac{1}{2}$. Each discrete value of the magnetic moment may couple with an external field or, as in our case, with the magnetic field produced at the nucleus by the crystal field and that due to the electron shell, so that the respective energy level will be split into a group of sublevels. In the case of Fe^{57} the excited state ($I = \frac{3}{2}$) splits into 4 energy levels and the ground state into 2 energy levels, as shown in Fig. 18. In accordance with the

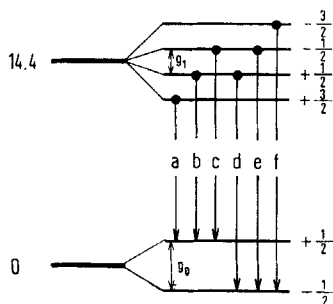


FIG. 18. Energy level scheme for the magnetic splitting of the ground state and the first excited state of Fe^{57} in metallic iron.

selection rule $\Delta m = 1, 0, -1$, the six possible transitions between the levels of the excited state and the ground state give six resonance lines in the spectrum. Figure 19 shows the velocity spectrum of metallic iron. The

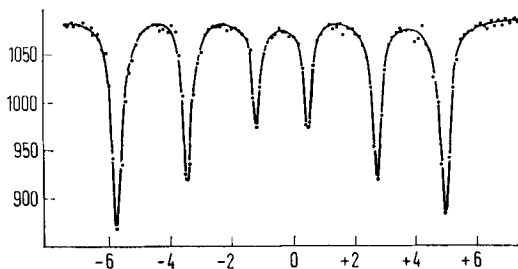


FIG. 19. Mössbauer spectrum of metallic iron at room temperature. Ordinate: transmission (arbitrary units). Abscissa: relative velocity between source and absorber (mm/sec).

splitting of the Fe^{57} ground state at 293°K is given by $g_0 = 3.924 \pm 0.008$ mm/sec, that for the excited state being 2.244 ± 0.005 mm/sec (16).

A detailed study of the Mössbauer spectrum of metallic iron was made by Hanna and associates (16, 44). The six components of the spectrum persist to temperatures in the neighborhood of the Curie point of iron (769°). Even at 766.2° the six lines may be partially resolved, but at 768.4 they coalesce to a single broad structure. Above the Curie point only a single narrow line is observable (see also refs. 38, 42).

7. Line Width

Observed line widths are, from what was said in Section II, made up of the line width of the source and the absorber. The broadening produced by a finite thickness of absorber depends on $\sigma_0 \times n \times f'$, where σ_0 is the cross section for resonance absorption, n is the thickness of the absorber, and f' is the Debye-Waller factor for the absorbing substance. This broadening was determined with the aid of the diagram based on the calculations of Margulies and Ehrmann (31). In order to obtain better comparisons, this component, which generally amounts to 0.1–0.4 mm/sec,

TABLE IV
LINE WIDTHS Γ_0 FOR VARIOUS RESONANCE ABSORBERS

Absorber	Line width Γ_0 (mm/sec)
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.248 ± 0.008
$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	0.240 ± 0.008
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	0.257 ± 0.007
$\text{Fe}(\text{COO})_2 \cdot 2\text{H}_2\text{O}$	0.230 ± 0.007
FeS (techn.)	0.9 ± 0.2
$\text{FePO}_4 \cdot 4\text{H}_2\text{O}$	0.441 ± 0.008
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	1.2 ± 0.2
$\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	1.6 ± 0.2
$\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$	0.33 ± 0.02
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0.28 ± 0.02
$\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$	0.235 ± 0.005
$\text{K}_3[\text{Fe}(\text{CN})_6]$	0.231 ± 0.005
$\text{Na}_2[\text{Fe}(\text{CN})_6\text{NO}] \cdot 2\text{H}_2\text{O}$	0.233 ± 0.005
Vacromium G	
(55% Fe, 25% Cr, 20% Ni)	0.387 ± 0.008
Fe (pure)	0.220 ± 0.006

is deducted from the measured values, thus eliminating the dependence on thickness and the temperature dependence arising from f' . Measurements with the same absorber at different thicknesses and temperatures are then in good agreement. A series of line widths Γ_0 obtained in this way are col-

lected in Table IV. It is seen that they are considerably greater in many cases than the value of $\Gamma_0 = 0.20$ mm/sec derived from the life of the 14.4-kev level of 1.0×10^{-7} sec. Disregarding very large values of the broadening ($\Gamma_0 = 0.35$ mm/sec), the approximate value of Γ_0 for Fe^{3+} salts is 0.31, for Fe^{2+} salts 0.24, for complex salts 0.23, and for metallic iron 0.22 mm/sec. The line broadening found by us (13, 24, 25, 26) for the Co^{57} source in platinum is thus 10% at the most, i.e., the source has practically the natural line width.

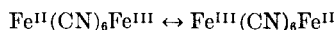
Line broadening for various absorbers may be due to different causes: (1) the Fe^{57} atoms may not be uniformly incorporated in the crystal lattice, leading to a blurring of δ and ϵ ; (2) very slow lattice vibrations may cause a change in the field gradient, which are not averaged as they are for higher frequencies; (3) magnetic interactions, even if these average up to zero; (4) with long spin correlation times the unresolved magnetic splittings give rise to a broad line.

8. Examples of Applications

The following sections describe the spectra of a number of iron compounds observed by us (13, 24, 25, 26).

a. Berlin Blue. The problem of Berlin blue appeared to us to be of special interest as its structure and color have been the subject of a great deal of speculative discussion for many years.

"Insoluble Berlin blue" results when a solution of potassium hexacyanoferrate(II), $\text{K}_4[\text{Fe}(\text{CN})_6]$, reacts with a solution containing Fe^{+++} ions in excess. It has the composition $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. The material is difficult to study chemically but with the aid of the Mössbauer effect it can be shown unambiguously that, contrary to earlier assumptions, well-defined oxidation states of +2 and +3 can be assigned to the iron atoms. They have discrete oxidation states rather than averaged values. Consequently the deep color of Berlin blue cannot be ascribed to fluctuating valencies or to resonance between structures such as



Robin (45) recently came to the same conclusion from a study of the absorption spectrum of "soluble Berlin blue."

The Mössbauer spectrum of "insoluble Berlin blue" is shown in Fig. 20a. It is made up by superposing the dotted curves. Curve I shows the line characteristic of $[\text{Fe}(\text{CN})_6]^{4-}$, while the spectrum consisting of Curves 2 and 3 represents a quadrupole splitting with the isomer shift characteristic of the Fe^{+++} ion. The ratio of intensities for the spectra 1 and (2 + 3),

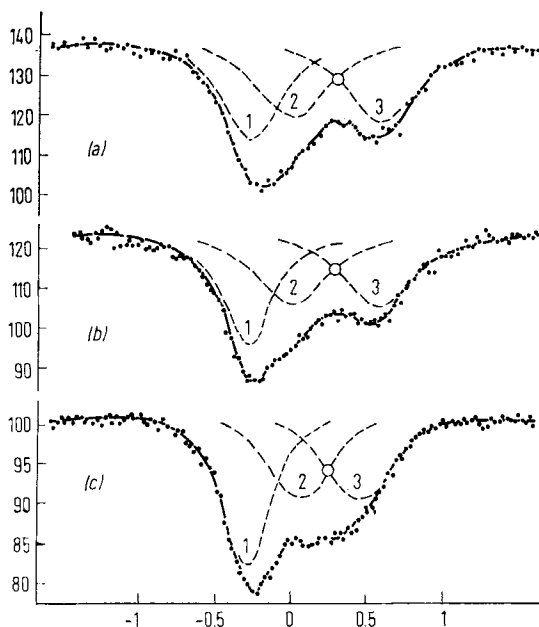
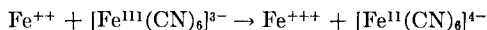


FIG. 20. Mössbauer spectrum of (a) insoluble Berlin blue,⁴ (b) Turnbull's blue, and (c) "soluble Berlin blue" at -130° . Ordinate: transmission (arbitrary units). Abscissa: relative velocity of source and absorber (mm/sec).

within the accuracy of measurement, is 3:4, corresponding to the ratio of iron atoms in the oxidation states of +2 and +3.⁴

The spectrum shown in Fig. 20b is that of the so-called "Turnbull's blue," obtained by mixing a solution of potassium hexacyanoferrate(III) with excess of a Fe^{++} solution. It may be supposed that the first reaction taking place is



The reaction products then combine to form "insoluble Berlin blue."

