

Advances in
INORGANIC CHEMISTRY
AND
RADIOCHEMISTRY

EDITORS

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VOLUME 5

1963

ACADEMIC PRESS INC.



NEW YORK

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ACADEMIC PRESS INC.

111 Fifth Avenue, New York 3, New York

United Kingdom Edition published by

ACADEMIC PRESS INC. (LONDON) LTD.

Berkeley Square House, London W.1

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 59-7692

PRINTED IN THE UNITED STATES OF AMERICA

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THE STABILIZATION OF OXIDATION STATES OF THE TRANSITION METALS

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I. Introduction and Scope

A number of reviews (39, 40, 41, 66) have been written on the stabilization of unusual oxidation states of transition metals, but, as time goes by, it becomes more and more apparent that, in this context, the word "unusual" is purely relative and sometimes meaningless. A transition metal atom, when examined in chemical combination, will be in an oxidation state that is stabilized by its chemical environment in the compound under examination. This stability may be either thermodynamic, i.e., due to an unfavorable free energy change associated with the most probable decompositions, or kinetic, i.e., due to an unfavorable free energy of activation associated with the most probable decompositions, generally an electron-transfer process between the metal and the ligand. The definition of a usual oxidation state refers to oxidation states that are stable in environments made up of those chemical species that were common in classical inorganic compounds, e.g., oxides, water and other simple oxygen donors, the halogens, excluding fluorine, and sulfur. Nowadays, however, such species constitute only a minority of the vast number of donor atoms and ligands that can be attached to metals, so that such a definition of normality has historical, but not chemical, significance. On the occasions, in this article, when it will be convenient, for the sake of brevity, to make use of the term "unusual oxidation state," it will be with this definition in mind.

This article will discuss the ways in which the chemical environment may stabilize a particular oxidation state and will attempt to rationalize the dependence of the oxidation state upon the various electronic promotion energies of the transition metal atom or ion and the pertinent properties of the chemical environment.

The concept of an oxidation state also requires some clarification. In ionic compounds, where there is little sharing of electrons between the metal and its environment, it is easy to give the term "oxidation state" a definition that has chemical significance, but as soon as the covalent contribution towards the bonding becomes significant, the concept of oxidation states becomes less precise and the discussion of the oxidation states of atoms in essentially covalent compounds has little physical reality.

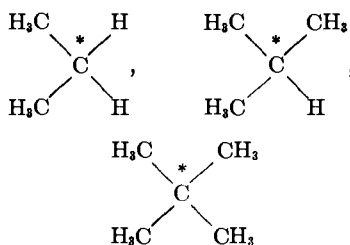
One of the basic empirical concepts that has been applied to coordination compounds is the Principle of Electroneutrality as propounded by Pauling (58). It is pointed out that, on the formation of a compound, charge is transferred wherever possible, to maintain the electroneutrality of each atom. Variations of up to $\pm\frac{1}{2}$ of an electronic charge (e), depending on the electronegativities of the atoms constituting the bond, are considered permissible, but any charge separation greatly in excess of this will lead to instability provided no other factors become important. Although difficulties arise in quantitatively defining an envelope for each atom within which the charge balance between the positive nucleus and the negative electrons can be assessed, it would appear that, if this electroneutrality principle is accepted, the physical reality of oxidation state vanishes unless one believes that in all complexes the metal atom strives to achieve a true oxidation state between -1 and $+1$ and that any deficiency or excess of electronic charge is spread as much as possible over the whole complex ion or molecule.

Provided that it is realized that the concept of an oxidation state can often have little chemical reality when applied to an atom engaged in bonding, there is no doubt that, as a working hypothesis to discuss the stoichiometry of compounds and to systematize the teaching of descriptive inorganic chemistry, the concept is extremely useful.

For the purposes of *this* article the term "oxidation state" will be defined formally in the usual way, e.g., as the charge left on the metal atom after all the attached ligands have been removed in their closed shell configurations, e.g., chlorine as Cl^- .

The definition of oxidation state by an analytical procedure works well when one can decide unambiguously which electron configuration to confer on the ligand when it is withdrawn. The outstanding cases that present difficulty are hydrogen which can be withdrawn as H^+ or H^- , nitric oxide which can be withdrawn as NO^- , NO^+ , or even NO (48), and the many important new complexes that contain metal-metal bonds. The

former cases can often be resolved by applying chemical knowledge of the way in which the ligand is behaving in the compound in question, i.e., in HCo(CO)_4 , the ability to form the sodium salt of the anion Co(CO)_4^- suggests that the hydrogen is protonic in character. In nitric oxide complexes the problem is more difficult to resolve unless one can determine the extent to which an odd electron is transferred to or from the nitric oxide molecule. The case of metal-metal bonding is of interest with respect to the parallel that it presents with the carbon-carbon bond in organic compounds. When the two atoms forming the bond have virtually identical electronegativities one must assume equal sharing of the bonding electrons with a result that the analytical definition of oxidation state splits bonds between like atoms homolytically, these bonds, therefore, being ignored in the computation of the oxidation state. This, unfortunately, gives rise to the paradox that in methane CH_4 the oxidation state of carbon is IV, whereas in ethane $\text{H}_3\text{C}-\text{CH}_3$ it is III, and the oxidation state of the asterisked C atoms in the compounds



and

are II, I, and 0, respectively. Chemically, all these carbon atoms resemble one another far more than do the carbon atoms in CH_4 and CCl_4 to which are both formally ascribed the oxidation state IV. Also, in the complexes $\text{Co}_2(\text{CO})_8$ or $\text{Mn}_2(\text{CO})_{10}$, where there is a metal-metal bond, the metals are in zero oxidation state. The discovery of compounds containing heteronuclear metal-metal bonds present difficulties that are less easily resolved (1, 13, 18, 37, 54, 65). It is proposed that these bonds be treated computationally as if they were homonuclear, unless there is a clear chemical reason for doing otherwise. It might be thought that the valency of the metal atom would be a more reliable concept to use than its oxidation state. The oxidation state of the atom is often, but by no means always, equal to the valency of the atom. The differences always arise in the cases that have just been discussed, i.e., those compounds whose electronic interactions are not self-evident from their composition. In order to assign a valency to an atom in a particular environment it is necessary to have some prior information about the mode of bonding. When applied to the case of carbon, the ambiguities that arise in the assignment of an oxidation

state in the above compounds do not appear in the assignment of a valency, which is always 4.

It should be realized that, since the concept of an oxidation state is only an artificial aid to the systematization of inorganic chemistry, effort should not be wasted in attempting to reconcile those areas of chemistry where the concept breaks down with the main mass of inorganic chemistry where it holds and is usefully applicable.

It has often been thought that magnetic and spectroscopic studies of transition metal complexes can give information about the oxidation state of the metal atom. These properties, however, arise mainly from the electrons *not* involved in chemical bonding and give little information about the electrons whose loss, or gain determines the oxidation state. An exception might be made of studies of characteristic infrared frequencies assigned to the metal-ligand bond or diagnostic bonds in the ligand itself which, in favorable circumstances, will provide information about the way in which the ambiguous ligands, e.g., H, NO, O₂, etc., are bound in the compound under examination.

It is necessary, finally, to define what will be meant, in this article, by a stable oxidation state. Stability that arises from kinetic considerations can lead to compounds that possess a whole spectrum of lifetimes ranging from those that are capable of existing indefinitely under suitable conditions to those which have only a transient existence and can only be demonstrated by an interpretation of kinetic data in *redox* reactions. The modern view of chemistry does not insist that isolation is a prerequisite of identification and, since modern techniques allow analysis and identification of transient molecules in a very short space of time, it is difficult to know where to draw the line. Rather than be forced, for the sake of consistency, to ignore all compounds that are thermodynamically unstable but kinetically stable, it is proposed to consider only those compounds that exist long enough for them to be isolated and characterized.

II. The Effect of the Environment upon the Stability of the Oxidation State of the Metal

A. GENERAL

The study of isolated atoms in high oxidation states simply requires the provision of sufficient energy to remove electrons from the atom and a means of observing the result before recombination can take place. The oxidation states produced will depend entirely on the ionization potentials of the atoms and the strength of the applied field. Such conditions obtain in high energy discharges, and arc and spark spectra show contributions from oxidation states far greater than those encountered in chemical com-

bination. Although the data obtained from these studies greatly assist our understanding of inorganic chemistry and will be drawn on extensively in the later part of this article, it is not necessary, in inorganic chemistry, to consider the chemical properties of isolated atoms or ions, in fact, an isolated atom does not have chemical properties (15). In an element or compound the atom under examination is always surrounded by chemical environment of like or unlike atoms. The atom and the environment interact and the stability of the possible oxidation states will depend upon the nuclear charge and electronic configuration of the atom and the properties of the environment.

The factors that determine the contribution of the metal to the stabilization of a particular oxidation state will be discussed in the next section and it is now necessary to examine the ways in which the environment interacts with the metal ion.

In general, the main influence of the environment will come from the nearest neighbors. The interaction can vary from the essentially electrostatic forces between ions to the complete electron exchange of the covalent bond. If the interaction is to remain essentially electrostatic it is necessary both for the anion to have minimum polarizability and for the cation to have minimum polarizing power. Polarization interaction will lead, either to significant covalent contributions to the bonding, which while not decreasing the formal oxidation state of the cation, reduces the positive charge in its vicinity, or to complete transfer of an electron from the anion to the cation, leading to a redox reaction. If the latter change takes place, the metal must have been not only in an oxidation state that is unstable with respect to its environment but also able to react with it. Such a situation is of interest to this discussion only when we consider the effect of a substitutionally labile environment. While realizing that a description of the interaction with the environment in terms of purely electrostatic or purely covalent bonds would be inadequate and probably misleading, it is convenient to discuss the extreme cases and to interpolate to achieve reality.

B. THE ELECTROVALENT COMPOUND

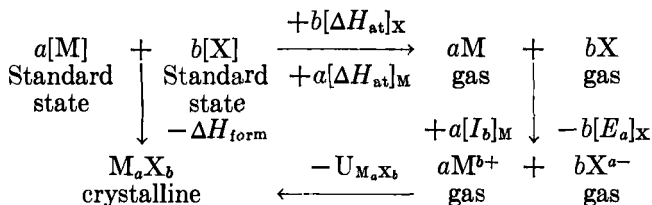
The first limiting type of compound to be discussed is that in which positively and negatively charged components of finite size are held together by a combination of electrostatic and repulsive forces in a crystalline lattice. The stability of a particular oxidation state of a cation in such a solid can be assessed by calculating the free energy of formation (ΔG_{form}^0) of the compound from its elements in their standard states. If (ΔG_{form}^0) is large and negative then the product will be very stable. This consideration, however, does not take into account the possibility of disproportionation into compounds other than the elements and this will be

discussed separately. Whereas it is not always easy to measure or calculate free energy charges, sufficient data are available to calculate the enthalpy of formation (ΔH_{form}). The two quantities are related by the expression

$$\Delta G = \Delta H - T\Delta S$$

and provided that $T\Delta S$ is small compared to ΔH it can be ignored. It should be noted that at 298°K $T\Delta S_{\text{form}}$ of sodium chloride is -6.45 kcal/mole, (7% of ΔH_{form}) and is mainly due to the entropy loss of the gaseous chlorine ($T\Delta S = 7.94$ for $\frac{1}{2}\text{Cl}_2$ at 298°K) (36). If the heat of formation of a salt is large, >50 kcal/mole, then this compound will be thermodynamically stable. When the heat of formation is small (either positive or negative), the stability may very well be controlled by the entropy of formation. Large positive enthalpies of formation indicate that the compound has little chance of existence.

It is possible to calculate a value for the heat of formation of an electrovalent compound by means of the well known Born-Haber cycle as follows:



The processes involved in this cycle are, (1) the conversion of the elements in their standard states to gaseous atoms and the provision of the appropriate heats of atomization $[\Delta H_{\text{at}}]$, (2) the conversion of the atoms to ions, processes involving the appropriate ionization potential of the metal $[I_b]_{\text{M}}$ and electron affinity of the nonmetallic element $[E_a]_{\text{X}}$, and, (3) the combination of these ions to form the crystalline solid which is accompanied by the release of the lattice energy U . Thus, if the heats of these individual reactions can be calculated independently, an approximate value can be obtained for the enthalpy of formation of the compound. The agreement between this value and the experimentally determined heat of formation will depend, not only upon the accuracy of the data used in the calculation, but also upon the validity of the simple electrostatic picture. The quantities are related by the simple expression:

$$-[\Delta H]_{\text{M}_a\text{X}_b} = -a[\Delta H_{\text{at}}]_{\text{M}} - b[\Delta H_{\text{at}}]_{\text{X}} - a[I_b]_{\text{M}} + b[E_a]_{\text{X}} + U_{\text{M}_a\text{X}_b}$$

The heats of atomization are often known accurately, the ionization potentials of the metals are known from spectroscopic measurements and the electron affinities of the nonmetallic elements can sometimes be measured

and often estimated. The lattice energy cannot be measured directly by an independent method but can be calculated in favorable circumstances. As it depends upon ionic charges and lattice geometry it can be evaluated approximately by comparison with other isomorphous compounds or by the various computational approximations that are available. Of all the thermal quantities used in the Born-Haber cycle, that most amenable to experimental measurement when the compound in question is known is the heat of formation. Thus one usually finds that electron affinities and lattice energies are often calculated using the Born-Haber cycle. Using the concept of the electrostatic bond and the Born-Haber cycle it is proposed now to see how the various properties of the environment affect the stability of a particular oxidation state when the bonding is essentially ionic. It will be convenient to limit this discussion to the monatomic ions of group V, VI, and VII and the B subgroups which are isoelectronic with the inert gases.

1. Heats of Atomization

The heats of atomization of many elements are known with reasonable accuracy. For elements that are gaseous and diatomic in their standard state, the heat of atomization is equal to one half of the bond dissociation energy. The heats of vaporization of liquid elements and the heats of melting or sublimation of solid elements must also be taken into account. Difficulties may sometimes arise when the electronic configuration of the element in its ground state requires some change during the process of atomization, e.g., the triplet-singlet transition of oxygen. Selected values of heats of atomization are given in Table I.

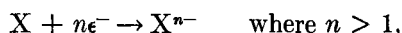
TABLE I
HEATS OF ATOMIZATION OF SOME ELEMENTS FROM THEIR
STANDARD STATES AT 298° (kcal/mole) (20)

<u>F</u>	<u>Cl</u>	<u>Br</u>	<u>I</u>
18.5	28.9	26.7	25.4
<u>O</u>	<u>S</u>		
59	57		
<u>N</u>	<u>P</u>	<u>As</u>	
113	75	60	
<u>C</u>	<u>Si</u>		
171	<105		

An important point is that the heats of atomization of anions will make only a small contribution to the stabilizing effects of the environments produced by these elements.* Apart from carbon, and to a lesser extent nitrogen, which require more than the average amount of energy, each need between 20–30 kcal/gm ion when compared on equal terms, i.e., one oxygen atom is equivalent to two fluorine atoms, etc.