When solutions of $\text{K}_4[\text{Fe}(\text{CN})_6]$ and Fe^{+++} salts or $\text{K}_3[\text{Fe}(\text{CN})_6]$ and Fe^{++} ions in a molar ratio of 1:1 are mixed, "soluble Berlin blue" of the composition $\text{KFe}[\text{Fe}(\text{CN})_6]$ is produced in the colloidal form. The Möss-

⁴ The method we have used in splitting up the spectrum into separate lines allows the energy to be determined exactly, but gives intensities with an accuracy of only about 30%. The ratio of intensities for the lines 1 and (2 + 3) does not correspond exactly to the required ratio 3:4. The mean of the intensity ratio obtained from many spectra of Berlin blue, however, was 0.72, which is near the theoretical value of 0.75.

bauer spectrum of "soluble Berlin blue" is shown in Fig. 20c. Line 1 corresponds to the hexacyanoferrate(II) ions, which are also present in this compound, while the doublet (lines 2 and 3) stems from Fe^{+++} ions. Intensities of 1 and (2 + 3) are in the ratio 1:1, corresponding to the ratio of Fe^{II} and Fe^{III} in the compound. It is thus a potassium iron(III) hexacyanoferrate(II). Assuming the structure for "soluble Berlin blue" proposed by Keggin and Miles (22), which is shown in Fig. 21; the results of our

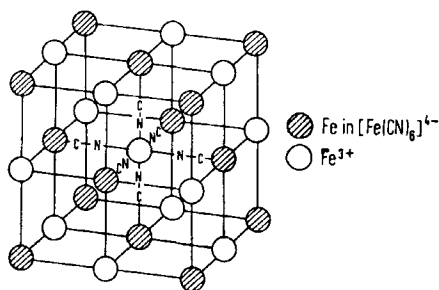
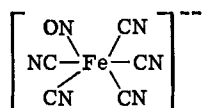


FIG. 21. Structure of "soluble Berlin blue." The potassium ions surround the central iron ion tetrahedrally (22).

investigation show that, if there are any bonds at all between iron and nitrogen, they can be only very weak and that iron in the $3+$ state occurs essentially as an ion. In the light of these results an X-ray structural study of insoluble Berlin blue would be particularly interesting. Finally, susceptibility measurements are in agreement with our data. Soluble Berlin blue has a magnetic moment of 5.72 Bohr magnetons per molecule of $\text{KFe}[\text{Fe}(\text{CN})_6]$, corresponding with five unpaired electrons per unit formula, as would be expected for a free Fe^{+++} ion.

It is notable in this connection that copper(II) and silver hexacyanoferrates(II), $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ and $\text{Ag}_4[\text{Fe}(\text{CN})_6]$, show single unsplit resonance lines with almost the same isomer shift as the potassium salt or the lines due to $[\text{Fe}(\text{CN})_6]^{4-}$ in $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. The copper(II) and silver hexacyanoferrates(III) give a Mössbauer spectrum with the strong temperature dependence characteristic of the $[\text{Fe}(\text{CN})_6]^{3-}$ ion.

b. Prussiates. The prussiates are a group of compounds in which one cyano group of the hexacyanoferrate ion is replaced by another ligand as, for example, in sodium nitrosyl prussiate, $\text{Na}_2[\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}]$ or sodium ammino prussiate, $\text{Na}_3[\text{Fe}^{\text{II}}(\text{CN})_5\text{NH}_3]$.



Nitrosyl prussiate ion

The Mössbauer spectrum of the first of these compounds is shown in Fig. 22. It consists of a doublet, the components of which are very widely split ($\epsilon = 1.723$ mm/sec at room temperature). The quadrupole splitting proves to be practically temperature independent. Similar quadrupole splittings of various magnitudes are found for other prussiates. Isomer shifts for prussiates lie in the region which is characteristic of complex compounds. As is discussed fully later, their magnitudes are characteristic of the nature of the bond between the ligands and the central iron atom.

As was described in the previous section, $[\text{Fe}(\text{CN})_6]^{4-}$ shows only a single unsplit resonance line. Because of the octahedral symmetry, the electrical field gradient and hence the quadrupole splitting is zero. The relationship is, however, different for prussiates, where the substituted ligands produce a different charge distribution, i.e., a finite field gradient is to be expected. This may have a positive or negative sign, according to the nature of the bond to the ligand in question.

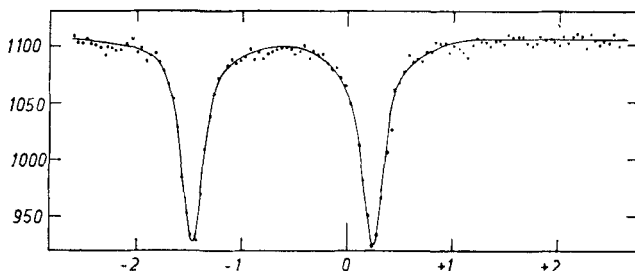


FIG. 22. Mössbauer spectrum of $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 3\text{H}_2\text{O}$. Ordinate: transmission (arbitrary units). Abscissa: relative velocity of source and absorber (mm/sec).

The cyano groups in hexacyanoferrate(II), $[\text{Fe}(\text{CN})_6]^{4-}$, are linked to the central iron atom by σ -bonds. In addition each bond has a π -component which prevents the build-up of a high negative charge on iron ("back donation"). The bond relationships are illustrated in Fig. 23 and are valid

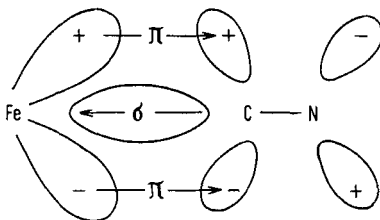
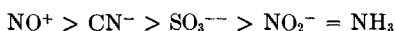


FIG. 23. Diagrammatic representation of bonding relationship between iron and a ligand with a Δ orbital.

in principle for all stable complexes. The π -bond removes charge from the central atom in accordance with the Pauling electroneutrality principle,

according to which the central atom can never have a charge greater than +1 or -1. As a result of the similar bond relationships occurring in all strong complexes, their isomer shifts all fall in a limited region situated in the position expected for Fe^0 .

When the cyanide ligand in $[\text{Fe}(\text{CN})_6]^{4-}$ is replaced by a ligand for which the π -bond has more weight, as in the example with NO^+ , the electron density of the $3d$ orbital, from which the electrons for the π -bond are derived, is diminished. As a result, the line shift of the nitroprussiate ion relative to hexacyanoferrate(II) is negative. If the cyano group is replaced by NH_3 or NO_2^- , which are unable to form π -bonds, the reverse effect occurs: a shift in the direction of higher δ values relative to $[\text{Fe}(\text{CN})_6]^{4-}$ is observed. Weak π -bonding is to be expected in the case of the sulfito complex $[\text{Fe}(\text{CN})_5\text{SO}_3]^{5-}$, since only the diffuse d orbitals of sulfur are available for π -bonding. The observed isomer shifts of prussiates thus fall into the sequence



with increasing positive values of δ as the strength of the ligand π -bonding decreases.

No account has been taken of the σ -donor effect of the various ligands in what has been said above. This is permissible since a small change in the σ -donor component has little influence on the total s electron density involved, especially as a hybrid is involved in which the s electrons play a secondary part. In this connection attention may be drawn to another phenomenon, which is also observed in other cases. The dependence of the shift for the prussiate ion on the mode of bonding of the separate ligands shows that the three π -bonds present in the octahedral complex $[\text{Fe}(\text{CN})_6]^{4-}$ are not divided among the remaining five cyano ligands if the sixth ligand is incapable of forming π -bonds. Instead the over-all π -bond component becomes smaller.

A π -bond of the separate ligand which is strong relative to CN^- leads to a positive field gradient, while for a weaker π -bond the field gradient is negative. It follows from what has been said above that only nitrosyl prussiate, $[\text{Fe}(\text{CN})_5\text{NO}]^-$, among the compounds studied, has a positive field gradient: for all others a negative field gradient must be assumed.

c. Carbonyls. Three iron carbonyls are known, namely, the pentacarbonyl, $\text{Fe}(\text{CO})_5$, the enneacarbonyl, $\text{Fe}_2(\text{CO})_9$, and the dodecacarbonyl, $\text{Fe}_3(\text{CO})_{12}$. The structures of the first two have been elucidated (11, 43) and are reproduced in Figs. 24 and 25.

In iron pentacarbonyl the five CO groups are arranged at the corners of a trigonal bipyramid. The σ -bond system is based on a $d_{z^2}sp^3$ hybrid, while the eight electrons in the d_{xy} , d_{xz} , d_{yz} , and $d_{x^2-y^2}$ orbitals serve to form

the π -bonds from iron to the CO ligands. The π -bonds prevent the accumulation of a high negative charge on the iron atom in an analogous way to that described in subsection 6b.

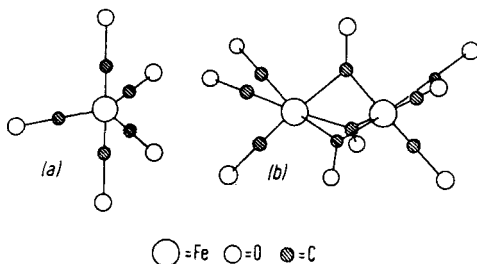


FIG. 24. Structure of iron pentacarbonyl (a).

FIG. 25. Structure of iron enneacarbonyl (b).