2. Electron Affinities

In recent years many independently evaluated electron affinities have been published and discussed in review articles. Although it is possible to evaluate single electron affinities for reactions of the type $X + e^- \rightarrow X^-$, it is still not possible experimentally to determine values for the addition of more than one electron. In general, the values quoted for reactions of the type



are obtained from the Born-Haber cycle assuming wholly ionic bonding. It is, therefore, not strictly correct to feed these data back into any other Born-Haber cycle. However, comparable values can be found for the electron affinity of oxygen $O + 2e^- \rightarrow O^{2-}$, from many oxides of the types M_2O and MO (47) and so it is not unreasonable to believe that the value is reasonably correct and that the original assumption that the bonding is essentially ionic does not depart significantly from the truth. Calculations based on extrapolation techniques also yield values similar to those found from heats of formation (48), but it should always be remembered that a

TABLE II
ELECTRON AFFINITIES, I.E., EXOTHERMICITY OF THE REACTION
 $X + e^- \rightarrow X^{a-}$ IN KCAL/MOLE (60)

	<u>F</u>	<u>Cl</u>	<u>Br</u>	<u>I</u>	<u>O</u>	<u>N</u>
(i) $X + e^- \rightarrow X^-$	83	88	82	75	54	-16
	<u>O</u>	<u>S</u>	<u>Se</u>			
(ii) $X + 2e^- \rightarrow X^{2-}$	-156	-80	-97			
	<u>N</u>					
(iii) $X + 3e^- \rightarrow X^{3-}$	-547					
	<u>C</u>					
(iv) $X + 4e^- \rightarrow X^{4-}$	-708					

* For metals in the early transition series, the heat of atomization is so large (e.g., W, 200 kcal/mole) that compounds are formed in lower oxidation states which involve metal-metal binding as well as covalent metal-halogen and ionic bonds. (See $MoCl_2$, p. 32.)

“theoretical” calculation can always approach the “right answer” provided that this is known beforehand.

Some accepted values are given in Table II. It is immediately apparent from Table II that the halogens possess an overwhelming advantage over all the other elements in the energetics of ionization. The addition of extra electrons to a negatively charged ion is energetically unfavorable in spite of the approach to a closed shell configuration because of the repulsion between the negative charges on the ion and on the electron. Thus, oxygen and nitrogen require a considerable amount of energy to form the O^{2-} and N^{3-} ions and were it not for the other compensating factor which will be discussed below, ionic oxides and nitrides would not be thermodynamically stable.

3. Lattice Energies

Continuing the purely electrostatic description of ionic compounds, it is necessary to consider the energy that is released when the ions are assembled in the crystalline lattice. This lattice energy makes a major contribution to the heat of formation of the compound. The calculation of lattice energies has been the subject of many reviews (21, 64) and it is not necessary to discuss the topic in great detail in this article. The “experimental” lattice energy is a quantity that can be calculated by means of the Born-Haber cycle provided the other data are known or can be estimated satisfactorily. In principle, it is possible to calculate the lattice energy in terms of a summation of the individual electrostatic interactions between lattice points, but it is necessary to know the charges, the lattice geometry and inter-nuclear distances for the compound in question. A comparison of the “experimental” and calculated lattice energy will give some indication of the extent to which the electrostatic model is correct and significant differences in the values obtained may indicate the extent to which covalent bonding is present.

It is possible to express the lattice energy in terms of the formula,

$$U = A \frac{N\epsilon^2}{r} Z_1 Z_2 \left(1 - \frac{1}{n} \right)$$

where ϵ , Z_1 , and Z_2 are the electronic and the ionic charges, N is Avogadro's number, r is a characteristic interionic distance, n the electron shell repulsion coefficient, and A is the Madelung constant (a structural coefficient that depends, amongst other things, upon the characteristic interionic distance, r used, and the relative number of anions to cations). The expression is not exact and more elaborate expressions have been derived to account for some of the other factors, e.g., Van der Waals's forces and zero point energy, that are involved but discussion of these refinements is not pertinent to the subject of this article. For other than simple structures all these expressions are not easy to apply and when it is necessary to pre-

dict the lattice energy without knowing the structure of the crystal they are useless.

Kapustinskii (35a) has developed an expression,

$$U = 287.2 \frac{\Sigma n Z_1 Z_2}{\tau_c + \tau_a} \left\{ 1 - \frac{0.345}{\tau_c + \tau_a} \right\}$$

where Σ_n is the number of ions per "molecule" of the compound and τ_c and τ_a are the Goldschmidt radii, referred to a coordination number of six.

While realizing the very approximate character of this treatment, it is possible to use it, in a crude quantitative fashion, to show how the various properties of the anion affect the lattice energy. It is clear, by inspection, that the smaller the radius of the anion, the greater will be the lattice energy. The charge of the anion makes a major contribution to the lattice energy.

Comparing M^+X^- with $M_2^+Y^{2-}$ and $M_3^+Z^{3-}$, if X, Y, and Z had identical radii the lattice energies for equivalent amounts of M would be in the ratio, 2:6/2:12/3, i.e., 2:3:4. In a similar way for a bivalent metal, $M^{2+}X_2^-$, $M^{2+}Y^{2-}$, and $M_3^{2+}Z_2^{3-}$ the ratios are 6:8:30/3 or 6:8:10 for a trivalent metal, $M^{3+}X_3$, $M_2^{3+}Y_2^{3-}$, and $M^{3+}Z^{3-}$ the ratios are 12:30/2:18, i.e., 12:15:18. Taking ionic radii into account it would appear that, from their charge alone, oxides benefit by about 150 kcal/equivalent of metal, and nitrides by 300 kcal/equivalent for univalent metals; 300 and 600 kcal/equivalent for bivalent metals; and 450 and 900 kcal/equivalent for trivalent metals with respect to fluorine. Thus, in spite of the extremely unfavorable energetics involved in the formation of anions that are isoelectronic with the inert gases, oxygen and nitrogen are able to compete adequately with fluorine in the formation of ionic compounds as a result of the increased lattice energy due to the increased anionic charge. That this compensation is inadequate can be seen by comparing the heats of formation of some ionic fluorides and oxides (kcal/mole).

<u>NaF</u>	<u>BaF₂</u>
136	286.9
<u>$\frac{1}{2}$Na₂O</u>	<u>BaO</u>
49.7	133.4

4. Stabilization of High Oxidation States in Electrovalent Compounds

The simple Born-Haber cycle can be used to show why compounds such as NaNe or NeCl or even NaF₂ are too unstable to exist.* These calculations

* See note added in proof on page 39.

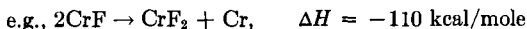
have often appeared in textbooks and review articles and need not be repeated here (26, 62). In general, they show that the lattice energy of the product is insufficient to compensate for the adverse ionization potentials or electron affinities. When such a treatment is applied to the problem of which environment is most suitable for the stabilization of the high oxidation states of the transition metals, the simplicity is lost. It is of interest to see why this should be so.

At first sight, it might appear that the halogens, since they are the only elements that take electrons exothermically to form anions with an inert gas configuration, should be most effective in stabilizing a high oxidation state in an ionic environment. In particular fluorine, because of the small size of its anion and its low heat of atomization, should be the most effective halogen. Since, however, the halide ions can only possess unit charge, the relative number of anions to cations will be large for a high oxidation state. Thus, for every M^{n+} cation that is present, n halide ions are required to maintain electrical neutrality, whereas the same function can be performed by $n/2$ divalent or $n/3$ trivalent anions. It is not unreasonable to expect that, since electrostatic forces are isotropic, they will function most effectively when the charge distribution around a particular ion is spherically symmetrical. This is possible only with 8:8, 6:6, 4:4, and 8:4 coordination and with any other arrangement the asymmetry of the electrostatic environment must lead to some directional polarization which may be sufficient, in certain cases, to lead to a significant departure from purely electrostatic bonding. The use of polyvalent anions brings its own drawback since the polarizability of the anion increases markedly with the charge, and unless prevented by the geometry of its environment and the orbitals available on the metal, the multiply charged anion will assume some covalent character in its bond with a cation possessing a high polarizing power. It would appear, therefore, that the highest oxidation state that can be stabilized in an essentially electrovalent compound is rarely greater than two, an observation that is in accordance with the Electroneutrality Principle.

5. Stabilization of Intermediate Oxidation States in Electrovalent Compounds

Up to this point the discussion has hinged on whether the compound of the metal in a particular oxidation state is thermodynamically stable with respect to its elements but such a consideration is inadequate because it is necessary, in addition, for the compound to be stable towards other modes of decomposition, e.g., disproportionation. Calculation shows that the heats of formation of all the fluorides of the first row transition elements in oxidation state I are negative and that these are therefore stable with

respect to their elements. However, it is also possible to show that the heat of disproportionation into the metal and a higher fluoride is also negative.



A similar situation obtains for TiF_2 which disproportionates as follows:



These considerations, while showing why it is not possible to produce pure crystalline specimens of univalent transition metal fluorides by direct reaction of the elements, also indicate how it might be possible to isolate the metal in oxidation state (I) in an ionic environment. In order for disproportionation to succeed it is necessary for the electrons to be transferred from one metal ion to another and this can be avoided if the ions are prevented from approaching one another too closely. If, therefore, the ions can be held in dilute solid solution they should be kinetically stable and observable. The production of detectable quantities of Fe^{I} in an ionic environment can be achieved by irradiating a solid solution of FeF_2 in NaF (29). The Fe^+ ion produced by electron capture is partly stabilized by interaction with the solvent environment since FeF might be expected to be isomorphous with NaF . There is no reason why, in favorable circumstances, the disproportionation should not be reversed as a result of isomorphic replacement in the solid solution. If the free energy of disproportionation is small, it is possible that it may be compensated by the free energy of solution of the lower oxidation state compound in the isomorphic solvent. This could be achieved by taking equivalent amounts of a suitable metal difluoride and the free metal and fluxing them with a large excess of sodium fluoride. If the above conditions are satisfied it is possible that a solid solution of the monofluoride in NaF may separate out as a stable phase on cooling.

6. *Complex Ions with Essentially Ionic Binding*

In previous sections the discussion has been concerned mainly with ionic lattice compounds in which it is not possible to pick out discrete chemical units other than the individual ions. However, one of the foundations of transition metal chemistry is the concept that the metal ion is surrounded by a fixed number of ligands. Since this coordination number is often not equal to the charge on the free ion and since it can be satisfied equally well by neutral molecules and charged ions, the resultant complex can be positively or negatively charged or even be uncharged. It remains however a chemical entity which is identifiable in the crystal and may, in favorable circumstances, retain its identity on going into solution. The lattice energy will still make a significant contribution towards the heat

of formation but much of the energy release will be due to the formation of the complex. The packing of complex ions in the lattice will be controlled almost entirely by the minimization of their mutual repulsion since the much smaller noncomplex anion, or cation will fit in suitable "holes" in the lattice. The coordination number of the metal will not be controlled by the desire to minimize the potential energy of the lattice and two other factors become of major importance. The first is the electronic configuration of the metal and the interactions between the ligands and the nonbonding electrons. The second is the extent to which the ligands displace charge towards or away from the metal.

The interaction between the ligands and the nonbonding electrons is only significant when these electrons are in a partly filled shell, especially a *d*-shell. The *d*-orbitals of a free transition metal ion are energetically degenerate, but on coordination the ligands approach sufficiently close to the ion for this degeneracy to be removed and solely by electrostatic interaction those orbitals which "point towards" the ligands are destabilized with respect to those which do not. The energy separation will depend upon the symmetry of the field and the effective field strength of the ligands and may be sufficient to change the spin multiplicity of the ion. This purely electrostatic picture is embodied in Crystal-Field theory and explains many of the properties of the complex that arise from these nonbonding electrons, i.e., visible absorption spectra and magnetism. This orientation of the ligands around the metal, apart from providing an optimum coordination number and geometry, places the ligands in a position where there is the possibility of overlap between filled orbitals on the donor atom and suitable empty orbitals on the metal. This produces a covalent contribution towards the bonding and the covalent-electrostatic picture is embodied in Ligand Field Theory but for essentially ionic complexes this latter refinement is unnecessary.

C. COVALENT BINDING IN COORDINATION COMPOUNDS

When we come to consider this other extreme picture of the metal-ligand bond, we find that it is no longer easy to separate the role of the metal from the role of the environment. The reciprocative character of covalent binding requires that the atoms attached to the metal will alter its bonding properties and will be altered themselves in return. Thus, when considering the factors which control the stability of a particular oxidation state of the metal, it is necessary to know something of the nature of the attached groups.

The ionization potential of the metal and electron affinity of the donor atom play only a minor role. It is still desirable to consider the promotion energies of electrons in both atoms forming the bond because it is often

necessary for electrons in the ground state of the atom to be promoted to higher levels in order to make way for covalent bonding. One well known case is that of carbon which has a ground state configuration $1s^2 2s^2 2p^2$ that must be changed, by promoting an electron to $1s^2 2s^2 2p^1 3s^1$ in order to make four orbitals available for bonding. A knowledge of the appropriate promotion energies for both the metal and the donor atom enables us to understand some of the factors controlling the stability of the system. This aspect is considered in more detail later on in this article (54). If this picture is taken as the start of our concept of covalent coordination the next process is to bring up to the free metal atom in its correct electron configuration, the appropriate number of ligands, each, one electron short of the closed shell configuration. The delocalization of the bonding electrons in the appropriate molecular orbitals provides the bonding energy and the strength and polarity of the resultant bond will depend upon the extent to which the bonding electrons experience the positive charge of the nuclei through the other shielding electrons. However close this representation may be to reality and however useful it may be in its application, it cannot be used in any discussion concerning the stabilization of oxidation states because at no stage is the metal ion oxidized. The concept of oxidation states as applied to covalent compounds was dealt with in the introduction to this article and the discussion need not be repeated here. If we wish to retain the concept of oxidation state as a useful method of correlating facts then it is necessary to picture the covalent bond as forming in a different way. We must take the free metal ion in the appropriate oxidation state and bring up to it the required number of ligands, each in their closed shell configuration, the bonds being formed by pairs of electrons originally located on the donor atoms. Not only is this the classical representation of the coordinate bond, but it is also the reverse of the process whereby the oxidation state of the metal is defined. The formation of the bond in this way leads to a transfer of charge from the ligand to the metal of up to one electron per ligand, if the electron pairs are equally shared, and therefore reduces its positive charge. The stabilization behavior can be understood relatively well if we apply the electroneutrality principle and expect to find instability when the charge on any one atom greatly exceeds $\pm 1\frac{1}{2}e$. The principle is less applicable to the electrovalent compounds that we have already discussed, since there, a greater charge separation is acceptable if the resultant increase in lattice energy provides adequate compensation. The transfer of charge towards the metal explains how coordination can stabilize a metal whose formal oxidation state is high. Often, the coordination number of the metal is greater than, or equal to, its formal oxidation state so that there is always an availability of electronic charge. However, with a metal ion in a high oxidation state it is also important that the donor

atom should have a strong enough hold on the shared electrons, i.e., a high electronegativity, in order to prevent the process being too efficient and leading to oxidation of the ligand. Only a few ligands are suitable for the stabilization of the very highest oxidation states. Neutral molecules in general are unsuitable because too much positive charge is transferred to them. A ligand such as water might be suitable but the transfer of positive charge to the hydrogen atom makes it too acidic to remain attached. Of the uninegative anions, the halides are the most important, but in most cases fluorine is the only one possessing sufficient electronegativity to prevent oxidation-reduction. The doubly charged anions can provide even more negative charge and the complex anion formed with a high coordination number would have a very high negative charge even when the metal is in its highest oxidation state. Of the monatomic divalent anions, oxygen is by far the best in stabilizing high oxidation states, partly because of the high electronegativity of oxygen. In general, four O^{2-} ligands are used, leading to a tetrahedral arrangement. In addition to the transfer of charge by the σ type coordinate bond, the oxygen has the capacity to donate more charge to the metal by way of a π -donor bond involving another pair of electrons. The stabilization of the highest oxidation states of transition metals as their complex oxyanion is well known, e.g., TiO_3^{2-} , VO_4^{3-} , CrO_4^{2-} , MnO_4^- , FeO_4^{2-} , as well as the neutral RuO_4 and OsO_4 . The ability of oxygen to form double bonds is paralleled by the other first row elements, carbon and nitrogen, and is ascribed in part to the size of the second quantum shell which is only separated from the nucleus by a 2-electron shell. The second row elements have an 8-electron penultimate shell and are unable to form double bonds as efficiently. Thus, sulfur is not as effective as oxygen in stabilizing high oxidation states so that although thiovanadates and thiomolybdates exist, any attempt to replace the oxygen in the chromate or permanganate ion results in oxidation of the sulfide to sulfur.

The ability of oxygen to form a donor π bond decreases to some extent down any group of the periodic table, and whereas the lighter members form oxyanion complexes the heavier members form hydroxyanions in the same oxidation state. Many examples are known in the p block elements e.g., $HClO_4$ and H_5IO_6 , $\{ClO_3OH, IO(OH)_5\}$; H_2SO_4 and $Te(OH)_6$. With transition metals in their highest oxidation states, the effect is shown in the increased tendency towards the formation of polyanions (cf., chromates and molybdates) where the polymerization is the result of oxygen acting as a bridging group.

As the bonding assumes a more covalent character, so the coordination of the metal tends to be controlled by the inert gas or nine orbital rule. Stability can be achieved by giving the metal the same electronic configuration in its complex as that of the next inert gas atom, i.e., $nd^{10}(n+1)s^2$.

$(n + 1)p^6$, and these electrons can be derived from nonbonding lone pairs on the metal or bonding pairs shared with the ligands. The rule can be extended to paramagnetic complexes if occupancy of an orbital by one electron is accepted as sufficient under the circumstances.

Intermediate oxidation states require less transfer of charge to and from the metal so that the bonding can be more electrovalent in character. Such complexes are amenable to ligand field treatments that require no great departure from the simple electrostatic picture.

The provision of an environment that will stabilize low oxidation states presents a new problem. As has already been shown, the ionic compounds of transition metals in their lowest positive oxidation state (+I), will usually disproportionate to gain stability. Covalent binding between the metal, in a low oxidation state, and the ligand will lead to excess negative charge being on the metal, a situation that would make the resulting complex unstable unless there were means whereby this excess charge could be returned to the ligands, usually by way of orbitals different from those used for the σ bonding. Therefore donor atoms which possess empty orbitals of suitable size and symmetry, e.g., the empty d orbitals of P, As, S, Se, or which are attached to a system that is able to conjugate with the metal, e.g.,



etc., should form stable complexes with the transition metals in their lowest oxidation states, provided they can form a sufficiently covalent σ bond.

D. THE STABILIZATION OF OXIDATION STATES IN SOLUTION

Consideration of the stabilization of a particular oxidation state in solution will introduce factors which have not, as yet, been discussed, and all of which derive from competition between the ligands and the solvent molecules for a place within the most important part of the environment of the metal, namely the first coordination sphere. The important contribution made by lattice energy in the solid compounds is now replaced by the equally important contribution made by the free energy of solvation. It should be noted that, because the entropy change now makes a very significant contribution to the free energy of the process, it can no longer be ignored as it was in the case of the solid compound and so we have to change from considering an enthalpy (lattice energy) to a free energy. Interaction between the metal and the solvent will produce new possibilities of destabilization and redox reactions between the metal and the solvent will have to be avoided. It is reasonable to believe that the high oxidation states are

stabilized in solvents that are not readily oxidized, e.g., water, liquid HF, and that low oxidation states are best stabilized in solvents not readily reduced, e.g., liquid ammonia. However, even when the complex is thermodynamically unstable with respect to its solvent environment, there may not be a suitable path for the electron transfer to take place and so kinetic metastability is achieved. This can arise, in inert complexes, because the solvent cannot readily displace a ligand and become directly bound to the metal. If, however, the complex is labile, there will be a rapid equilibration between the ligands and the solvent molecules for a place in the coordination sphere and, if the equilibrium products are unstable, redox processes will rapidly follow. For instance, iridium(VI) is stabilized as the volatile IrF_6 , (as also is Pt^{VI}), but with excess water, hydrolysis is instantaneous and the hydrolyzed species give oxygen, ozone, and $\text{Ir}(\text{OH})_4$. However, as we have already seen, oxygen can stabilize high oxidation states very well, and the normal behavior of a high oxidation state fluoride in water is to hydrolyze to give the oxide or oxyanion of the metal in the same oxidation state. When one considers the cases in which a particular oxidation state is stabilized thermodynamically by its immediate environment (i.e., coordination) the cobalt(II)–cobalt(III) system presents a classical example. The reduction potential for $[\text{Co}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$ is greater than the oxidation potential of water and so the simple hydrated Co^{III} ion is unstable with respect to its aqueous environment and is reduced, albeit slowly in the absence of catalysts, to Co^{II} . However, on coordination with other ligands, e.g., ammonia, amines, cyanide etc., the situation is reversed and the higher oxidation state is stabilized with respect to the lower, since the reduction potential is less than that required for the oxidation of water. Looking at this from the point of view of the Co^{II} species, we find that, although the oxidation potential of $\text{Co}(\text{NH}_3)_6^{3+}$ is more positive than the reduction potential of water to give hydrogen, it is less positive than the reduction potential of oxygen in water to give hydroxide. Therefore an aqueous cobalt(II) ammine solution is stable in the absence of oxygen, but in its presence will be oxidized to cobalt(III). The problem can be restated in terms of the oxidation-reduction potential of the solvated metal ion and the relative magnitude of the stability constants of the complexes of the metal in its various oxidation states with the ligand under examination.

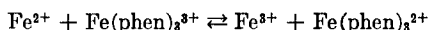
If K_n and K_{n+1} are the over-all stability constants for the complex of the metal in oxidation states n and $(n + 1)$ then the change in oxidation potential of the metal caused by the addition of sufficient of the ligand is given by

$$E_{\text{complex}}^{\circ} = E_{\text{hydrate}}^{\circ} - \frac{RT}{F} \ln \frac{K_n}{K_{n+1}}$$

Thus the argument now turns on what factors determine the relative stability constants of the same ligand with the various oxidation states of the metal.

As a generalization one can say that if the ligand uses only σ bonding then, if it is more polarizable than the solvent, it will favor the higher oxidation states. If the ligand requires π bonding in addition, e.g., CO, then it will favor a low oxidation state, because here the effective nuclear charge of the metal will be lower and so draw on the d , electrons less and leave them free to engage in π bonding.

The electron configuration of the metal ion is also of supreme importance. The stability of the d^6 spin-paired configuration will destabilize adjacent oxidation states making oxidation, or reduction easy in the presence of a ligand whose field is sufficient to cause spin pairing. This is seen in the stabilization of Ni^{IV} by arsine chelates. These factors can be demonstrated in the case of iron. The oxidation potential of the $\text{Fe}_{\text{aq}}^{2+} \rightarrow \text{Fe}_{\text{aq}}^{3+} + e^-$ couple is -0.74 volts, inadequate to cause an oxidation of ferrous to ferric by the reduction of water but sufficient for the couple to reduce oxygen in the presence of water. One of the factors involved in this couple is the high acidity ($\text{p}K \sim 2$) of the hydrated ferric species and its subsequent stabilization contribution to the higher oxidation state. The oxidation potential for $\text{Fe}(\text{CN})_6^{4-} \rightarrow \text{Fe}(\text{CN})_6^{3-} + e^-$ is -0.36 volts, i.e., more in favor of the ferric complex, since the cyanide is acting essentially as a strong σ bonder. However, with ligands that derive much of their stability from π bonding the situation is reversed. Dipyriddy and phenanthroline stabilize the Fe^{II} state in aqueous solution even in the presence of oxygen, the oxidation potential being now in the order of -1.1 volts. Thus the larger number of d , electrons in the lower oxidation state and the smaller effective nuclear charge they experience increases the stability of the lower oxidation state complex. It is of interest to note that the stabilization of the ferrous phenanthroline complex with respect to the ferric complex is greatly decreased by increasing the acidity of the solution. With sulfuric acid the equilibrium constant for the reaction



changes from 1.6×10^7 in $0.05 M \text{H}_2\text{SO}_4$ to 15 in $8 M$ sulfuric acid (42). This change is said to be due to the increase in the stability of the ferric complex in high acid solution although no independent assessment of the behavior of the ferrous complex appears to have been made in this acid range.

An interesting sidelight to the stabilization of oxidation states in solution is the effect of ionic strength. $\text{K}_2\text{Ir}^{\text{IV}}\text{Br}_6$ is stable in aqueous solution with respect to $\text{K}_3\text{Ir}^{\text{III}}\text{Br}_6$ but if sufficient potassium nitrate added the Ir^{IV}

is completely reduced to Ir^{III} with the liberation of bromine (22). This effect is caused by the different effects of ionic strength upon the two redox couples involved.

For the $\text{IrBr}_6^{3-}/\text{IrBr}_6^{2-}$ couple $E^0 = -0.99$ volts at zero ionic strength whereas for the $\text{Br}^-/\frac{1}{2}\text{Br}_2^0$ couple $E^0 = -1.08$ volts. Because of the greater ionic charge of the lower oxidation state complex the oxidation-reduction potential of the $\text{Ir}^{\text{III}}\text{--Ir}^{\text{IV}}$ system will increase with increasing ionic strength. This will not be matched by the bromine-bromide couple which in fact is affected in the opposite direction and a stage is reached where the redox potentials cross and IrBr_6^{2-} is able to oxidize bromide to bromine.

III. Survey of Oxidation States of Various Electron Configurations

A. GENERAL

We shall discuss the various nonbonding configurations starting with the $(n-1)d^{10}ns^2$ arrangement working back to the $(n-1)d^0$ in turn. When comparing the properties of chemical compounds in which the binding is essentially electrostatic it is most convenient to think in terms of isovalent sequences, e.g., the similarity of the bivalent transition series (excepting Cr^{II} and Cu^{II}). On the other hand when comparing compounds in which the binding is essentially covalent, and most of the compounds which we consider fall into this category, one finds much closer similarity if one thinks in terms of isoelectronic sequences. As an example, the d^6 arrangement is specially favorable for the formation of spin paired d_{π}^6 complexes. Thus we find, in the first transition series, oxidation states extending all the way from $-I$, in the $[\text{V}(\text{CO})_6]^-$ ion, to $+IV$, in the $[\text{NiF}_6]^{2-}$ ion.

In the discussion of each configuration no attempt will be made to list a large number of examples of the oxidation states but suitable examples are given in each case and special attention is directed towards oxidation states which have been established recently.

B. DISCUSSION OF NONBONDING CONFIGURATIONS

1. Oxidation States with a $(n-1)d^{10}ns^2$ Configuration

This survey starts most conveniently with a discussion of an electron configuration which is trivial so far as transition elements are concerned, but it provides a necessary background to the detailed examination of the transition metals. In the following table are shown the oxidation states of the transition metals, and of some nearby elements for comparison, which possess the $d^{10}s^2$ configuration and which, at least formally, could arise.

Those shown in heavy type [i.e., **Zn^{II}**] have been observed experimentally while those in light type are, as yet, unknown. It should be emphasized, however, that some of the "unknown" oxidation states to which we shall refer are unknown probably because of the lack of purposeful attempts to obtain them.

The $(n-1)d^{10}ns^2$ Configuration				
Cu^{-I}	Zn⁰ (Metal)	Ga^I (Ga ⁺ (GaCl ₄) ⁻)	Ge^{II} GeCl ₂	As^{III} (AsCl ₃)
Ag^{-I}	Cd⁰ (Metal)	In^I (In ⁺ (AlCl ₄) ⁻)	Sn^{II} (SnCl ₂)	Sb^{III} (SbCl ₃)
Au^{-I}	Hg⁰ (Metal)	Tl^I (TlCl)	Pb^{II} (PbSO ₄)	Bi^{III} (BiCl ₃)

The oxidation states III for the elements As, Sb, and Bi and II for Ge, Sn, and Pb are well known; the I state occurs for each of the elements Ga (24), In (16) and Tl but is much more stable for Tl than for the two lighter elements of the triad. The *relative* ease with which the $d^{10}s^2$ goes to the d^{10} configuration for these three series of elements is illustrated by the following table which shows the ionization potentials for the process $(n-1)d^{10}ns^2 \rightarrow (n-1)d^{10}$ (of relevance in ionic compounds) and also the energy required to effect the promotion $ns^2 \rightarrow ns^1np^1$, a measure of the separation between the ns and np levels; this gives an idea of the ease of forming covalent compounds which use all the electrons in the outermost valency shell.

	Zn	Cd	Hg
Sum of 1st and 2nd ionization potentials (volts)	27.35	25.90	29.19
$ns^2 \rightarrow ns^1np^1$ Promotion energy (volts)	4.01	3.74	4.67

Of particular relevance for us are the data for the triads Zn⁰, Cd⁰, Hg⁰ and Cu^{-I}, Ag^{-I}, Au^{-I}. For the first of these triads the ns^2 configuration for the ground state of the atom represents a quasi-inert gas (cf. He); hence these elements show a definite tendency to pass to the monatomic state. This is, of course, correlated with their relatively low boiling points, with a minimum at mercury for which the energy required to reach the valence state ($6s^16p^1$) is a maximum. No *compounds* of zerovalent Zn, Cd, and Hg have been reported; it seems unlikely that the use of ligands requiring $d_{\pi}-p_{\pi}$ or $d_{\pi}-d_{\pi}$ bonds will effect this stabilization because, in this case, the donation of d electron pairs by the metal for the necessary π bond

formation with the ligand is difficult owing to the high ionization potential of an electron from the d^{10} shell (54). If such complexes are isolated, however, it is likely that ligands having highly polarizable electron pairs will be required, e.g., a complex of the type $K_4[HgL_4]$. The relatively high (estimated) electron affinities of Cu(1.4 ev), Ag(1.2 ev) and Au(2.4 ev) suggest that, in some ways, these could behave like halogen atoms and become negatively charged, forming Cu^{-I} , Ag^{-I} , and Au^{-I} ions, respectively. Given the right cation A^+ with an appropriate lattice energy for the resulting salt, there seems no reason why compounds of the type $[A^+][Au^-]$ might not be prepared; thus the salt-like properties of Cs^+Au^- support this (67).