The trigonal bipyramidal arrangement of ligands leads to a finite electrical field gradient around the central iron atom which shows itself in the splitting of the iron resonance lines. The Mössbauer spectrum of $\text{Fe}(\text{CO})_5$ is shown in Fig. 26. It consists of two lines, the separation of which corresponds to a quadrupole splitting of 2.53 mm/sec (-133°C).

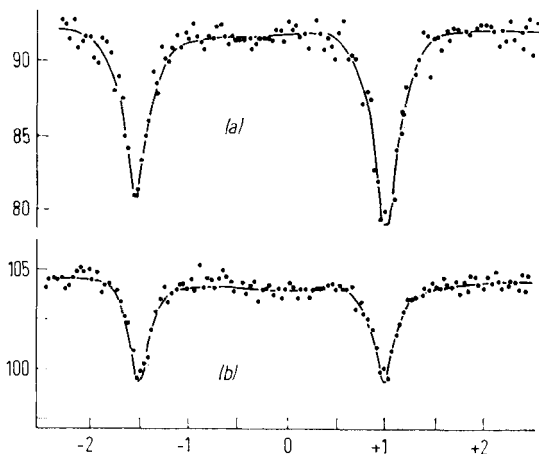


FIG. 26. Mössbauer spectrum of (a) undiluted $\text{Fe}(\text{CO})_5$, (b) $\text{Fe}(\text{CO})_5$ in tetrachloroethane. Ordinate: transmission (arbitrary unit). Abscissa: relative velocity of source and absorber (mm/sec).

The isomer shift amounts to -0.47 ± 0.08 mm/sec (-133°C). A notable feature of the spectrum of iron pentacarbonyl is that the left component of the doublet is smaller than the right. Kalvius *et al.* (21) showed by rotation of the sample that this arose from a preferred orientation of the

molecular field with respect to the direction of irradiation, and concluded that the field gradient and quadrupole moment were positive. Such a preferred orientation can occur readily in the crystallization of $\text{Fe}(\text{CO})_5$, which is liquid above -21°C . Variation in the procedure may lead to different intensity relationships for the two lines. On the other hand we found that, using frozen solutions of $\text{Fe}(\text{CO})_5$ in tetrachloroethane, the doublet consisted of two lines of equal intensity, showing that a homogeneous phase was present.

From the fact that frozen solutions may be used in studying the Mössbauer effect, two important possibilities for further application emerge: (1) isolated molecules or ions may be investigated independently of influences of the crystal lattice; (2) substances may be studied which cannot be isolated in the solid form or are stable only in solution.

In iron enneacarbonyl, $\text{Fe}_2(\text{CO})_9$, each iron atom is approximately octahedrally surrounded so that it can be assumed that the σ -bonded system is made up of $d_{e_g}^2 sp^3$ hybrids. Each of the terminal carbonyl groups contributes two electrons to the iron atom to which it is linked and each bridge CO group one, so that each iron atom has 17 electrons at its disposal, counting its own eight. Since the compound is diamagnetic the two "lone"

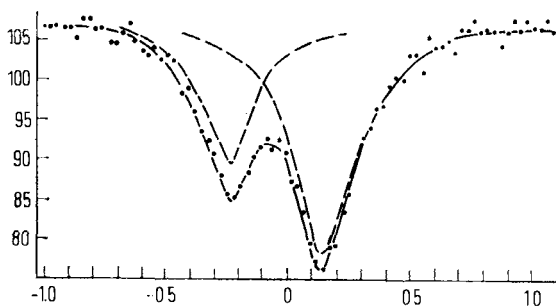
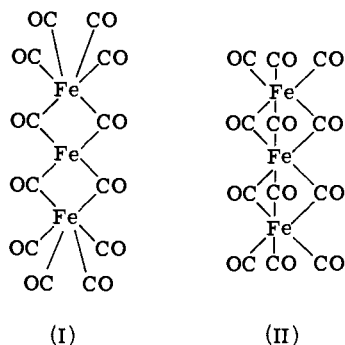


FIG. 27. Mössbauer spectrum of $\text{Fe}_2(\text{CO})_9$. Ordinate: transmission (arbitrary units). Abscissa: relative velocity of source and absorber (mm/sec).

electrons must pair their spins in some way. The relatively short iron-iron distance found by crystal structure studies led to the supposition that there may be a covalent iron-iron bond. The results of our investigations are, however, in favor of a suggestion made by Orgel (39), according to which only a weak coupling of the unpaired electron spins suffices to explain diamagnetism of $\text{Fe}_2(\text{CO})_9$. This could be brought about, for example, by the carbonyl bridges. The Mössbauer spectrum of iron enneacarbonyl is shown in Fig. 27. It exhibits a small quadrupole splitting as would be expected from the symmetrical environment of the iron atoms. The doublet

components are of different sizes and have an intensity relationship from which later discussion shows that the field gradient has a positive sign.

The structure of iron dodecacarbonyl, $\text{Fe}_3(\text{CO})_{12}$, has so far not been elucidated. From infrared spectroscopy Mills (32) favored the second of the much discussed structures I and II which have been proposed. Dahl and Rundle (6), on the other hand, believe the assumption that the three iron atoms are arranged linearly, which has been supported by many authors, is incorrect. Dahl and Rundle prefer a structure in which the iron atoms are situated at the corners of a triangle.



The Mössbauer spectrum of the compound is reproduced in Fig. 28. It consists of three lines, the two outer of which correspond. The quadrupole splitting deduced from their separation is 1.09 mm/sec. The middle line is somewhat broadened relative to the other two, which may be due to a small

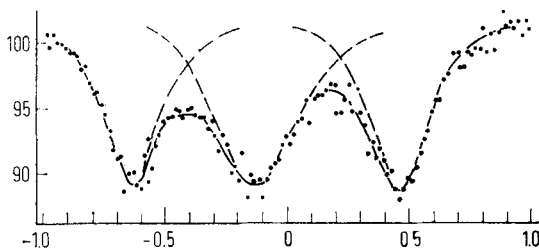


FIG. 28. Mössbauer spectrum of $\text{Fe}_3(\text{CO})_{12}$. Ordinate: transmission (arbitrary units). Abscissa: relative velocity of source and absorber (mm/sec).

unresolved quadrupole splitting. The shape of the spectrum may be interpreted only on the basis of a structural model in which the iron atoms are in a line and the outer two are equivalent. Only the first of structures I and II can be reconciled without any difficulty with the results of our experiments and with the diamagnetism of the compound. In structure I the two outer iron atoms have an octahedral bond arrangement, while the middle

iron atom makes use of a tetrahedral d^3s hybrid. In accordance with this, one would expect the two outer iron atoms, four terminal CO ligands of which are opposite two bridging CO groups, to show a positive field gradient and splitting of the resonance line. On the other hand, the tetrahedrally surrounded central iron atom should give a single resonance line. This spectrum postulated for a molecule with structure I is in fact observed. The small broadening of the middle line can be understood readily as the result of a small distortion of the tetrahedral bonds. The electron configuration which has been described will also account for the diamagnetism.

In the hypothetical structure II, all three iron atoms would use d^2sp^3 hybrids for bonding so that the t_{2g} orbitals of each iron atom would remain occupied by four electrons. The somewhat different disturbance of the octahedral symmetry for the inner and outer iron atoms would lead to a different splitting of the corresponding $3d$ electron terms. This would explain the observation that there is a strong temperature-dependent quadrupole splitting for the outer iron atoms and a small one for the inner one. This electron configuration fails, however, to provide an explanation of the diamagnetism of the compound.

Figure 29 shows the Mössbauer spectrum of $\text{Fe}(\text{CO})_4\text{I}_2$ in which, in contrast to $\text{Fe}(\text{CO})_5$, the left line is stronger than the right. This again stems from the fact that the crystals are arranged with a preferred orientation, a phenomenon which can occur in powdered crystals and which is

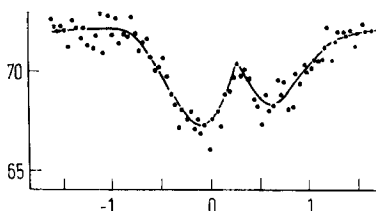


FIG. 29. Mössbauer spectrum of $\text{Fe}(\text{CO})_4\text{I}_2$. Ordinate: transmission (arbitrary units). Abscissa: relative velocity of source and absorber (mm/sec).

often encountered in X-ray investigations. If the line in the spectrum belonging to the state $m = \pm\frac{3}{2}$ lies at more positive velocities than that belonging to the state $m = \pm\frac{1}{2}$, the field gradient is positive. If the reverse is true it is negative (see in this connection refs. 13, 25). A thorough investigation of the iron carbonyls and of $\text{Fe}(\text{CO})_4\text{I}_2$ has also been made by Herber *et al.* (18).

d. Potassium Ferrate(VI) and Potassium Ferrate(III). Potassium ferrate(VI), K_2FeO_4 , shows in its Mössbauer spectrum a very broad unsplit resonance line which is shifted to the left, with a δ value of about -1.20 mm/sec at -120°C . The absence of quadrupole splitting results from the

tetrahedral symmetry of the complex $[\text{FeO}_4]^-$ ion. It is possible to find, from the position of the absorption line and the lack of splitting, which of the two possible bond hybrids directed towards the corners of the tetrahedron is used for the σ -bond system. According to Watson's calculation (53) for an sp^3 hybrid, a δ value would be expected which lies substantially lower than that measured. The $3d$ orbitals of iron would then be occupied by only two electrons, so that the screening action on the s electron density would be very small. Wertheim and Herber came to the same conclusion (55). In addition a temperature-dependent splitting should be observed with sp^3 hybridization.