2. Oxidation States with an $(n-1)d^{10}ns^1$ Configuration

This configuration, involving an unpaired s electron is commonly unstable, having the properties of a free radical. However, the existence of apparent s^1 compounds is common, stability being achieved, either by disproportionation to produce two different ions with s^0 and s^2 configurations, e.g., as in $Ga^I[Ga^{III}Cl_4]$, or by metal-metal bond formation (e.g., as in Ga_2S_2 (27), Hg_2Cl_2 or in Au_2 in the gas phase). There do not appear to be any known examples of paramagnetic s^1 compounds in the 1st, 2nd, and 3rd long periods.

The *formal* $d^{10}s^1$ configuration is expected to arise in the cases shown in the table below:

The $d^{10}s^1$ Configuration					
Ni^{-I} [Ni ₂ (CO) ₈] ²⁻	Cu⁰ (Metal)	Zn^I	Ga^{II} Ga ₂ S ₂	Ge^{III} R ₃ Ge—GeR ₃	As^{IV}
Pd^{-I}	Ag⁰ (Metal)	Cd^I	In^{II}	Sn^{III} R ₃ Sn—SnR ₃	Sb^{IV}
Pt^{-I}	Au⁰ (Metal)	Hg^I Hg ₂ Cl ₂	Tl^{II}	Pb^{III} R ₃ Pb—PbR ₃	Bi^{IV}

In the As, Sb, and Bi triad so-called quadrivalent compounds, e.g., SbCl₄ (35), are known but these are now considered to involve a mixture of Sb^{III} and Sb^V. In the Ge, Sn, and Pb triad examples of both mixed (+II and +IV) oxidation states (e.g., in plumbous plumbate Pb₃O₄) and metal-metal bonding (e.g., in Ph₃Pb—PbPh₃) are known. As pointed out above, for Ga, In, and Tl, mixed (+I and +III) (see Fig. 1) oxidation states arise (e.g., in Ga^I[Ga^{III}Cl₄]) and also metal-metal bonding (e.g., Ga₂S₂). Coming to the Zn, Cd, and Hg triad, metal-metal bonding is well known in the mercurous halides but no similar derivatives of zinc or cadmium have been described. Also, no *complex* compounds of any of these elements

in the oxidation state +I have been reported. Recently, several complexes have been prepared in which gold has an oxidation state of zero, the gold atom being attached to a different metal atom in the same oxidation state. The combination of Au^0 with metals having d^9 and d^7 configurations, for example, has been effected (18). Thus, the following reaction involving a

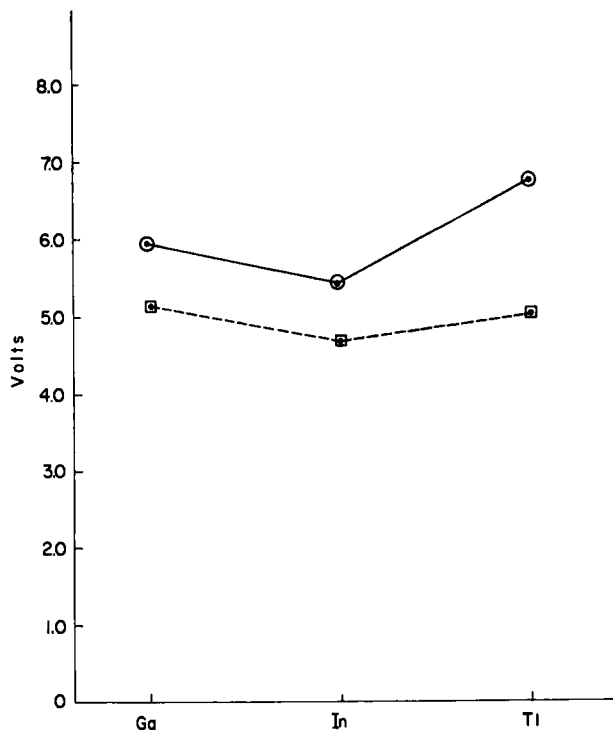


FIG. 1. \circ — \circ Promotion energy $ns^2 \rightarrow nsnp$ of M^+ ion; \square — \square $IP_2 + IP_3$: scale to be multiplied by 10 (second and third ionization potentials). (From Nyholm *Proc. Chem. Soc.* pp. 286, 287, 288, 1961).

d^9 atom, $\text{Ph}_3\text{P} \rightarrow \text{Au-Cl} + \text{Na}^+[\text{Co}(\text{CO})_4]^- \rightarrow \text{Ph}_3\text{P} \rightarrow \text{Au-Co}(\text{CO})_4$ takes place readily in alcohol solution, the yellow gold cobalt complex being precipitated. Similarly the reaction $\text{Ph}_3\text{P} \rightarrow \text{AuCl} + \text{Na}^+[\text{Mn}(\text{CO})_5]^- \rightarrow \text{Ph}_3\text{P} \rightarrow \text{Au-Mn}(\text{CO})_5 + \text{NaCl}$ gives rise to a complex involving a d^7 , Mn^0 atom. Iron gives rise to a similar derivative having the formula $(\text{Ph}_3\text{P} \rightarrow \text{Au})_2\text{Fe}(\text{CO})_4$.

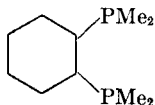
Finally, the only example of the oxidation state $-I$ for the triad Ni, Pd, and Pt seems to be the carbonyl hydride $\text{H}_2[\text{Ni}_2(\text{CO})_6]$, (32) it being assumed that the hydrogen atom in this compound is essentially cationic.

3. Oxidation States with the d^{10} Configuration

This is one of the commonest arrangements and gives rise to stable oxidation states from $+VII$ of the halogens to $-II$ for iron as in $\text{Na}_2\text{Fe}(\text{CO})_4$.

The d^{10} Configuration				
Fe^{-II} [Fe(CO) ₄] ²⁻	Co^{-I} [Co(CO) ₄] ⁻	Ni⁰ Ni(CO) ₄	Cu^I CuCl	Zn^{II} ZnCl ₂
Ru^{-II} [Ru(CO) ₄] ²⁻	Rh^{-I} [Rh(CO) ₄] ⁻	Pd⁰ [Pd(CN) ₄] ⁴⁻	Ag^I AgCl	Cd^{II} CdCl ₂
Os^{-II} [Os(CO) ₄] ²⁻	Ir^{-I} [Ir(CO) ₄] ⁻	Pt⁰ [Pt(Diphosphine) ₂]	Au^I AuCl	Hg^{II} HgCl ₂

Perhaps the only problem calling for comment is the relative rarity of compounds of Pd and Pt of oxidation state zero. Thus it has been shown recently (14) that certain triphenylphosphine complexes in which the Pt atom appeared to have an oxidation state of zero are in fact dihydrides of Pt^{II}. Nevertheless Chatt and co-workers (11a) have prepared Pd⁰ and Pt⁰ derivatives of the diphosphine

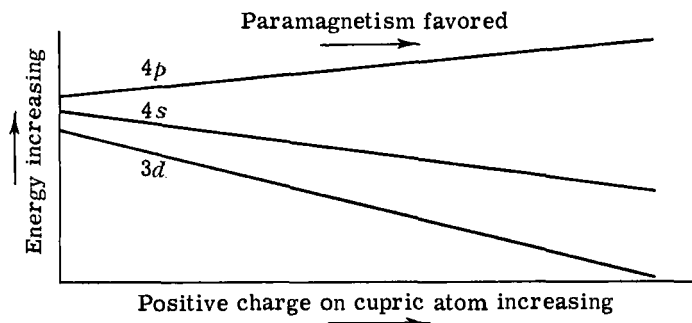


of the type [Pt(chelate)₂]⁰. Where strong double bonding appears to be an essential feature necessary for the attachment of the ligand (e.g., with CO), the isolation of complexes of Pd⁰ and Pt⁰ seems to be much more difficult. Thus, all attempts to prepare the carbonyls Pd(CO)₄ and Pt(CO)₄ have so far proven unsuccessful. It is suggested that if $d\pi$ bonding from the metal to the ligand is important for the stability of metal carbonyls, then the instability of Pd(CO)₄ and Pt(CO)₄ might be explained by the reluctance of the d^{10} Pd⁰ and Pt⁰ atoms to donate electrons to the ligand for $d\pi$ bond formation; the ionization potentials of the spin paired free atom configurations Cr⁰(d^6), (as in Cr(CO)₆); Fe⁰(d^8), (as in Fe(CO)₅); Ni⁰(d^{10}), (as in Ni(CO)₄) are respectively 4.1, 3.9, and 5.7 volts (3). However, in marked contrast, the ionization potentials for the d^{10} atoms Pd⁰ and Pt⁰ are respectively 8.1 and 8.3 volts. It is suggested that, as with Cu⁰, Ag⁰, and Au⁰, the stabilization of Ni, Pd, and Pt in the oxidation state 0 is most likely to be effected by using a negatively charged ligand; thus, Nast (49) has succeeded in preparing acetylides of the type K₄M(C≡C—Ph)₄ (M=Ni, Pd). These are similar to the corresponding cyano complexes K₄Ni(CN)₄ and K₄Pd(CN)₄.

4. Oxidation States with the d^9 Configuration

This is the first case where an unpaired d electron is involved and hence paramagnetism is to be expected. As we shall emphasize, however, this d^9 configuration shows a marked tendency to reach the d^{10} configuration, especially in covalent compounds. In passing, it is of interest to ask why atoms

containing unpaired d electrons are fairly common but those with unpaired s and p electrons are relatively rare. A pointer to the reason for this is obtained by noting that the d^9 configuration becomes progressively less stable as the binding becomes more covalent, e.g., in the hypothetical ion $[\text{Cu}(\text{CN})_4]^{2-}$, or as the negative charge on the atom increases. Conversely, paramagnetism is most pronounced in essentially ionic d^9 compounds, e.g., salts like cupric fluoride. It is suggested that the unpaired d electron becomes progressively less stable as its energy approaches that of the bonding orbitals. The higher the positive charge on the cupric atom the more the d orbitals is "drawn in" away from the sphere of the bonding electrons.



The d^9 configuration can reach the stable diamagnetic d^{10} arrangement in several ways: (1) by metal-metal bonding as in $\text{Co}_2(\text{CO})_8$; (2) by oxidation of the ligand as when the cupric ion and the cyanide ion come into contact in aqueous media; (3) by disproportionation, e.g., $3\text{Au}^{2+} \rightarrow 2\text{Au}^{3+} + \text{Au}^0$. There are several factors which decide which of these will occur; of special importance are the relative values of the lattice energy of the salts produced as compared with the promotion energy required to reach the tervalent state.

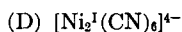
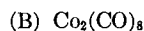
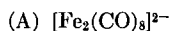
The following data are of interest in order to understand the relative stabilities of the oxidation states of Cu, Ag, and Au.

IONIZATION POTENTIALS IN VOLTS			
	Cu	Ag	Au
1st I. P. (Ionization potential)	7.72	7.57	9.22
2nd I. P.	20.29	21.48	20.45
Sum of 1st and 2nd I. P.	28.01	29.05	29.67
3rd I. P.	37.08	34.82	30.5
Sum of 2nd and 3rd I. P.	57.37	56.30	50.95
Promotion energy for $d^{10} \rightarrow d^9s^1$			
($^1S \rightarrow ^3D$) $J = 3$	2.72	4.85	1.86

These data show that to reach the tervalent state gold requires less energy than do copper or silver. Also, the energy required to form an M^{+3} ion starting from the M^+ ion is considerably less for gold than it is for the other two elements. However, more energy is required to reach the Au^{2+} ion starting from the uncharged atom than for either copper or silver; hence it is not difficult to understand why the oxidation state $+II$ in gold so readily passes to a mixture of $+III$ and $+I$.

The d^9 Configuration			
Fe^{-I} [Fe ₂ (CO) ₈] ²⁻	Co⁰ Co ₂ (CO) ₈	Ni^I [Ni ₂ (CN) ₈] ⁴⁻	Cu^{II} CuCl ₂
Ru^{-I}	Rh⁰ Rh ₂ (CO) ₈	Pd^I	Ag^{II} [AgPy ₄] ²⁺
Os^{-I}	Ir⁰ Ir ₂ (CO) ₈	Pt^I	Au^{II}

Only in the cases of Cu^{II} and Ag^{II} and in the compound $K_3Ni^I(CN)_4$ has paramagnetism been observed. In all other cases diamagnetism is the rule, with metal-metal bonding. The way in which this arises in the $[Fe_2^{-I}(CO)_8]^{2-}$ ion, $Co_2^0(CO)_8$, the $[Ni_2^I(CN)_8]^{4-}$ ion and in cupric acetate is shown in Fig. 2.



It is of interest to note that, whereas metal-metal bond formation in $Co_2(CO)_8$ was once generally believed to be a consequence of the proximity of the two Co atoms which were bound by bridging CO groups, it is now considered likely that it is the metal-metal bond formation which causes the CO bridging. Dahl (20a) has shown recently that the structure of rhodium carbonyl involves a metal-metal bond without any bridging CO groups. He suggests that when the radius on the metal atom becomes small enough this enables the CO groups to come close enough together to act as a bond between the metal atoms in addition to the metal-metal bond. Obviously, in cobalt carbonyl there is then some rearrangement of the stereochemistry since the metal-metal bond is a bent one.