In potassium ferrate(III) each iron atom is surrounded tetrahedrally by four oxygen atoms. The tetrahedra are linked at their edges. The δ value of potassium ferrate(III) is only about 0.22 mm/sec more negative than $\delta_{\text{Fe}^{+++}}$, i.e., the s electron density in the ferrate(III) is not much greater than in the free Fe^{+++} ion. The small shift is caused by the small contribution which the sp^3 hybrid makes to the s electron density, for the bonds between oxygen and iron are purely σ in character. That the contribution of the sp^3 hybrid is so small is probably related, *inter alia*, to the fact that a hybridized $4s$ electron increases the s electron density less than a normal $4s$ electron and that the bonds are also already strongly heteropolar.

e. Potassium Dithioferrate(III). In potassium dithioferrate(III), KFeS_2 , the $[\text{FeS}_2]^-$ ions are arranged in chains of FeS_4 tetrahedra linked by their edges. As in the case of KFeO_2 , the chains may be considered as multi-center ions. While KFeO_2 shows magnetic splitting up to at least several hundred degrees, this occurs for KFeS_2 only at low temperatures. Figure 30a shows the spectrum of KFeS_2 with a pure quadrupole splitting at 25° , while in Fig. 30b there is an additional magnetic splitting at -145° . The spectra with pure quadrupole splitting may be interpreted in the usual way, but it should be noted that, in the case of magnetic splitting, the electrical quadrupole splitting must also be taken into account.

Compared with a spectrum showing pure magnetic interaction, the four inner lines in the figure are somewhat shifted to the right and the two outer lines are shifted to the left, so that the spacing of the outer lines to the right and left are no longer equal. The intensities of the lines relative to one another are those which would be expected for magnetic splitting with a finite thickness of absorber. This is in agreement with the observed position of the lines. Figure 31a shows schematically how the spectrum in Fig. 30b arises: the magnetic interaction first leads to splittings of the ground state and the first excited state of Fe^{57} characterized by g_0 and g_1 ; these combine to give the structure shown in Fig. 31b, taking into account the approximate ratio of the magnitudes of the magnetic moments. The substates of the excited state with $m = \pm \frac{3}{2}$ are then displaced to lower values and that with

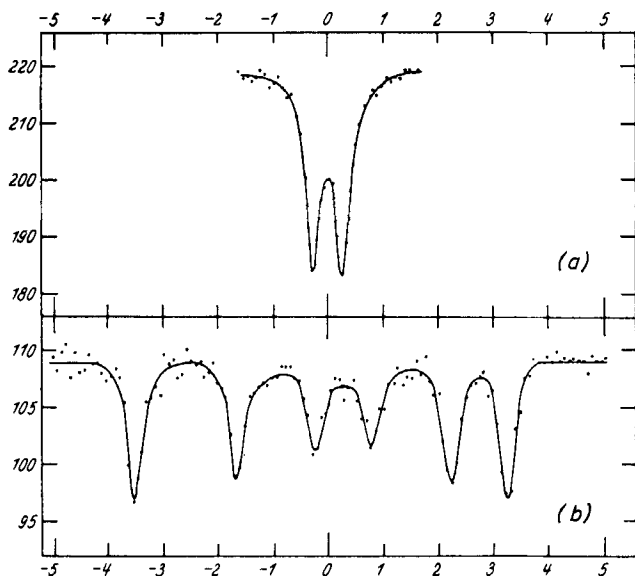


FIG. 30. Mössbauer spectrum of KFeS_2 : (a) at 25° , and (b) at -145° . Ordinate: transmission (arbitrary units). Abscissa: relative velocity of source and absorber (mm/sec).

$m = \pm \frac{1}{2}$ raised by the electrical quadrupole interaction. The six possible transitions are indicated in the spectrum. If the asymmetry parameter of the field gradient $\eta = (V_{xx} - V_{yy})/V_{zz}$ (see p. 480) disappears and the direction of the magnetic field coincides with the main axis of the field gradient, the shifts of the excited substates (Fig. 31a) are exactly $\epsilon/2$ (as

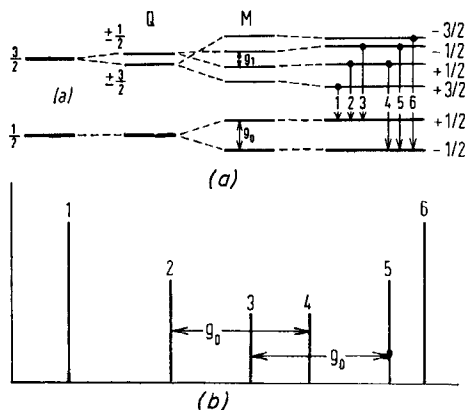


FIG. 31. (a) Energy level scheme for the superposition of quadrupole splitting and magnetic splitting. (b) Spectrum to a first approximation.

they are without a magnetic field, when they lead to a quadrupole splitting of ϵ), and a lowering of the excited substates with $m = \pm \frac{3}{2}$ and a raising of those with $m = \pm \frac{1}{2}$ correspond to a negative field gradient. In the general case, these shifts are neither equal in amount nor can conclusions be drawn from them directly about the sign of the field gradients.

The interpretation of spectra such as that in Fig. 30b may be made on the basis of the scheme shown in Fig. 31a: g_0 is obtained as the distance between the lines 2 and 4 or 3 and 5; δ is obtained as the mean value of the positions of lines 1, 2, 5, and 6 or 1, 3, 4, and 6 since the sum of the energies of interaction E_n for the four excited substates must be zero in this case: E_n is obtained similarly from the positions of the corresponding lines. Since only three of the four E_n values are independent because of the condition $\Sigma E_n = 0$, the five quantities, g_1 , ϵ , η , θ , and φ may now be determined if two of them can be evaluated in another way (θ and φ are polar and azimuthal angles of the magnetic field in the coordinate system of the field gradient).

The magnetic field at the nucleus is obtained from g_0 and the magnetic moment of the ground state of Fe^{57} . Since our standardization of velocities is based on the value $g_0 = 3.96$ mm/sec for metallic iron at 25° , and this corresponds to a field at the nucleus of 333 kilogauss, the measured values of g_0 must be multiplied by a factor of 84.09 kilogauss/mm/sec in order to obtain the magnetic field at the nucleus. For KFeS_2 the magnetic field at the nucleus decreases from 206 kilogauss at -145° to zero at -28° , but for KFeO_2 from 515 kilogauss at -123° only to 490 kilogauss at 75° . This shows the existence of a high transition point for the latter compound.

Figure 32 shows δ for KFeS_2 as a function of temperature. Near the transition point there is a deviation from the otherwise normal and approximately linear relationship. If the isomer shift is assumed to be inde-

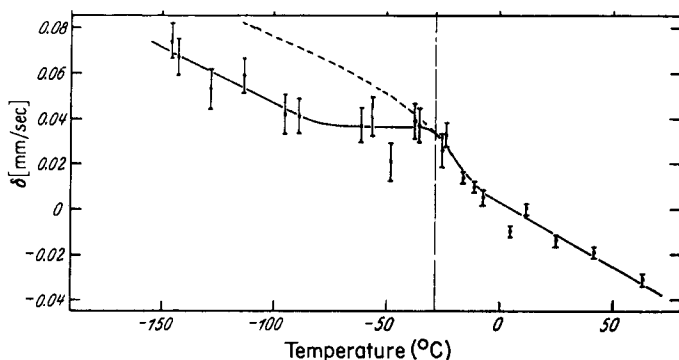


FIG. 32. Shift δ in the spectrum of KFeS_2 as a function of temperature. Ordinate: shift (mm/sec). Abscissa: temperature ($^\circ\text{C}$).

pendent of temperature, $-\partial\delta/\partial T$ is proportional to the specific heat. This is known to have a maximum at the Curie or Neel point, which the dotted curve leads one to expect. The deviation below the transition point may be explained by a temperature-dependent component of the isomer shift which is approximately proportional to the magnetic field.

f. Silicates Containing Iron. A number of typical silicates containing iron have been studied by De Coster, Pollak, and Amelinckx (9, 40). The Mössbauer absorption spectra were obtained, unless otherwise noted, with powdered silicate samples and are shown in Figs. 33–35. The isomer shifts given in this section refer to Co^{57} in Cr. The half width Γ of stainless steel as absorber was 0.48 mm/sec for the source used.

Epidote, $\text{Ca}_2(\text{Al}, \text{Fe}^{3+})_3[\text{OH}(\text{SiO}_4)_2]$, contains only one sort of Fe(III) ions, which are surrounded by O^{2-} ions. Accordingly the spectrum shows only a doublet, the center of which shows an isomer shift of 0.53 mm/sec⁵ characteristic of Fe^{3+} ions. The quadrupole splitting observed was $\epsilon = 2.07$ mm/sec. This large splitting was caused by a strong electrical field gradient resulting from the anisotropic environment. An even larger splitting for Fe^{3+} ions was observed earlier by Shirane *et al.* (47) for Fe_2TiO_5 ($\epsilon = 3.5$ mm/sec).

Augite, which may be described as a mixture of layers of acmite, $\text{NaFe}(\text{SiO}_3)_2$, and diopside, $\text{CaMg}(\text{SiO}_3)_2$, layers, contains SiO_4 tetrahedra joined by two oxygen bridges into chains. Iron in acmite is trivalent while that which partially replaces magnesium in the diopside layers is bivalent. A quadrupole splitting would be expected for both resonance lines because of the unsymmetrical environment. The spectrum of augite is reproduced in Fig. 33. It can be resolved readily into two doublets (dotted curves), the strongest of which shows an isomer shift of 1.37 mm/sec characteristic of Fe^{2+} ions while that for the second (0.54 mm/sec) is typical of the Fe^{3+} ion. The measured value of the quadrupole splittings of the first and second doublets are 2.18 and 1.08 mm/sec, respectively.

Tourmaline, which may be represented by the formula $(\text{Na}, \text{Ca})(\text{Mg}, \text{Li}, \text{Fe}, \text{Al})_3(\text{Al}, \text{Fe}, \text{Mg})_6[(\text{OH})_4(\text{BO}_3)_3\text{Si}_6\text{O}_{18}]$ is, like augite, a silicate with $\text{Si}:\text{O} = 1:3$. The oxygen tetrahedra which surround each silicon atom are linked by two corners and form closed rings rather than infinite chains. The relatively complex structure of the spectrum reproduced in Fig. 34 shows at once that the iron in this mineral is present in various states and environments. The authors have resolved the spectrum into three doublets. The first two bands are due to Fe^{2+} ions ($\delta = 1.15$ mm/sec or 1.40 mm/sec; $\epsilon = 2.10$ mm/sec or 2.61 mm/sec). Since the isomer shifts are different for the two Fe^{2+} ions, the authors discussed the result in terms of different

⁵ The shifts for the Co^{57} source in chromium used by the authors were about 0.4 mm/sec higher than for a source of Co^{57} in platinum.

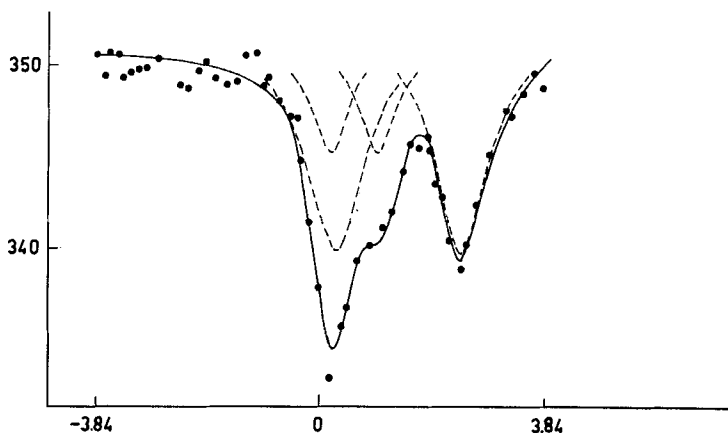


FIG. 33. Mössbauer spectrum of augite. Radiation source Co^{57} in Cr (9). Ordinate: transmission (arbitrary units). Abscissa: relative velocity of source and absorber (mm/sec).

configurations relative to the OH groups, i.e., to the different positions of the protons. The protons influence the $\pm\frac{1}{2}$ levels but not the $\pm\frac{3}{2}$ levels. The difference in interaction energy between protons and the $\pm\frac{1}{2}$ state is $0.51 \pm$

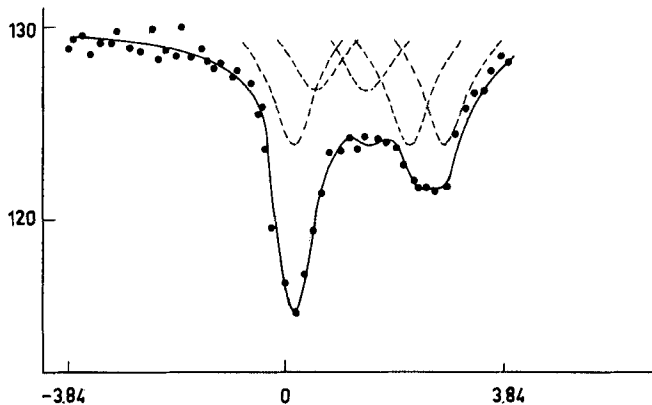
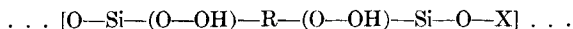


FIG. 34. Mössbauer spectrum of tourmaline. Radiation source Co^{57} in Cr (9). Ordinate: transmission (arbitrary units). Abscissa: relative velocity of source and absorber (mm/sec).

$0.07 \text{ mm/sec} = 5.8 \pm 0.8 \text{ Mc/sec}$. The third doublet is attributed to the presence of Fe^{3+} ions, although the observed isomer shift of 0.95 mm/sec is very high. The quadrupole splitting was 0.91 mm/sec .

Biotite is a micaceous mineral. The sequence of layers is of the type (10):



The lattice position R may be occupied by Mg^{++} , Al^{+++} , Fe^{++} , Li^+ , and Mn^{++} , while the X positions may be occupied by Na^+ or K^+ (56). Silicon may be partially replaced by aluminum, the missing positive charge being compensated for by replacement of a bivalent ion in the R layer by a trivalent iron ion. The structure of biotite described by Wyckoff (57) contains iron in two different environments, which may be described as distorted octahedra.

Figure 35 shows the Mössbauer spectrum of a single crystal of biotite. It consists of two bands A and B, the first of which is sharper than the second. This excludes the possibility that we are dealing with the quadrupole splitting of a single line. Rather, it supports the assumption that there are two different types of iron atom, each of which gives rise to a

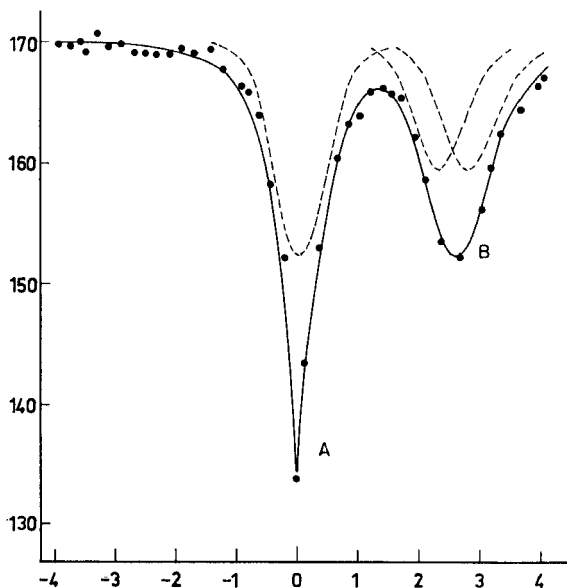


Fig. 35. Mössbauer spectrum of biotite. Radiation source Co^{57} in Cr (40). Ordinate: transmission (arbitrary units). Abscissa: relative velocity of source and absorber (mm/sec).

doublet. The centers of the doublets fall in the region characteristic of Fe^{++} ions. Resolution of the spectrum into two doublets is shown by the dotted curves in Fig. 35. The components of each doublet on the left almost coincide and are separated by 0.05 mm/sec at the most. They produce the resonance band A ($\delta = 0.022$ mm/sec). The components of the two doublets on the right lie at 2.43 and 2.83 mm/sec. The isomer shifts for the two

types of iron are 1.23 and 1.42 mm/sec, the quadrupole splittings being 2.41 and 2.81 mm/sec.

Staurolite, olivine, and actinolite give spectra which consist of a doublet. Olivine, $(\text{Mg,Fe})_2(\text{SiO}_4)$, belongs to the structures with discrete anions. The tetrahedra in $\text{Ca}_2\text{Mg}_{2-5}\text{Fe}_{0-3}[\text{OHSi}_4\text{O}_{11}]_2$ form bands, and staurolite may be described as cyanite, $\text{Al}_2\text{O}[\text{SiO}_4]$, into which $\text{Fe}(\text{OH})_2$ layers are built. In all these cases bivalent iron is in an octahedral environment and accordingly gives rise to a spectrum which is split into a doublet. The isomer shifts and quadrupole splittings are shown in Table V.