5. Oxidation States with the d^8 Configuration

The d^8 configuration gives rise to a wide range of oxidation states varying from Cr^{-II} to Cu^{III} . Paramagnetism, with two unpaired electrons, is very uncommon, having been observed only in the cases of Cu^{III} (K_3CuF_6),

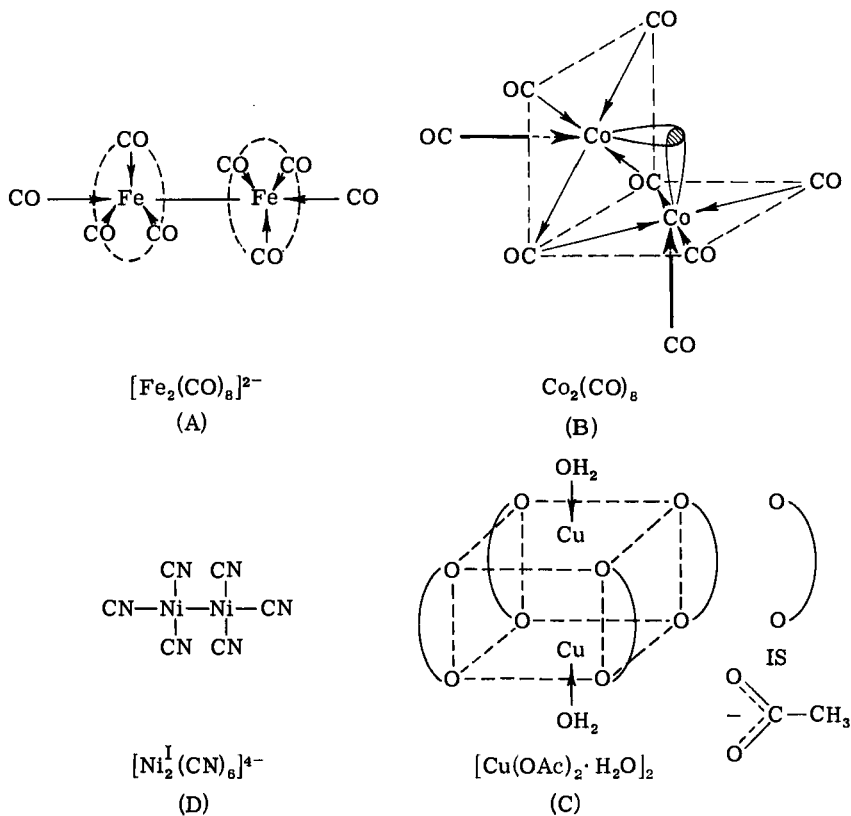


FIG. 2. Diamagnetism in metal-metal bonding.

The d^8 Spin-Paired Configuration

Cr^{-II} [Cr(CO) ₆] ²⁻	Mn^{-I} [Mn(CO) ₅] ⁻	Fe⁰ Fe(CO) ₅	Co^I [Co(RNC) ₅] ⁺	Ni^{II} [NiDiars. ₂] ²⁺	Cu^{III} [CuO ₂] _n ⁻
Mo^{-II} [Mo(CO) ₆] ²⁻	Tc^{-I}	Ru⁰ Ru(CO) ₅	Rh^I [Rh(RNC) ₄] ⁺	Pd^{II} [PdCl ₄] ²⁻	Ag^{III} [AgF ₄] ⁻
W^{-II} [W(CO) ₆] ²⁻	Re^{-I} [Re(CO) ₅] ⁻	Os⁰ Os(CO) ₅	Ir^I [Ir(RNC) ₄] ⁺	Pt^{II} [PtCl ₄] ²⁻	Au^{III} [AuCl ₄] ⁻

in the well known octahedral (e.g., $[\text{Ni}(\text{NH}_3)_6]^{2+}$) and tetrahedral (e.g., $[\text{NiCl}_4]^{2-}$ nickel(II) compounds and in palladium difluoride (6).

The diamagnetic spin paired configuration gives rise to square four-coordinate or tetragonal six-coordinate, arrangements. More recently, it has been recognized that five-coordination is also very common for the d^8 spin paired configuration. As discussed elsewhere (5), five-coordination arises most readily when the $(n-1)d \rightarrow np$ separation is a minimum. This state of affairs is favored if (1) the formal charge (oxidation state) of the metal atom is a minimum and (2) the effective nuclear charge is as small as possible. The first of these clearly increases as we pass along the sequence. $[\text{Cr}^{II}(\text{CO})_6]^{2-}$, $[\text{Mn}^{I}(\text{CO})_6]^-$, $\text{Fe}^0(\text{CO})_5$, $[\text{Co}^I(\text{PhNC})_5]^+$, $[\text{Ni}^{II}\text{Cl}_2\cdot 2\text{Et}_3\text{P}]$ leading to the frequent occurrence of square-four coordination with Ni^{II} . With regard to the second item, we find that shielding decreases as we go down the periodic table in any vertical triad e.g., $\text{Co}^I \rightarrow \text{Rh}^I \rightarrow \text{Ir}^I$. As an illustration of this it is found that Co^I forms a penta-isocyanide cobalt complex whereas the Rh^I and Ir^I complexes are *four*-coordinate. Little work has been done on $\text{Ru}(\text{CO})_5$ and $\text{Os}(\text{CO})_5$ and it is of interest to note that in the light of the above, Os^0 is quite likely to give rise to square four coordinate complexes.

Perhaps the most interesting new oxidation states which have been stabilized recently are those in which the metal atom is in the $-I$ or $-II$ state. The $-I$ state for Mn and Re are known in the ions $[\text{Mn}(\text{CO})_5]^-$ and $[\text{Re}(\text{CO})_5]$.²² Recently, Kaesz (33) has isolated certain carbonyls and carbonyl halides of technetium, namely $\text{Tc}_2(\text{CO})_{10}$, $\text{Tc}(\text{CO})_5\text{I}$ and $[\text{Tc}(\text{CO})_4\text{I}_2]_2$. There is little doubt that the corresponding $[\text{Tc}(\text{CO})_5]^-$ ion will be obtained in due course. The $-II$ oxidation state occurs in ions of the type $[\text{M}(\text{CO})_6]^{2-}$ where $\text{M} = \text{Cr}, \text{Mo},$ and W . They are formed from the hexacarbonyls by reduction with sodium in liquid NH_3 (8, 9).

6. Oxidation States with a d^7 Configuration

We have here an odd number of electrons, and when it is borne in mind that this configuration is one electron short of the stable d^8 arrangement, it is not surprising that oxidation states with a d^7 configuration are not widespread, particularly in spin-paired complexes. Spin-free complexes with 3 unpaired electrons are formed by Co^{II} (e.g., octahedral $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and tetrahedral $[\text{CoCl}_4]^{2-}$) and Ni^{III} (e.g., octahedral K_3NiF_6). No spin-free Fe^I compounds are known but possibly this spin-free oxidation state may be stabilized by inclusion in a suitable host lattice which favors a tetrahedral arrangement, e.g., in a lattice of the type $\text{K}_3\text{M}^I\text{Cl}_4$.

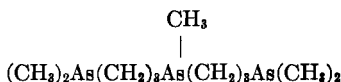
The known oxidation states having spin-paired d^7 configurations are given in the following table:

The d^7 Spin-Paired Configuration

Cr^{-I} [Cr ₂ (CO) ₁₀] ²⁻	Mn⁰ Mn ₂ (CO) ₁₀	Fe^I [Fe Diars.(CO) ₂ I] ⁰	Co^{IIa} [Co Diars. ₂] ²⁺	Ni^{III} K ₃ NiF ₆
Mo^{-I} [Mo ₂ (CO) ₁₀] ²⁻	Tc⁰ Tc ₂ (CO) ₁₀	Ru ^I	Rh ^{II}	Pd^{III} PdF ₃
W^{-I} [W ₂ (CO) ₁₀] ²⁻	Re⁰ Re ₂ (CO) ₁₀	Os ^I	Ir ^{II}	Pt ^{III}

^a Compounds with three unpaired electrons, e.g., CoSO₄·7H₂O are, of course very common.

This configuration, if paramagnetic, is expected to favor square planar four-coordination or tetragonal six-coordination. The latter occurs in compounds of the type [Ni^{III}(Diarsine)₂Cl₂]Cl (53) and the former in certain Co^{II} complexes of which the simplest example is Co^{II} protoporphyrin. It should also be emphasized that five-coordination is by no means uncommon, the arrangement being presumably square pyramidal. Examples include NiBr₃·2Et₃P (34) and CoI₂·Triarsine (4), where Triarsine has the formula



In the case of Fe^I, a d^7 spin-paired paramagnetic complex [Fe^I(Diarsine)-(CO)₂I]⁰ has been prepared (51). However, as with the d^9 configuration, the tendency towards metal-metal bonding increases as the oxidation state decreases and thus the carbonyl of Mn⁰ is dimeric as in Mn₂(CO)₁₀; replacement of one CO group by Ph₃P leads to rupture of the metal-metal bond, the monomeric paramagnetic [Mn(CO)₄Ph₃P]⁰ being formed (31). If, however, one uses (PhO)₃P the metal-metal bond is retained. It is not easy to decide just what is the major influence in effecting rupture of the Mn-Mn bond. A study (18) of the compounds produced using a variety of donors suggests that stability of the Mn-Mn bond is enhanced by using ligands which do not leave too high a positive charge on the metal atom, i.e., have polarizable donor σ pairs of electrons but which have little capacity for π bond formation. Both of these factors tend to minimize contraction of the d orbital containing the unpaired electron and hence favor overlap. The carbonyl compounds of Re⁰ and Tc⁰ (33) are now known and have properties similar to those of Mn₂(CO)₁₀. Lastly, we come to the -I oxidation state, which occurs in the dimeric complex ion [Cr₂(CO)₁₀]²⁻. Similar derivatives of Mo and W are known (8, 9).

Before leaving the d^7 configuration it is important to note that caution

is required when assigning oxidation states if metal-hydride formation is possible. Thus, certain diamagnetic rhodium compounds originally believed to have the formula $[\text{Rh}(\text{hal})_2 \cdot 3\text{Ph}_2\text{AsMe}]_2$ with a metal-metal bond, have since been shown to owe their diamagnetism to the fact that the Rh atom is trivalent, the formula being actually $\text{HRh}(\text{hal})_2 \cdot 3\text{Ph}_2\text{AsMe}$ (44).

7. Oxidation States with the d^6 Configuration

This is a very common arrangement for spin-paired complexes, but the only spin-free d^6 oxidation states are those of Co^{III} in octahedral K_3CoF_6 , of Fe^{II} in octahedral $[\text{Fe}(\text{NH}_3)_6]\text{Cl}_2$ and of Fe^{II} in tetrahedral complexes, e.g., $[\text{Ph}_3\text{MeAs}]_2\text{FeCl}_4$ (25). No spin-free Mn^{I} complexes are known but as with Fe^{I} it is possible that this oxidation state can be stabilized in a suitable host lattice.

The known oxidation states having a spin-paired d^6 configuration are very extensive, the d_e^6 arrangement being specially favorable for a regular octahedral arrangement.

The d^6 Spin-Paired Configuration					
V^{-I} [V(CO) ₆] ⁻	Cr⁰ Cr(CO) ₆	Mn^I Mn(CO) ₅ I	Fe^{II} [Fe(CN) ₆] ⁴⁻	Co^{III} [Co(NH ₃) ₆] ³⁺	Ni^{IV} [NiF ₆] ²⁻
Nb^{-I} [Nb(CO) ₆] ⁻	Mo⁰ Mo(CO) ₆	Tc^I Tc(CO) ₅ I	Ru^{II} [Ru(CN) ₆] ⁴⁻	Rh^{III} [RhCl ₆] ³⁻	Pd^{IV} [PdCl ₆] ²⁻
Ta^{-I} [Ta(CO) ₆] ⁻	W⁰ W(CO) ₆	Re^I Re(CO) ₅ I	Os^{II} [Os(CN) ₆] ⁴⁻	Ir^{III} [IrCl ₆] ³⁻	Pt^{IV} [PtCl ₆] ²⁻

The octahedral spin paired complexes of Ni^{IV} , Pd^{IV} and Pt^{IV} ; of Co^{III} , Rh^{III} , and Ir^{III} ; and of Fe^{II} , Ru^{II} , and Os^{II} are well known but one point of interest calls for comment. The IV state for Ni is now well known but no facile generalization can be made as to relative stabilities of Ni^{IV} and Pd^{IV} unless the ligand used be specified. Thus using Cl^- , $[\text{PtCl}_6]^{2-}$ is much more stable than the readily reduced $[\text{PdCl}_6]^{2-}$ and the $[\text{NiCl}_6]^{2-}$ ion is unknown. However, for ions of the type $[\text{M}^{\text{IV}}(\text{Diarsine})_2\text{Cl}_2]^{2+}$ the stability appears to be $\text{Pt}^{\text{IV}} \gg \text{Ni}^{\text{IV}} > \text{Pd}^{\text{IV}}$ (28). Presumably the relative order of the promotion energies involved changes with the residual charge on the metal atom.

The oxidation state $-I$ appears to occur in the $[\text{V}(\text{Dipyridyl})_3]^-$ ion but the location of the electrons is uncertain (30).

8. Oxidation States with the d^5 Configuration

The spin-free arrangement, even though it involves a half-filled d -shell is limited in its occurrence to Fe^{III} and Mn^{II} . The spin-paired d^5 arrange-

ment is expected to be associated with an octahedral stereochemistry; indeed, stable d^5 octahedral complexes are known for oxidation states from +IV (in $\text{K}_2\text{Ir}^{\text{IV}}\text{F}_6$) to 0 (in $\text{V}(\text{CO})_6$) and perhaps -I (in the $[\text{Ti}(\text{Dipyridyl})_3]^-$ ion).

The d^5 Spin-Paired Configuration					
Ti^{-I} [TiDipy ₃] ⁻¹	V⁰ V(CO) ₆	Cr^I [CrDipy ₃] ⁺	Mn^{II} Mn(CN) ₆ ⁴⁻	Fe^{III} [Fe(CN) ₆] ³⁻	Co^{IV} [CoF ₆] ²⁻
Zr ^{-I}	Nb ⁰	Mo ^I	Tc^{II} [Tc Diars. ₂ I ₂] ⁰	Ru^{III} [Ru(CN) ₆] ³⁻	Rh^{IV} [RhCl ₆] ²⁻
Hf ^{-I}	Ta ⁰	W ^I	Re^{II} [Re Diars. ₂ Cl ₂] ⁰	Os^{III} [Os(CN) ₆] ³⁻	Ir^{IV} [IrCl ₆] ²⁻

Oxidation states which have been stabilized recently include Re^{II} and Tc^{II} as Diarsine complexes of the type $[\text{M}^{\text{II}}(\text{Diarsine})_2\text{Cl}_2]^0$ (23), Cr^{I} as $[\text{Cr}^{\text{I}}(\text{Dipyridyl})_3\text{ClO}_4]$ and V^0 as the carbonyl $\text{V}(\text{CO})_6$ (10, 61). Earlier doubts as to whether this carbonyl is dimeric and diamagnetic or monomeric and paramagnetic have been resolved in favor of the latter. Thus $\text{V}(\text{CO})_6$ is the only known carbonyl which does not obey the "nearest inert gas" rule. The absence of d^5 compounds of the remaining elements to the bottom left hand corner of this table probably reflects more the lack of purposeful work on this subject than inherent difficulties in their stabilization.

9. Oxidation States with the d^4 Configuration

The d^4 configuration is of special interest in many ways because it is known to give rise to 0, 2, or 4 unpaired electrons and to coordination numbers of 4, 6, and 7. Regarding the spin-free complexes of atoms with 4 unpaired electrons, we find that this highly paramagnetic state arises with Cr^{II} and Mn^{III} only. From simple crystal field theory one expects a square planar arrangement for *four*-coordinate spin-free d^4 complexes and a tetragonal arrangement if the coordination number is six. This is certainly true for $[\text{CrCl}_4]^{2-}$ and $\text{CrCl}_2 \cdot 2\text{Py}$. The spin-free oxidation states of +I (V^{I}) and +IV (Fe^{IV}) have not been reported. The failure to prepare $\text{K}_2\text{Fe}^{\text{IV}}\text{F}_6$ is curious for although one has to break the d^5 shell of Fe^{III} to achieve this, the relative ease with which Fe^{IV} can be stabilized with diarsine and Fe^{VI} with oxygen suggests that this is not the main problem to be overcome.

The oxidation states in which the d^4 configuration has two unpaired electrons are shown in the Table below. In an octahedron this indicates a d_{xy}^4 arrangement and is observed for a wide range of oxidation states. The sole example of the +VI state (of Pt) is PtF_6 (?) and similarly only one example of +V, KIrF_6 is known. The +IV state is represented by Fe, Ru, and Os with compounds of the type $[\text{M}^{\text{IV}}(\text{Diarsine})_2\text{Cl}_2][\text{ClO}_4]_2$

The d^4 Configuration				
Cr^{II} Cr(CN) ₆ ⁴⁻	Mn^{III} [Mn(CN) ₆] ³⁻	Fe^{IV} [Fe Diars. ₂ Cl ₂] ²⁺	Co ^V	Ni ^{VI}
Mo^{II} [Mo Diars. ₂ I ₂] ⁰	Tc^{III} [Tc Diars. ₂ Cl ₂] ⁺	Ru^{IV} [RuCl ₆] ²⁻	Rh ^V	Pd ^{VI}
W^{II} [W Diars. ₂ I ₂] ⁰	Re^{III} [Re Diars. ₂ Cl ₂] ⁺	Os^{IV} [Os Diars. ₂ Cl ₂] ²⁺	Ir ^V K[IrF ₆]	Pt ^{VI} PtF ₆

[M^{IV} = Fe (55) or Os (56)] or K₂M^{IV}Cl₆ (M^{IV} = Ru or Os). As with the Ni, Pd, and Pt triad, we find that whereas the Cl⁻ ion will stabilize the two heavier elements, diarsine is needed to stabilize Fe^{IV}. Once again, as with Pd^{IV}, we find that the complex ion [Ru^{IV}(Diarsine)₂Cl₂]²⁺ is much less stable than the corresponding complex Fe^{IV} ion. (It is of interest to note that the Co, Rh, and Ir sequence might be expected to show similar behavior. In fact Ir^{IV} is quite stable in the compound K₂IrCl₆ whereas, although Rh^{IV} can be prepared as Cs₂Rh^{IV}Cl₆ the compound loses chlorine rapidly if moist. It is more effectively stabilized by including it in a host lattice such as [NH₄]₂PtCl₆. Experience with the Fe, Ru, and Os and Ni, Pd, Pt triads suggests that the [Co^{IV}(Diarsine)₂Cl₂]²⁺ should perhaps be less difficult to prepare than [Rh^{IV}(Diarsine)₂Cl₂]²⁺).

Coming to the oxidation state +III, the complex cyanide K₃Mn(CN)₆ has been known for many years but Re^{III} and Tc^{III} in octahedral complexes have been obtained only recently (23). In both cases, the complex formed was of the type [M^{III}(Diarsine)₂Cl₂]⁺Cl⁻. The +II state can be stabilized in the case of Cr^{II} as the complex cyanide and recently a series of d^4 octahedral complexes of Mo^{II} of the type [Mo^{II}(Diarsine)₂Cl₂]⁰ (46) have been prepared. The assigned octahedral structure is supported by the fact that the compounds are isomorphous with the corresponding Tc^{II} and Re^{II} complexes. The spin-paired d^4 oxidation state +I for vanadium has not yet been reported.

Finally, we come to the diamagnetic d^4 complexes. These are of three kinds (a) those in which the metal atom is (presumably) four-coordinate; (b) those in which it is definitely seven-coordinate and (c) those in which metal-metal bonding must be invoked. The best examples of the first of these types are the Re^{III} halide derivatives, e.g., Re₂Cl₆ and the [ReCl₄]⁻ ion. Recent investigations (2) have indicated that Re₂Cl₆ is dimeric in a variety of solvents and this supports—but does not confirm—the generally accepted halogen bridged tetrahedral structure like anhydrous ferric

Footnote added in proof: It has now been shown by Cotton and also by Ferguson *et al.* (personal communications) that the [ReCl₄]⁻ ion is in fact trimeric in the solid state. The [Re₃Cl₁₂]³⁻ unit involves a central group of three Re atoms in a triangle.

chloride. Similarly, it has been shown that the $[\text{ReCl}_4]^-$ is apparently monomeric in solution. The hypothesis that the Re^{III} is tetrahedral with a d_7^4 configuration would, as pointed out by Orgel, explain the diamagnetism. However, all attempts to establish this tetrahedral arrangement have so far proven unsuccessful.* One expects that Mo^{II} and W^{II} might give rise to similar d_7^4 complexes, e.g., $\text{K}_2\text{Mo}^{\text{II}}\text{Cl}_4$ but so far all attempts to isolate these have proven fruitless. Similarly, $\text{Os}^{\text{IV}}\text{Cl}_4$ shows no evidence of the properties expected if it were in fact tetrahedral and monomeric.

The seven-coordinate diamagnetic complexes are derived from certain carbonyl compounds wherein the governing rule appears to be the desire on the part of the metal to reach the nearest inert gas configuration. Since there are four nonbonding electrons occupying two d orbitals only, there are clearly seven orbitals available for bond formation. Such compounds are formed by Mo^{II} and W^{II} , e.g., by the reaction (52). $\text{Mo}^0 \text{Diarsine}(\text{CO})_4 + \text{I}_2 \rightarrow \text{Mo}^{\text{II}} (\text{Diarsine})(\text{CO})_3\text{I}_2 + \text{CO}$. Finally, we have compounds in which metal-metal bonding is invoked. The best examples of this are the derivatives of the bivalent molybdenum halides. In general these can be looked upon as derived from a basic cation of the formula $[\text{Mo}_6\text{Cl}_8]^{4+}$. The structure

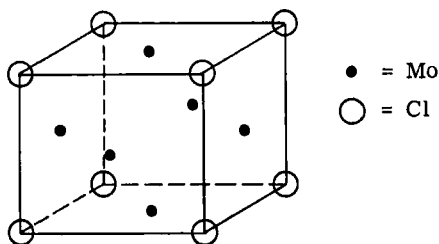


FIG. 3. Structure of $[\text{Mo}_6\text{Cl}_8]^{4+}$.

of this is shown in Fig. 3. The eight Cl atoms occupy the corners of a cube and the six molybdenum atoms are in the middle of the six faces. Six groups now have to be attached, one to each Mo atom normal to the faces of the cube. In the compound $[\text{Mo}_6\text{Cl}_8]^{4+}[\text{Cl}^-]_4 \cdot 2\text{H}_2\text{O}$ there are clearly four chlorine ions and two water molecules. However, unless one invokes some kind of pairing of d electrons between molybdenum atoms, such a complex is expected to be paramagnetic. The symmetry of the d_4 orbitals permit such pairing of electrons and if one regards each Mo as having in effect a valency of six one can understand the magnetic properties and the absence of color in these derivatives (59, 63).

10. Oxidation States with a d^5 Configuration

Two possibilities arise in this instance, those compounds which contain *three* and those which contain only *one* unpaired electron. We discuss these

* See note added in proof on page 40.

in turn. The spin-free d^3 configuration is specially favorable for octahedral coordination and the extent to which this d^3 configuration is able to give rise to a wide range of oxidation states is shown in the following table:

The d^3 (Spin-Free) Configuration				
V^{II} [V(H ₂ O) ₆] ²⁺	Cr^{III} [Cr(NH ₃) ₆] ³⁺	Mn^{IV} [MnF ₆] ²⁻	Fe^V [FeO ₄] ³⁻	Co^{VI}
Nb^{II}	Mo^{III} [MoCl ₆] ³⁻	Tc^{IV} [TcCl ₆] ²⁻	Ru^V [RuF ₆] ⁻	Rh^{VI}
Ta^{II}	W^{III} [W ₂ Cl ₉] ³⁻	Re^{IV} [ReCl ₆] ²⁻	Os^V [OsF ₆] ⁻	Ir^{VI} [IrF ₆] ⁰

Perhaps the most interesting are the compounds of Mo^{III}, W^{III}, Tc^{IV}, Re^{IV}, Os^V, and Ir^{VI}, since three unpaired electrons is the greatest number observed in any compounds in the second two transition series. Again, not much is known of the oxidation state +II arising with d^3 complexes of V^{II}, Nb^{II}, and Ta^{II}.

The spin-paired d^3 complexes contain only one unpaired electron and if we assume that spin pairing occurs because the third orbital is used for bond formation, seven-coordination results. This occurs in the complex cyanide of Mo^{III}, K₄Mo(CN)₇·2H₂O, and in certain W^{III} complexes such as [W^{III}Diarsine(CO)₃Br₂]⁺Br⁻ (57). Similar paramagnetic seven-coordinate derivatives are expected with Tc^{IV} and Re^{IV} and with Nb^{II} and Ta^{II} but no examples have yet been reported.

11. Oxidation States with a d^2 Configuration

We consider first the spin-free compounds, containing two unpaired electrons. These are expected to arise for the oxidation states shown in the table. The spin free d^2 configuration is of special interest in connection with

The d^2 (Spin-Free) Configuration				
Ti^{II} Na ₂ TiCl ₄	V^{III} [V(H ₂ O) ₆] ³⁺	Cr^{IV} K ₂ CrF ₆	Mn^V K ₃ MnO ₄	Fe^{VI} K ₂ FeO ₄
Zr^{II}	Nb^{III}	Mo^{IV}	Tc^V	Ru^{VI} K ₂ RuO ₄
Hf^{II}	Ta^{III}	W^{IV}	Re^V	Os^{VI} OsF ₆

the formation of tetrahedral complexes since the d_{γ}^2 configuration gives a half filled d_{γ} shell. It is no accident, therefore, that in the first transition series the oxidation states from +II to +VI are all associated with tetra-

hedral complexes—although an octahedral arrangement is also possible (e.g., with V^{III}). The isolation of $Na_2Ti^{II}Cl_4$ (45) is a good example of the way in which an oxidation state may be stereochemically stabilized. The stability of the compound K_2FeO_4 is presumably related to this also, K_2FeO_4 being isomorphous with K_2SO_4 .

The d^2 Spin-Paired Configuration				
Ti^{II}	V^{III}	Cr^{IV}	Mn^V	Fe^{VI}
Zr^{II}	Nb^{III}	Mo^{IV} [Mo(CN) $_8$] $^{4-}$	Tc^V [Tc Diars $_2$ Cl $_4$] $^+$	Ru^{VI}
Hf^{II}	Ta^{III}	W^{IV} [W(CN) $_8$] $^{4-}$	Re^V [Re Diars $_2$ Cl $_4$] $^+$	Os^{VI}

The second possibility is, of course, diamagnetism, and this is expected to be associated with eight coordination. Running along the two heavier transition series, examples of this include: for the oxidation state +IV, $K_4Mo(CN)_8$ and $K_4W(CN)_8$; for the oxidation state +V, the complex cyanides $K_3Tc(CN)_8$ and $K_3Re(CN)_8$ (19) and the diarsine complexes of the type $[M^V(Diarsine)_2Cl_4]ClO_4$, where $M^V = Tc^V$ and Re^V (23). Surprisingly, corresponding Ru^{VI} , Os^{VI} compounds have not yet been prepared and the +III state for Nb and Ta appears to have been little investigated.

12. Oxidation States with a d^1 Configuration

These are expected to arise for the elements shown in the following table and, as may be seen, it is of common occurrence.

The d^1 Configuration				
Ti^{III} [Ti(H $_2$ O) $_6$] $^{3+}$	V^{IV} VCl $_4$	Cr^V [CrO $_4$] $^{3-}$	Mn^{VI} [MnO $_4$] $^{2-}$	Fe^{VII}
Zr^{III} ZrCl $_3$	Nb^{IV} NbCl $_4$	Mo^V MoCl $_5$	Tc^{VI} TcCl $_6$	Ru^{VII} [RuO $_4$] $^-$
Hf^{III} HfCl $_3$	Ta^{IV} TaI $_4$	W^V WBr $_5$	Re^{VI} ReF $_6$	Os^{VII} [OsO $_4$] $^-$

A survey reveals that this configuration is associated with a wide range of coordination numbers extending from four to eight. In complexes where the binding is essentially covalent as in metal carbonyls, we expect a coordination number of eight. This observed in the case of complexes of Re^{VI} , e.g., the $[Re^{VI}(CN)_8]^{2-}$ ion, and the recently reported $[Tc^{VI}(CN)_8]^{2-}$ ion. Similarly Mo^V and W^V give rise to octacyanides of the type

$[\text{Mo}^{\text{V}}(\text{CN})_8]^{3-}$. These latter have a structure based on a dodecahedral arrangement which can be visualized as arising from two interlacing tetrahedra, one of which has been slightly flattened while the other is slightly elongated (cf. Fig. 4). Quadrivalent vanadium also gives rise to a structure of this type; vanadium tetrachloride and diarsine react to form the compound $\text{VCl}_4 \cdot 2$ Diarsine (17) which is isomorphous with the corresponding titanium complex. The structure of this is shown in Fig. 4. No similar diarsine derivatives of niobium or tantalum have yet been prepared; in view of the greater ease with which eight coordination arises in the second two transition series one might expect eight coordinate derivatives of Nb^{IV} and Ta^{IV} to arise also. The unusual eight-coordination for quadrivalent vanadium is

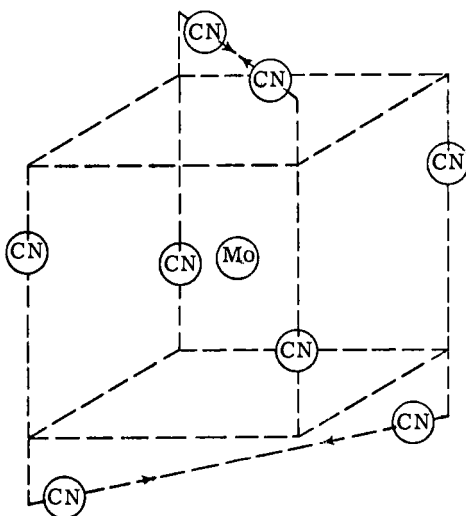


FIG. 4. Structure of $[\text{Mo}^{\text{V}}(\text{CN})_8]^{3-}$.

noteworthy. Presumably, the bonds are sufficiently ionic to ensure that bond pair-bond pair repulsions are relatively small. Six coordination is very common and is exemplified by the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion and by compounds such as ReF_6 . Four coordinate complexes of the type $[\text{MO}_4]^{2-}$ are well known for Mn^{VI} and recently the corresponding Re^{VI} and Tc^{VI} derivatives have been isolated (38). The single d_γ electron has practically no effect upon the regular tetrahedral stereochemistry, $\text{BaMn}^{\text{VI}}\text{O}_4$ being isomorphous with BaSO_4 . The oxidation state V for chromium also arises in a presumably tetrahedral complex ion of the type $[\text{Cr}^{\text{VO}}_4]^{3-}$ described first by Klemm (41) and co-workers and recently investigated in more detail by Bailey and Symons (3).