TABLE V
ISOMER SHIFT, QUADRUPOLE SPLITTING, AND LINE
WIDTHS OF SOME SILICATES (SOURCE Co^{57} IN CR)

Silicate	δ (mm/sec)	ϵ (mm/sec)	Γ (mm/sec)
Staurolite	1.14	2.22	0.88 ± 0.05
Olivine	1.35	3.04	0.70 ± 0.04
Actinolite	1.32	2.41	1.06 ± 0.09

Bronzite, $(\text{Mg,Fe})_2\text{Si}_2\text{O}_6$, also contains Fe^{++} ions and again gives a spectrum consisting of a doublet. The intensities of the two components of the doublet are somewhat different, an observation which has been made in other cases (e.g., for $\text{Fe}(\text{CO})_5$; see p. 467): it may be attributed to a preferred orientation of the bronzite crystallites.

g. Iron π -Complexes. Ferrocene or dicyclopentadienyl iron, $\text{Fe}(\text{C}_5\text{H}_5)_2$, a "sandwich" compound, in which the iron atom lies between two five-membered aromatic hydrocarbon rings (Fig. 36) and ferricinium salts, e.g.

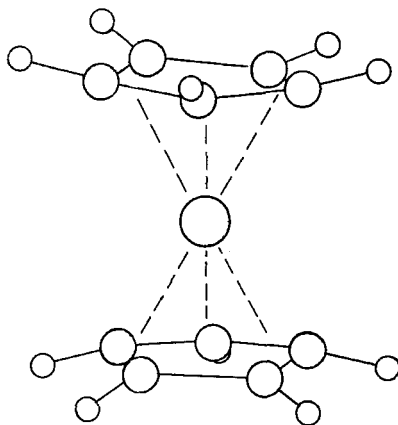


FIG. 36. Structure of ferrocene $\text{Fe}(\text{C}_5\text{H}_5)_2$.

$[\text{Fe}(\text{C}_8\text{H}_8)_2]\text{Br}$, have been investigated by Wertheim and Herber (55). Both compounds display approximately the same isomer shift, equal to 0.65 mm/sec (295°K) or 0.52 mm/sec relative to a Co^{57} source measured in stainless steel. The quadrupole splittings of the two compounds, on the other hand, are very different: ϵ for ferrocene at 20°K is 2.3 mm/sec, whereas the ferricinium ion exhibits only a small quadrupole splitting of about 0.2 mm/sec, which shows itself as a broadening of the line. In spite of the fact that strong screening of the s electrons by the ten $3d$ electrons is to be expected in ferrocene, the observed isomer shift is relatively small. In order to account for this low value, Herber *et al.* suggested that the 4s electrons participate to the extent of about 30% in the bonding. Another explanation would be the formation of π -bonds from iron to the cyclopentadienyl rings (back donation), which would involve electrons of the d_{yz} and d_{zx} orbitals. The very small quadrupole splitting in ferricinium salts is, according to Zahn *et al.* (58), due to a fortuitous compensation of the large electrical field gradients of the σ and π orbitals, on the one hand, and of the δ orbitals, on the other.

Study of a series of ferrocene derivatives shows that the bonding of the iron atom is virtually unaffected by ring substitution. Neither the isomer shift nor the quadrupole splitting changes appreciably on such substitution (55).

The small isomer shift in the cyclooctatetrene complexes $(\text{C}_8\text{H}_8)\text{Fe}_2(\text{CO})_3$ and $(\text{C}_8\text{H}_8)[\text{Fe}(\text{CO})_3]_2$ is also indicative of a well-developed π -bond system. The shifts, which were measured at 78°K, and were referred to Co^{57} in chromium, amounted to 2.3 ± 0.1 mm/sec and 1.8 ± 0.1 mm/sec. The almost equal shifts show that the environment of the iron atoms must be very similar in the two compounds. In keeping with this assumption, the line widths in the two compounds are found to be approximately the same (0.32 and 0.33 mm/sec). All observations support the conclusion made from NMR and infrared studies that the C_8H_8 rings in both compounds are planar. Table VI gives the quadrupole splittings of some iron π -complexes with cyclooctatetrene as ligand.

TABLE VI
QUADRUPOLE SPLITTINGS IN IRON π -COMPLEXES

Complex	ϵ (mm/sec)
$(\text{C}_8\text{H}_8)\text{Fe}(\text{CO})_3$	1.23
$(\text{C}_8\text{H}_8)[\text{Fe}(\text{CO})_3]_2$	1.32
$(\text{C}_8\text{H}_8)_2\text{Fe}(\text{CO})_3$	1.60
$(\text{C}_8\text{H}_8)[\text{C}_2(\text{CN})_4]\text{Fe}(\text{CO})_3$	0.86

h. Miscellaneous Compounds. α -Dipyridyl reacts readily with iron(II) chloride to form the complex $[\text{Fe}(\text{dipyr})_3]\text{Cl}_2$, the bonding being quite similar to that in hexacyanoferrate(II). The σ -bond system is a d^2sp^3 hybrid and a transfer of charge from the iron atom to the ligands is made possible by delocalized $p\pi$ orbitals. The Mössbauer spectrum of the compound shows a small quadrupole splitting which is practically temperature independent, confirming that the octahedral symmetry is somewhat distorted by the bifunctional ligands.

The spectrum of pyrites and marcasite, the disulfides of iron, FeS_2 , shows a similar largely temperature-independent quadrupole splitting. The shift for the two compounds shows that, in agreement with Klemm's magnetic measurements, iron is in the +2 oxidation state and not in the +4. The shift also falls in the range which is characteristic of complex compounds. In these two compounds, iron uses what are essentially d^2sp^3 hybrids for its bonding, the bonds having extensive covalent character. Pyrite has a rock salt lattice with dumbbells formed by two sulfur atoms ($\text{S}-\text{S} = 2.14 \text{ \AA}$) situated with their mass centers at the sites of the chloride ions. The iron atoms are then in an environment which is not strictly octahedral and this is responsible for the small quadrupole splitting.

i. Chemistry of Surfaces. Brady *et al.* (3) have opened up this interesting range of applications of Mössbauer spectroscopy. All the experiments described so far were directed towards the study of the chemistry of the absorber but, in certain problems, it is better to vary the radiation source in a suitable way. A carrier-free solution of $\text{Co}^{57}/\text{Fe}^{57}$ is added to the supernatant solution from which $\text{Fe}(\text{II})$ oxalate has been precipitated and the precipitate is filtered after some time. The Mössbauer spectrum of the radiation emitted by the material adsorbed on the surface of the precipitate is then studied, using an absorber consisting of nonmagnetic stainless steel. It is found that there is the same isomer shift and the same quadrupole splitting as in the spectrum of a Co^{57} source (on copper) with an iron(II) oxalate absorber. It is found that more than 40% of the Fe^{57} atoms adsorbed onto the surface occupy lattice sites corresponding to those in crystalline inactive iron(II) oxalate. Clearly extensive recrystallization has occurred or there has been exchange with layers of atoms below the solid surface. Analogous investigations, in which a cobalt(II) oxalate precipitate was used, led to similar results.

9. General Interpretation of Various Effects in the Mössbauer Spectroscopy of Fe^{57}

a. Temperature Shift. Temperature shifts, $-\partial\delta/\partial T$, for complex salts lie between 0.03 and 0.04 (mm/sec)/ 100° but otherwise are in the range 0.05–0.06 (mm/sec)/ 100° . With the aid of $-\partial\delta/\partial T$, the contributions of

the temperature shift to the total line shifts at low temperatures (-130°) and their differences for individual compounds may be estimated. This is needed in the discussion of finer differences. The specific heat decreases regularly with decreasing temperature, apart from the behavior at transition points (Curie point, etc.). The value of δ less the temperature shift of the absorber consequently lies between the values at -130° given in Table III and the values extrapolated to -273° , i.e., the contribution of the temperature shift to δ at -130° between 0 and $143 \times \partial\delta/\partial T$. The mean value for complex salts is -0.025 (mm/sec)/ 100° and for other compounds it is -0.04 (mm/sec)/ 100° , while differences within the two groups are of the order of 0.01 (mm/sec)/ 100° .

b. Influence of the Crystal Lattice. As may be seen from Table III, the value of δ changes little if ions such as Fe^{2+} , Fe^{3+} , $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$, or $[\text{Fe}^{\text{VI}}\text{O}_4]^{2-}$ are incorporated in different crystal lattices. The same is true for molecules such as $\text{Fe}(\text{CO})_5$, as may be seen from measurements on frozen solutions. The value of δ is thus primarily characteristic of the isomer shift of the particular iron ion or molecule. Influences of the crystal lattice on the isomer shift, as in the case of the temperature shift, must be examined in the light of more exact studies of the isomer shift. Valuable conclusions can then be drawn from small differences. Thus, for example, the value of δ for Fe^{2+} and Fe^{3+} salts changes by about 0.08 mm/sec, and for $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ in the form of K^+ , NH_4^+ , Cu^{2+} , and Ag^+ salts by about 0.06 mm/sec. These differences can no longer be explained by the temperature shift, but clearly depend for the most part on differences in the isomer shift. They may be explained by the fact that the ionic character in the copper and silver salts is reduced and that a small covalent component enters into the bonding. Occupation of the $3d$ orbitals is reduced as a result of this covalent component, and as a result the $3s$ electron density at the site of the nucleus is increased because of reduced screening. Differences which occur in the isomer shift of Fe^{2+} and Fe^{3+} salts may be explained similarly, the small value of δ for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in relation to that for $\text{Fe}(\text{COO})_2 \cdot 2\text{H}_2\text{O}$ being particularly striking.