The quadrivalent state occurs in VCl_4 which is again regular tetrahedral.

No $[\text{Ti}^{\text{III}}\text{Cl}_4]^-$ complexes have yet been reported but the ease with which the corresponding $[\text{VCl}_4]^-$ complexes can be prepared by employing a suitable solvent suggests that these should be capable of being prepared. No stable complexes of tervalent zirconium or hafnium have been reported but the tervalent halides are well known (50). They display only very weak paramagnetism and this appears to indicate strong antiferromagnetic interaction in the crystal.

13. Oxidation States with the d^0 Configuration

Oxidation states embodying this configuration extend all the way from the univalent K, Rb, and Cs triad to the heptavalent elements of Mn, Tc, and Re. The first break occurs at iron, no Fe^{VIII} compounds being known. Ru^{VIII} and Os^{VIII} are known as their tetroxides but the previously reported octafluoride of osmium has recently been shown to be in fact the hexafluoride. It is of interest to note that if the nine-orbital rule were obeyed, complexes having a coordination number 9 are possible. The only possible example of this is the strontium nonahydrate ion of unknown structure. Gillespie, (25a) however, has suggested that a 3:3:3 structure is the most likely configuration for this ion. Eight-coordination occurs in the bis-diarsine complexes of quadrivalent titanium, zirconium, and hafnium, the structure being shown in Fig. 4.

Oxidation States with a d^0 Configuration								
A⁰	K^I	Ca^{II}	Sc^{III}	Ti^{IV}	V^V	Cr^{VI}	Mn^{VII}	Fe^{VIII}
Element	KCl	CaCl ₂	ScCl ₃	TiCl ₄	VF ₅	$[\text{CrO}_4]^{2-}$	$[\text{MnO}_4]^-$	
Kr⁰	Rb^I	Sr^{II}	Y^{III}	Zr^{IV}	Nb^V	Mo^{VI}	Tc^{VII}	Ru^{VIII}
Element	RbCl	SrCl ₂	YCl ₃	ZrCl ₄	NbCl ₅	MoF ₆	$[\text{TcO}_4]^-$	RuO ₄
Xe⁰	Cs^I	Ba^{II}	La^{III}	Hf^{IV}	Ta^V	W^{VI}	Re^{VII}	Os^{VIII}
Element	CsCl	BaCl ₂	LaCl ₃	HfCl ₄	TaCl ₅	WCl ₆	$[\text{ReO}_4]^-$	OsO ₄

IV. Summary

In this article we have endeavored to show that the "formal" oxidation state adopted by transition metal in a compound depends, not only upon the nature of the metal and its electronic configuration, but also upon its environment. The fundamental controlling factor appears to be the stability of an electrically neutral situation around the metal and indeed around every atom in the system, and, although it is not possible to convert this principle of electroneutrality to a quantitative basis, it remains, nevertheless, a good working hypothesis with which to assess the stability of a

particular compound. The major departure from this principle occurs in the ionic lattice compounds where the loss of stability due to the departure from electroneutrality is more than compensated by the gain in lattice energy. In these compounds the major factors influencing the stability of an oxidation state are the relevant ionization potentials of the metal and the lattice energy of the product and, to a lesser extent, the appropriate electron affinities of the nonmetallic component. In general, provided a closed electron shell on the metal is not broken into, the increase in the lattice energy due to the greater cationic charge will compensate for the increased ionization potential. The limits of stability are reached, not as a result of the energetics of the ionic system, but as a result of the increased polarizing power of the metal ion in the higher oxidation states, especially the relatively small transition metal ions. Thus no anion is sufficiently unpolarizable to resist covalent bond formation in the higher "formal" oxidation state compounds and the factors involving the stability of the covalent compounds become of major importance.

Further considerations arise when we consider the transition metals where the number and arrangement of the *nonbonding d* electrons have a considerable effect upon the stability of the compound. It was pointed out in the preceding section that certain electronic configurations were less stable than others. The stability of a more than half filled *d* shell is far greater when there is an even number of *d* electrons than when this is odd, compare d^6 , d^8 , and d^{10} with d^7 and d^9 , whereas no similar sharp distinction exists in a shell which is half filled or less. This is attributed to the steadily increasing effective nuclear charge as the *d* shell nears completion, which causes the bonding to become more covalent in character, and, in doing so, draws the bonding electrons in towards the nonbonding shell. As a result it is easier for the unpaired electron on one atom to interact with one on another atom and either be shared or transferred.

Certain electron configurations favor stabilization of a regular tetrahedral or octahedral environment, e.g.,

Regular tetrahedron d^0 , d^2 , $d^4_{(\text{SF})}$, $d^5_{(\text{SF})}$, $d^7_{(\text{SF})}$, d^{10}

Regular octahedron d^0 , d^3 , $d^5_{(\text{SF})}$, $d^6_{(\text{SF})}$, d^8 , d^{10}

(SF = spin free, SP = spin paired)

and, no doubt, the provision of a suitable forced geometry by the environment might stabilize an otherwise unusual oxidation state, e.g., Fe^{I} in a tetrahedral environment.

Finally, it should be stressed that the absence of an example of a metal in a particular oxidation state need not reflect the inherent instability of that particular oxidation state but possibly the lack of purposeful research.

It is to be hoped that this article will make easier the task of those whose purposeful research will find examples of hitherto uncharacterized oxidation states of the transition metals.

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NOTES ADDED IN PROOF

p. 10. Note 1.

Following observations of the high electron affinity of PtF_6 (>161 kcal/mole) [Bartlett, N., and Lohmann, D. H., *J. Chem. Soc.* p. 5253 (1962)], the stabilization of Xe(I) in the compound, $\text{Xe}^+[\text{PtF}_6]^-$, was predicted and achieved [Bartlett, N., *Proc. Chem. Soc.* p. 218 (1962)]. This

breaking of the "prejudice barrier" has lead very rapidly to the isolation and characterization of XeF_2 , XeF_4 , XeF_6 , and $[\text{XeO}_4]^{2-}$, and the great interest that has been aroused in this field will lead, in a short time, to an extensive chemistry of the once "inert" gases.

p. 32. Note 2.

It has now been shown [Robinson, W. T., Fergusson, J. E., and Penfold, B. R., *Proc. Chem. Soc.* p. 116 (1963)] that the complex ion in CsReCl_4 is the trimeric $[\text{Re}_3\text{Cl}_{12}]^{3-}$ with each Re atom essentially seven-coordinate.

OXIDES AND OXYFLUORIDES OF THE HALOGENS

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Introduction

The existence of oxy-compounds of chlorine, bromine, and iodine has been known for a long time, and chlorine oxides, in particular, were the object of numerous investigations. These were limited, however, to physico-chemical measurements, apart from work on hydrolysis or ammonolysis and on the respective oxidizing powers. Thus, especially in the 1920's and 1930's, the mechanism of formation and decomposition of these oxides became largely understood. Photochemical decomposition processes were

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also studied and a whole range of physical properties was determined. Subsequently, the structures of these compounds were determined by the use of electron diffraction and of infrared or Raman spectroscopy.

Only isolated studies of chemical reactions capable of being applied for preparative purposes were made. The reason for this may be that large-scale manipulation of the chlorine oxides is dangerous because of their explosive properties. Apart from dichlorine heptoxide, appreciable progress in the study of the chemical reactions of these oxides has been made only in the last ten years. Our knowledge of the oxides of bromine and iodine is still quite slight, and their polymeric character makes it difficult to make statements about definite compounds. Only a little is so far known about the chemistry of these oxides.

Directly related to the halogen oxides or anhydrides of the halogen oxyacids are the acid fluorides of the type XO_2F and XO_3F (where X = chlorine, bromine, or iodine), some of which may be made directly by fluorinating the oxides. These compounds have been intensively studied in recent years and ClO_3F , in particular, has excited considerable interest. Compounds of the type XOF are not yet known. Interhalogens with the formula XF , which may be considered as fluorides of the acids XOH , will not be discussed here.

Finally, some reference may be made to the oxygen compounds of fluorine. They stand in a special relationship to the oxygen compounds of the remaining halogens since they should be considered rather as fluorides of oxygen. This stems from the fact that the electronegativity of fluorine is greater than that of oxygen and is implicit in the usual method of formulation as OF_2 , O_2F_2 , etc. The special position of the oxy-compounds of fluorine is also apparent from their completely different stoichiometry compared with the halogen oxides. This leads to the conclusion that, except in the case of OF_2 , the structures and bonding are quite different. Nevertheless, a comprehensive description of these compounds seems desirable because of their contrast to the halogen oxides. It is also very topical because of the interest which the high oxidizing power of the oxygen compounds of fluorine has excited.

In this review new results on the chemistry of the halogen oxides, oxygen-fluorine compounds and halogen acid fluorides are presented. The results of older work are also discussed insofar as this seems necessary to characterize a compound as fully as possible with regard to its typical physical properties and, particularly, its chemical reactions. In those cases where several measurements or different results are available for certain physical properties, the more recent work is considered.

1. Oxygen-Fluorine Compounds

Only two oxygen compounds of fluorine, OF_2 and O_2F_2 , were known until lately. Very recently A. V. Grosse proved the existence of O_3F_2 and

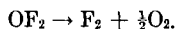
thus confirmed the finding of Japanese workers which till then had been regarded with skepticism. Grosse succeeded finally in synthesizing the oxide O_4F_2 . Practically nothing is known, however, about the chemical reactions of this class of compound.

A. OXYGEN DIFLUORIDE OF_2

Oxygen difluoride was first obtained by Lebeau and Damiens (106) by electrolyzing KHF_2 in presence of water. Shortly afterwards they discovered a further preparative method based on the action of fluorine on aqueous caustic soda solution (107). These methods have remained unchanged in principle up to the present time. Finally, Engelbrecht and Nachbaur (48) studied the preparation of OF_2 and proposed the electrolysis of 80% aqueous hydrofluoric acid: this gives an anode gas containing 58% of OF_2 , the remainder being oxygen.

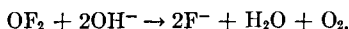
The most important physical properties are shown in Table I. Vapor pressures between $-195^\circ C$ and $-145^\circ C$ may be represented by the equation $\log_{10} p_{mm} = 7.2242 - 555.42/T$ (172). The density of liquid OF_2 as a function of temperature is given by $d = 2.1315 - 0.00469 T$ (150). Critical data are (1): $T_c = -58.0 \pm 0.1^\circ C$; $V_c = 97.6 \text{ cm}^3/\text{mole}$; $p_c = 48.9 \text{ atm}$.

Recent dipole moment measurements gave a value of $0.1759 \pm 0.0010 D$; this has been interpreted as indicating a contribution of 2.1% of an ionic structure $O^{2+}(F^-)_2$ (28). [Note added in proof: Pierce *et al.* (147a) gave a value of $0.297 \pm 0.005 D$ for the dipole moment.] Both the photochemical and the thermal decomposition of oxygen fluoride were investigated by Schumacher (72, 99). The thermal reaction occurs unimolecularly at $250^\circ C$ to $280^\circ C$ according to the equation



The theoretical prediction that a first order reaction should go over into one of second order at a certain pressure was first verified in the case of OF_2 by Schumacher (177).

Investigations on OF_2 reported so far are almost entirely physicochemical in character, and there are only isolated publications on its reactions. Exploratory studies of the action of OF_2 on solid inorganic compounds have demonstrated that its reactivity as a fluorinating agent is less than that of elementary fluorine (150). In aqueous solution it acts more as an oxidizing agent, in keeping with the strong affinity of fluorine for hydrogen (86, 106, 150, 195). Thus bromide and iodide are oxidized to bromine or iodine; prolonged reaction with aqueous alkalis yields oxygen:



B. DIOXYGEN DIFLUORIDE O_2F_2

Ruff and Menzel (151, 152) obtained O_2F_2 as an orange-red solid deposit on passing a stream of fluorine containing oxygen through a glow discharge,

TABLE I
PROPERTIES OF OXYGEN-FLUORINE COMPOUNDS

	OF ₂	O ₂ F ₂	O ₃ F ₂	O ₄ F ₂
M.p. (°C)	-223.8 (152)	-163.5 (153)	-189 (98)	Solid at -196; liquid at -183 (78)
B.p. (°C)	-145.3 (172)	-57.0 (152)		> -183 (78)
Decomposition temperature (°C)		> -57.0	> 158 (98)	
Trouton's Constant	20.65 (150)	21.2 (153)		
Density (gm/ml at °C)	1.521 at -145.3 (1)	1.736 at -157.0 (153)	1.756 at -163 (98)	
Heat of formation (kcal mole ⁻¹)	-7.6 ± 2 (53)	+4.73 ± 0.30 (97)	+6.24 ± 0.75 (97)	
IR-Spectrum	(91) (19)	(31)		
Microwave spectrum		(87)		

the discharge tube being cooled in liquid air. The compound melts at -163.5°C to a cherry red liquid which decomposes rapidly to O_2 and F_2 in the neighborhood of its boiling point, -57°C . Thermal decomposition, which was measured between -60° and -25°C , is homogeneous and unimolecular (69, 70).

Vapor pressures measured below -100°C are represented by the equation $\log_{10} p_{\text{mm}} = 7.515 - 1000/T$ (153). Liquid densities are given by $d = 2.074 - 0.00291 T$ (153). The dipole moment is $1.40 D$ (87). For other physical properties see Table I.

Grosse succeeded recently in measuring directly the heat evolved in the decomposition of liquid O_2F_2 at -83°C into gaseous oxygen and fluorine, as well as that for the decomposition of liquid O_3F_2 at -152°C (97). From these values the heats of formation of gaseous O_2F_2 and O_3F_2 at 25° (see Table I) and the corresponding bond energies were calculated.

C. TRIOXYGEN DIFLUORIDE (OZONE FLUORIDE) O_3F_2

A compound with the composition O_3F_2 was first reported by Aoyama and Sakuraba (2, 3). Their discovery was not, however, generally accepted, possibly because an exact quantitative analysis was not given and because the possibility that oxygen was dissolved in O_2F_2 was not excluded. The existence of O_3F_2 as a definite compound was first confirmed by Kirshenbaum and Grosse in 1959 (98). An oxygen-fluorine mixture (3:2) was converted quantitatively into O_3F_2 in a glow discharge (2100–2400 volts; 25–30 ma) at a total pressure of 12 ± 1 mm and at liquid air temperature; the yield was 3–4 gm of O_3F_2 per hour.