c. Quadrupole Splitting. The quadrupole splitting, ϵ , which arises from the interaction of the electrical field gradient with the quadrupole of the excited Fe^{57} nucleus, is proportional to

$$\frac{\partial^2 V}{\partial z^2} \sqrt{1 + \eta^2/3}$$

where

$$\eta = \left(\frac{\partial^2 V}{\partial x^2} - \frac{\partial^2 V}{\partial y^2} \right) / \frac{\partial^2 V}{\partial z^2}$$

the asymmetry parameter, and $\partial^2 V/\partial x^2$, $\partial^2 V/\partial y^2$, and $\partial^2 V/\partial z^2$ (abbreviated V_{xx} , V_{yy} , and V_{zz}) are the components of the field gradient. The coordinate system may in addition be chosen so that

$$|V_{xx}| \geq |V_{yy}| \geq |V_{zz}|$$

We then have

$$-1 \leq \eta \leq +1$$

and

$$1 \leq \sqrt{1 + \eta^2/3} \leq 1.16$$

The quantity ϵ is approximately proportional to $\partial^2 V/\partial z^2$. With the aid of ϵ and $\Delta\epsilon/\Delta T$ in columns 4 and 5 of Table III, it is possible to obtain an over-all picture of how the electrical field gradient varies in different compounds. The values, which have been rounded, have been determined for ϵ at -130° and for $\Delta\epsilon/\Delta T$ in the range -130° to $+25^\circ$. The mean slope $\Delta\epsilon/\Delta T$ has been used in place of $\partial\epsilon/\partial T$ because deviations from linearity are observed for some compounds, i.e., $\partial\epsilon/\partial T$ decreases with decreasing temperature in the case, for example, of some Fe^{2+} salts.

The values of ϵ for the compounds investigated in the ranges shown appear in Fig. 16. Considering the temperature dependence of the quadrupole splitting (Fig. 16) it will be noted that for Fe^{3+} salts and $[\text{Fe}(\text{CN})_6]^{3-}$ it is relatively large, with values of $-\Delta\epsilon/\Delta T = 0.06\text{--}0.43$, whereas iron in an oxidation state of $+2$ in complexes with octahedral covalent bonding shows a very small temperature dependence of the quadrupole splitting: it is of the order of <0.01 (mm/sec)/ 100° .

For closed electron shells or half-shells, and with almost no effect due to the remaining crystal lattice, the splitting is given by the charge distribution on the ion, complex ion, or molecule in question. An over-all picture of possible splittings is obtained from simple symmetry considerations. It is $\epsilon = 0$ if there are at least two 3- or more-fold rotational axes (3-fold or more), and $\eta = 0$ if there is only one such axis. The field gradient will not be altered if a charge is mirrored at the center. Accordingly for $[\text{Fe}^\text{II}(\text{CN})_6]^{4-}$ a value of $\epsilon = 0$ is to be expected, and for the prussiates, in which CN groups are replaced by another ligand, $\epsilon \neq 0$ and $\eta = 0$. In $[\text{Fe}^\text{II}(\text{dipyridyl})_3]^{2+}$, in which iron also uses octahedral d^2sp^3 orbitals in bonding, there is no strictly 3-fold axis because of the bidentate nature of the ligands, and a small splitting is to be expected. For $\text{Fe}(\text{CO})_5$, which forms a trigonal bipyramid, there is only one 3-fold axis and thus $\epsilon \neq 0$ and $\eta = 0$ is to be expected. If iron d^3s orbitals are used in forming the σ -bonded structure of $[\text{Fe}^\text{VI}\text{O}_4]^{2-}$, which follows from the lack of splitting and from the value of δ , the $3d$ half-shell which does not participate in the

hybridization is closed. The value of ϵ should then be zero because of the tetrahedral symmetry. In $[\text{Fe}^{\text{III}}\text{S}_2]^-$ and $[\text{Fe}^{\text{III}}\text{O}_2]^-$ with sp^3 configurations, the chain structure of the anion should give rise to a small splitting. All these expectations are fulfilled, as may be seen from a glance at the table. Thus values of ϵ may be predicted reasonably well.

d. Bond Character. Like the values of the quadrupole splitting, those of the isomer shift are characteristic of the way in which iron is bonded. The ideas on the relationship between isomer shifts and s electron densities, which were developed by Walker *et al.*, have already been mentioned (p. 454). The values of δ , measured by us, referred to Co^{57} in platinum as a radiation source and those expected for configurations from $3d^4$ to $3d^8$ are shown in Fig. 37.

In Fig. 37, $[\text{Fe}^{\text{VI}}\text{O}_4]^{2-}$ has the highest s electron density at the nucleus of iron. For this ion, bonds based on sp^3 or d^3s hybrids could be assumed. The first possibility can, however, be discarded at once, for with the $3d^2$ configuration and a $4s$ contribution, a considerably greater s electron density would be expected (see Fig. 13). The absence of quadrupole splitting leads to the same conclusion. There must therefore be d^3s hybridization. If, in keeping with the model of the donor bond, one electron of iron is included in each of the four hybrid orbitals so that the formal configuration $3d^5 4s^1$ results, one obtains the right order of magnitude for the shift, the observed value of which lies between $3d^5$ and $3d^4$. The greater s electron density compared with $3d^5$ is to be explained in terms of the $4s$ contribution.

As a first approximation the rough picture of bonding which has already been employed is useful. The application of more exact functions for the $3d^n 4s^m$ configurations, which take account, for example, of $4s$ - $3s$ screening, and also the consideration, in part at least, of the actual bonding hybrid functions, should result in considerable improvement in the calculation of line shifts, δ . Probably the components of the hybrid functions may be replaced to a good approximation by the components of the functions from which the hybrid functions are formed by linear combination, though the orbitals concerned must then be occupied in a suitable way. Using first the simplified picture of the covalent bond, where one electron of the bonding orbital is assigned to iron, one has, in place of the full occupation of one spin direction, half occupation of both spin directions. In general, this leads in the case of a $3d$ orbital to a somewhat stronger screening of the $3s$ electrons and, in the case of the $4s$ orbital, to a somewhat larger contribution to the s electron density.

The line shifts of iron bonded in a complex all fall in the same range irrespective of the formal oxidation number, as may be seen from Figs. 12 and 37. Metallically bonded iron also falls in just the same range. To explain this phenomenon we must recall the Pauling electron neutrality principle,

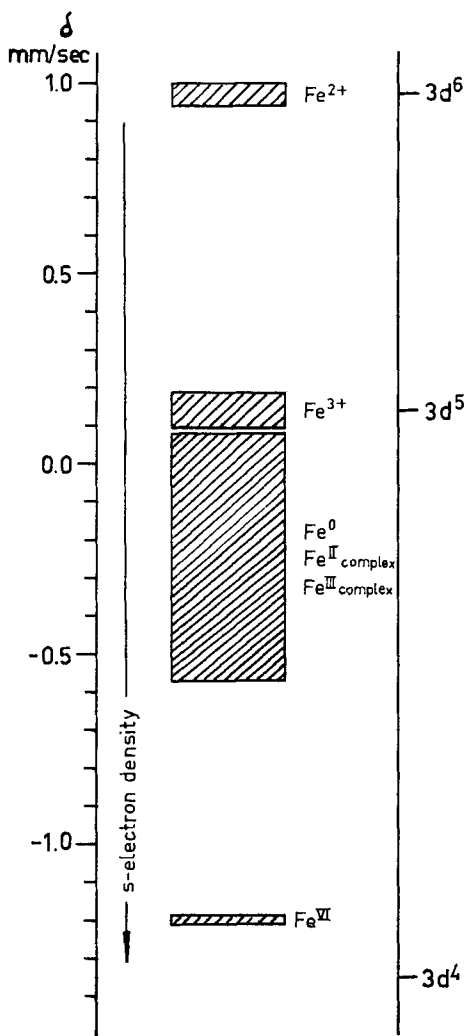


FIG. 37. Characteristic ranges for the shift δ with theoretical values for the configuration $3d^n$.

according to which the charge adjusts itself between the central atom and its covalently bonded ligands in such a way that the effective charge on the central atom remains between -1 and $+1$. This charge adjustment may be brought about in many cases by π -bonds, which occur in addition to σ -bonds. In other cases, however, as for example for $[\text{FeO}_4]^{2-}$ with O^{2-} ligands, this mechanism is impossible. In such circumstances charge adjustment is brought about by increase in the ionic component of the σ -bond.

Where possible, relatively strong π -bonds occur in addition to σ -bonds in all the complexes considered. These are formed between the 3 orbitals of iron which are not involved in σ -bonding and suitable orbitals of the ligands. In this way 3d electrons and the s electron density at the nucleus increase. For Fe^0 with dsp^3 bonding four π -bonds are possible, while for $\text{Fe}^{II}(d^2sp^3)$ three and for $\text{Fe}^{III}(d^2sp^3)$, because of the missing electron, only two π -bonds can be formed. With maximum π -bond formation there are in all three cases five 3d electrons and a decrease of the formal charge to -1 . This explains the practically identical δ values for $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$. The fact that $\text{Fe}(\text{CO})_5$ shows almost the same δ value may be understood in terms of the stronger π -bonding of CO ligands compared with CN^- ligands.

From the δ values of metallically bonded iron in Table II it follows that, with the introduction of metals which are more electronegative than iron, the s electron density at the iron nucleus becomes smaller. Introduction of more positive metals causes it to increase as is shown, for example, by the values for Cr and Mn given by Walker *et al.* (52). On the whole, δ values vary in accordance with Pauling's scale of electronegativities. More electro-positive metals withdraw more 4s electrons from iron, as indeed would be expected. In place of the effective $3d^7 4s^1$ configuration of metallic iron, which has been variously proposed, the configuration $3d^{6.4} s^x$ with $x > 1$ seems to us to be more suitable since the 4s electrons play the chief role, according to what has been said. Occupation of the 3d levels by more than six electrons is also less probable.

Relatively small line shifts δ are, however, attributable to the isomer shift if the differences due to the influence of the crystal lattice on the isomer shift and the differences of the temperature shift are sufficiently small. These small differences may be used to determine the relative strengths of bonding of the various ligands, although absolute values for the strength of the π -bond cannot be given directly.

The prussiates, for example, are especially suitable for these investigations. If the new ligand establishes a stronger π -bond with the iron than CN^- , the 3d occupation is reduced and one obtains a bigger s electron density at the iron nucleus and a positive field gradient. Correspondingly, a weaker π -bond gives a lower s electron density and a more negative field gradient. Since the field gradient disappears in $[\text{Fe}(\text{CN})_6]^{4-}$, one has with stronger π -bonding the field gradient of a positive, and with weaker π -bonding that of a negative charge distribution in the direction of the substituents. A review of the behavior of various substituents for the CN^- group in $[\text{Fe}(\text{CN})_6]^{4-}$ is given in Section III, B, 8, b.

In principle, analogous investigations may also be made for $\text{Fe}(\text{CO})_5$. Similar relationships would be expected when a CO group is replaced, i.e.,

for weaker π -bonding components of the new ligands a smaller s electron density may be anticipated. Because of the different symmetry the behavior of the field gradient will, however, be different from that for prussiates. An over-all description is given by a simple model: negative charge is withdrawn in the direction of the bond from the spherically symmetrical charge distribution $3d^{10}4sp^3$. The field gradient corresponds to that in the center of a trigonal bipyramid at the corners of which there are equal positive charges at the same distance from the center. This gives a large positive field gradient, as is observed for $\text{Fe}(\text{CO})_5$. If a π -bond is removed, this means that the positive charge at one corner of the bipyramid is reduced. The field gradient will become zero if this positive charge decreases to half its initial value and will become negative on further reduction. Depending on the strength of the π -bond which is removed, the field gradient may become smaller or even negative. The values of δ and ϵ for the compound $\text{Fe}(\text{CO})_4\text{I}_2$, which results when one CO group in $\text{Fe}(\text{CO})_5$ is substituted by I_2 , are in good agreement with this conception. No π -bond is formed in this case between I_2 and Fe because the $5p$ and $5d$ orbitals of iodine are too diffuse for a bond.

10. Mössbauer Spectroscopy of Sn^{119}

As may be seen from the data in Table I, the isotope Sn^{119} should be very suitable for studying the Mössbauer effect. γ -Quanta of 24-keV energy are emitted in the transition from the first excited state to the ground state. The conversion coefficient α is 7.3. It follows from the Doppler theory that the energy ΔE with a relative velocity v of source and absorber is $\Delta E = (v/c)E$ with E being the γ -ray energy, i.e., for a 24-keV γ -quantum, 8×10^{-8} eV per cm/sec.

A large number of tin compounds were investigated by Kistner and associates (28). The observed isomer shifts and quadrupole splittings are shown in Table VII. The isomer shifts relate to a white tin source and fall in three regions which appear to be characteristic of Sn^{2+} and Sn^{4+} compounds and of tin in alloys.

In interpreting the observed shifts, the authors related them to the most probable electron configurations of tin in these compounds. The ordinate in Fig. 38 shows the number of $5p$ electrons of the tin, while the abscissa gives the number of $5s$ electrons. Starting from the assumption that the sp^3 configuration is present in gray tin or that the sum of the s and p electrons is 2 for compounds in which tin has an oxidation number of +2, (i.e., the shifts lie on the line $s + p = 2$, and mainly in the region of $s = 2$), there are a number of regions in the diagram in which the members of the various classes of compound should fall. Compounds of tin in which it has an oxidation number of +4 should fall in a region which lies to the right

TABLE VII
 ISOMER SHIFTS AND QUADRUPOLE SPLITTINGS OF Sn^{119}

Compound	δ (mm/sec)	ϵ (mm/sec)
SnF_2	+0.85	1.58
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	+1.09	1.24
SnBr_2	+1.38	—
SnSO_4	+1.41	0.90
SnO	+0.13	1.30
SnS	+0.85	1.13
SnF_4	-2.77	2.03
$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	-2.26	—
SnBr_4	-1.32	—
SnI_4	-1.19	—
$\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$	-2.82	—
SnO_2	-2.54	—
SnS_2	-2.23	0.80
Mn_4Sn	+0.70	—
Sn in Fe, Ni, Co	-1.00	—
SnNb_3	-1.00	—
SnV_3	-0.98	—
Sn_2Ir	-0.79	—
SnPt	-0.65	—
SnAu	-0.18	—

of the point $s = 0$, $p = 0$; in these a small total number of electrons is to be expected. That this total number is not equal to zero expresses the fact that the bond is covalent to some extent in character in these tin(IV) compounds. Kistner *et al.* have tentatively drawn in the diagram lines of constant isomer shift, i.e., of constant s electron density on the nucleus. The straight lines run almost parallel to the ordinate, from which it may be deduced that the p electrons do not screen the s electrons to any considerable extent.

Detailed studies of tin compounds have also been carried out by Goldanski *et al.* (14a).

IV. Prospect

An attempt has been made in the foregoing pages to describe the nature of the Mössbauer effect and its significance in chemistry. Looking back on what has been said in the various sections about the conclusions reached with the aid of the Mössbauer effect on the structure of iron compounds and the nature of the bonding, it is probably true to say that Mössbauer spectroscopy is no less fruitful than other physical methods. Moreover, it is able to solve problems which, in many cases, other methods are unable to answer. The study of other compounds will clarify many points where,

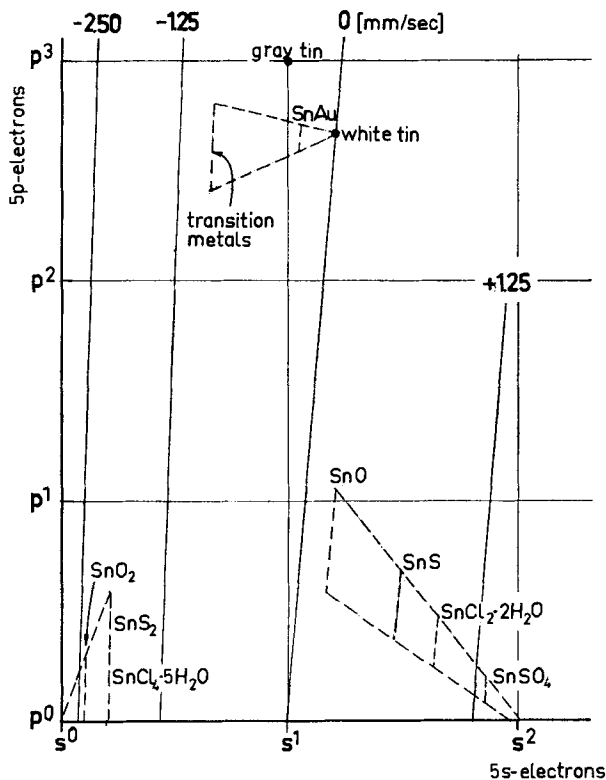


FIG. 38. Schematic coordination of isomer shifts in Sn(II) and Sn(IV) compounds and in Sn alloys (28).

at the moment, because of the relatively small amount of empirical information, only speculation is possible. Further progress will also doubtless come from the extension of the measurements to the nuclei of other elements. Even if Mössbauer spectroscopy, because of the lack of suitable isotopes, is incapable of application to all areas of chemistry—and this is true of almost every method—it will be able in many cases to contribute to the solution of chemical problems.

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