In the meantime a further method of forming O_3F_2 was found, based on the decomposition of NF_3 with O_2 in a glow discharge (3700 volts; 20 ma; 0.6 torr) (134). A mixture of O_3F_2 and O_2F_2 condenses in the discharge tube, which is cooled with liquid nitrogen. Under these conditions NF_3 is clearly broken down completely since no compound containing the N—F bond can be condensed.

Properties (98). Ozone fluoride is a blood red viscous liquid, which remains liquid at -186°C and is thus readily distinguished from O_2F_2 . The endothermic compound decomposes quantitatively and exothermally at about -158°C according to the equation



It may be boiled under reflux in the temperature range -177° to -159°C at 0.1 to 1.5 torr with only a little decomposition, and it may also be distilled.

Vapor pressures, which were measured between -194° and -159°C , are represented by the equation: $\log_{10} p_{\text{mm}} = 4.7277 - 520.7/T$. The liquid

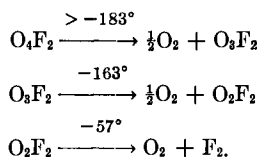
density is given by $d = 2.357 - 0.00676 T$. Ozone fluoride is one of the strongest oxidizing agents known; like O_2F_2 , it is appreciably more reactive than OF_2 , F_2 , or mixtures of O_2 and F_2 , but by itself is not explosive. Organic compounds or other oxidizable materials inflame instantly or even explode.

At -157°C , O_3F_2 is readily soluble in $CFCl_3$ or CF_2Cl_2 over the whole concentration range. On the other hand it is insoluble at -196°C in liquid fluorine, nitrogen or oxygen. Gaseous fluorine does not react with ozone fluoride at -196°C , but if the fluorine is activated by a discharge (3000–4000 volts; 30–60 ma), quantitative decomposition to O_2F_2 takes place:



D. TETRAOXYGEN DIFLUORIDE (OXAZONE FLUORIDE) O_4F_2

Grosse *et al.* (78) were able to isolate yet another oxygen fluoride, O_4F_2 , which separated as a red-brown solid in a discharge tube at -196°C using an O_2 - F_2 total pressure of 5–15 torr and with a discharge operated at 840–1280 volts and 4.5–4.8 ma. The possibility of dissolved oxygen or ozone was excluded. At -183°C O_4F_2 is a liquid with a vapor pressure less than 1 torr. Liquid O_4F_2 may be kept, at least for some hours, at -183°C . Slow decomposition to oxygen and ozone fluoride occurs between -183° and -163° . Thus the following sequence of decomposition reactions for the oxygen fluorides may be set out:



E. THE STRUCTURE OF OXYGEN-FLUORINE COMPOUNDS

The structure of the angular molecule of OF_2 (symmetry C_{2v}) was elucidated through its infrared spectrum (19, 91) and by the use of electron diffraction (85). The most probable values for the bond distance r_{O-F} is 1.418 Å, that for the valency angle being 103.2° . On the basis of the microwave spectrum Jackson (87) discussed a structure for O_2F_2 which was of the peroxide type. The following spread of possible values was given for the various parameters:

$$\begin{array}{l} r_{F-O} = 1.44 - 1.54 \text{ Å}; r_{O-O} = 1.28 - 1.48 \text{ Å}; \\ \angle O-O-F = 109^\circ - 110^\circ; \text{dihedral angle} = 75-85^\circ \end{array}$$

Grosse concluded from a comparison of the estimated bond energy in O_2F_2 with that in other compounds that there was considerable resonance

stabilization. Further discussions would be out of place in view of the very incomplete state of our knowledge of F_2O_2 ; this is even more true of O_3F_2 and O_4F_2 .

II. Oxy-Compounds of Chlorine

Four oxides of chlorine have so far been isolated: in orders of increasing oxidation number of the halogen they are Cl_2O , ClO_2 , Cl_2O_6 , and Cl_2O_7 . Their physical properties are given in Table II.

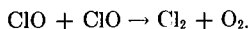
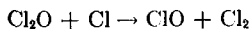
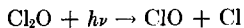
In addition the occurrence of ClO has also been established. This radical occurs both in the course of the decomposition of the chlorine oxides and also in reactions leading to their synthesis. The radical ClO has also been detected in an oxyhydrogen flame to which chlorine has been added. The radicals BrO and IO also occur in analogous conditions and indirect evidence for OF has been obtained in electron bombardment experiments. It has not, however, been possible so far to isolate ClO .

The existence of ClO_4 , which was postulated by Gomberg, has not been confirmed. There was no indication of this compound either when Gomberg's experiments were repeated or in the course of the examination of a series of reactions of silver perchlorate with halogens in the most diverse organic solvents (80). It has, however, been discussed in relation to the decomposition of Cl_2O_7 . According to Hùdepohl (84), the Gomberg reaction ($2AgClO_4 + I_2 \rightarrow 2AgI + 2ClO_4$) should be formulated as follows:



A. DICHLORINE MONOXIDE Cl_2O

Dichlorine monoxide may, according to Podenstein and Kistiakowski (24, 181, 194), be obtained as a brown solid by passing a mixture of chlorine and dry air in a ratio between 1:2 and 1:3 over HgO , and condensing the product in a vessel cooled in liquid air. The compound is extraordinarily unstable and may be exploded by shock or impact. It is also decomposed by light. The photochemical decomposition to chlorine and oxygen (60, 178) proceeds by a primary cleavage into ClO and Cl .



The chlorine-sensitized decomposition occurs similarly according to the following mechanism:

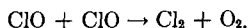
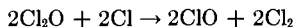
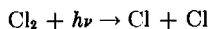


TABLE II
PHYSICAL PROPERTIES OF THE OXIDES OF CHLORINE

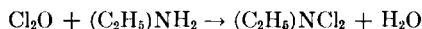
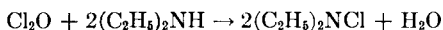
Oxide/Property	Cl ₂ O	ClO ₂	Cl ₂ O ₆	Cl ₂ O ₇
Molecular weight	87	67.5	167	183
M.p. (°C)	-116 (75)	-59 (96)	- +3.5 (76)	91.5 (77, 209)
B.p. (°C)	2.0 (75)	11.0 (96)	203 (calc.) (76)	80 (77)
Vapor pressure at 0°C	699 (75)	490 (96)	0.31 (76)	23.7 (77)
log p_{mm}	+7.87 - 1373/ T (75)		+7.1 - 2070/ T Liquid +9.3 - 2690/ T Solid between -40°C and +20°C (76)	+8.03 - 1818/ T (77)
Trouton's constant	22.5 (75)	23.0 (96)	21 (76)	23.4 (77)
Heat of vaporization (kcal mole ⁻¹)	6.20 (75)	6.52 (96)	9.5 (76)	8.29 (77)
Heat of formation (kcal mole ⁻¹)	-18.26 (207)	25.0 ± 1.5 (53)		
Density (gm cm ⁻³ at °C)		1.64 at 0° (33)	2.02 at 3.5° (54)	1.86 at 0° (125)
Electron diffraction	(43)	(43)		
IR spectrum	(82)	(82, 138, 188, 203)		(14, 188)
Raman spectrum		(102)		(61)
Microwave spectrum	(88)	(13)		

Dichlorine monoxide is shown to be angular by its infrared spectrum (82), from electron diffraction studies (32, 43, 142) and from the microwave spectrum (88). The most probable value for the bond distance $r_{\text{Cl-O}}$ is 1.701 Å, and for the valency angle $\angle \text{ClOCl}$ is $110.8 \pm 1.0^\circ$. The microwave spectrum shows that the molecule has substantial ionic character: a contribution of about 25% by the component Cl^+OCl^- has been suggested.

Reactions of Cl_2O : Dichlorine monoxide is readily soluble in water and is partially decomposed to hypochlorous acid in an equilibrium reaction; hypochlorite is formed with aqueous alkali. The course of ammonolysis was formerly represented by the equation (181)



but new studies (101) have shown that monochloramine and nitrogen chloride may also be isolated and are therefore very probably intermediates. In order to obtain evidence bearing on the course of the reaction, and particularly on the primary step in ammonolysis, the action of Cl_2O on alkyl amines was studied as a model reaction. Both mono- and di-alkylamines were converted into the corresponding chloramines (101).

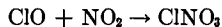


Further investigations are needed, however, to show how far this observation is applicable to the ammonia reaction.

The reaction of dichlorine monoxide with the oxides of nitrogen, and especially with NO_2 and N_2O_5 , has been studied in detail (59, 126, 127, 157). In every case the product is chlorine nitrate, ClNO_3 , which was first discovered by Martin and Jacobsen (128) in studying the system $\text{ClO}_2\text{-NO}_2$. The following set of reactions leading to the formation of ClNO_3 may be formulated on the basis of the kinetic studies of Martin and his co-workers (126), in which monofluorotrichloromethane, CFCl_3 , and trifluorotrichloroethane, $\text{CF}_2\text{Cl}\cdot\text{CFCl}_2$, were used as solvents:

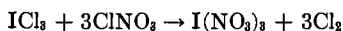
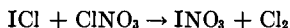
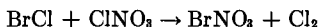


It was found that Cl_2O does not react directly with N_2O_5 either in the gas phase or in solution, but reacts instead with the NO_2 produced in the decomposition of N_2O_5 , and the latter process therefore controls the over-all reaction. The actual step leading to formation of chlorine nitrate in these reactions seems to be



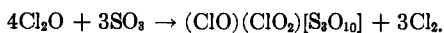
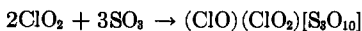
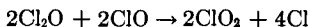
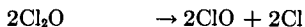
in every case.

Simultaneously and independently Schmeisser and Fink (59, 157) succeeded in carrying out the reaction between dichlorine monoxide and nitrogen pentoxide on a preparative scale. The larger quantities of chlorine nitrate which it was possible to make in this way allowed it to be used in the synthesis of inorganic acyl nitrates [e.g., $\text{CrO}_2\text{Cl}_2 + 2\text{ClNO}_3 \rightarrow \text{CrO}_2(\text{NO}_3)_2 + 2\text{Cl}_2$] and led to the first isolation of bromine nitrate and the iodine nitrates INO_3 and $\text{I}(\text{NO}_3)_3$ (158, 159):



The reaction of nitric oxide and dinitrogen trioxide with Cl_2O at -78°C led mainly to N_2O_4 and chlorine (101). The occasional appearance of chlorine nitrate in the reaction makes it probable that it is also an intermediate in this case, since it can form dinitrogen tetroxide with nitric oxide ($\text{ClNO}_3 + \text{NO} \rightarrow \text{NONO}_3 + \frac{1}{2}\text{Cl}_2$) (158). It is impossible, however, to draw any firm conclusions above the course of the reaction from these purely preparative studies. The same is true of the interaction of dichlorine monoxide and nitrosyl chloride at -78°C , which yields chlorine, chlorine nitrate and N_2O_4 (126).

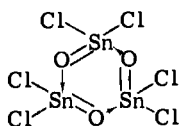
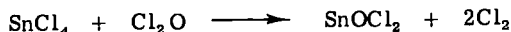
The reaction of Cl_2O with SO_3 was first investigated by Schützenberger (174–176). On passing Cl_2O over SO_3 he obtained a deep red liquid, which crystallized to bright red needles of m.p. 55°C . He ascribed the composition $\text{Cl}_2\text{O} \cdot 4\text{SO}_3$ to this compound, which decomposed explosively if it was heated rapidly. A fresh study of this reaction (201), in which an SO_3 solution in CFCl_3 was added dropwise to a Cl_2O - CFCl_3 mixture at above -27° , also gave red crystals which melted at 56°C and were therefore identical with Schützenberger's product. This compound is not, however, a simple adduct but a chlorosyl-chloryl trisulfate, $(\text{ClO})(\text{ClO}_2)(\text{S}_3\text{O}_{10})$, which is also produced by the interaction of SO_3 and ClO_2 . When SO_3 reacts with Cl_2O it seems that ClO_2 is formed as an intermediate; the following mechanism was proposed for the reaction (201):



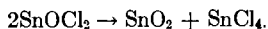
Recently Dehnicke discovered in the action of Cl_2O on metallic chlorides a method for the preparation of anhydrous oxychlorides (39–41). Dichlorine

monoxide was passed as gas into the liquid chloride. These reactions take place very exothermally at room temperature without thermal decomposition of any significant part of the Cl_2O . Oxychlorides corresponding with the highest oxidation state always result because of the strong oxidizing action of Cl_2O and Cl_2 .

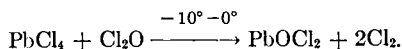
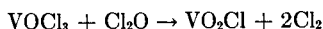
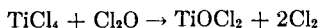
Tin tetrachloride forms a white, amorphous and very hygroscopic oxychloride according to the equation



The oxychloride is high molecular in substance; according to molecular weight determinations it is trimeric. A ring-structure is proposed. It disproportionates at 155°C into tin dioxide and tin tetrachloride:

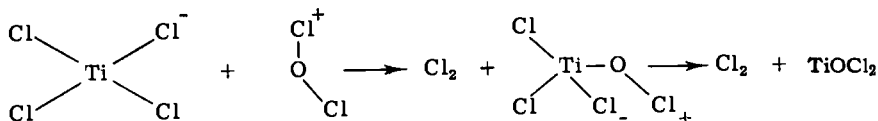


The pale yellow TiOCl_2 produced from TiCl_4 is crystalline. With VOCl_3 , Cl_2O forms orange red crystalline VO_2Cl , which decomposes at 150°C into V_2O_5 and VOCl_3 . Amorphous PbOCl_2 is violet:

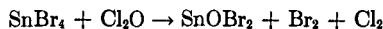


Tantalum pentachloride in carbon tetrachloride solution yields TaOCl_3 or $\text{Ta}_2\text{O}_3\text{Cl}_4$, according to the quantity of Cl_2O used. The oxychlorides give addition compounds with pyridine or POCl_3 , except in the case of PbOCl_2 .

There are indications that the reactions take place through the intermediate formation of hypochlorites. In the case of titanium tetrachloride, for example, the following reactions are possible:



The transformation of metal halides to oxychlorides can be applied directly to the corresponding bromides (liquid or molten). By the action of gaseous Cl_2O on tin or titanium tetrabromide the hitherto unknown oxybromides SnOBr_2 and TiOBr_2 are formed (42). These also give adducts with pyridine.



Similar experiments with the halides of boron and aluminium were made by Schmeisser and Aubke (169), though these were directed not so much to the preparation of oxychlorides as to the preparation of anhydrous oxides at low temperatures. When boron trichloride or tribromide in solution in CFCl_3 at -30°C is decomposed with Cl_2O , flocculent B_2O_3 is precipitated and may be isolated by distilling off the solvent or filtration, and freed from halogen or excess of Cl_2O in vacuo at 70°C . The resulting hygroscopic B_2O_3 is found to be amorphous to X-rays. The same B_2O_3 is formed from undiluted BCl_3 and Cl_2O in the liquid state at -78°C . An analogous reaction occurs with Cl_2O and AlBr_3 at temperatures up to -20°C , though so far no halogen-free oxide has been obtained. Aluminium trichloride does not react with Cl_2O .

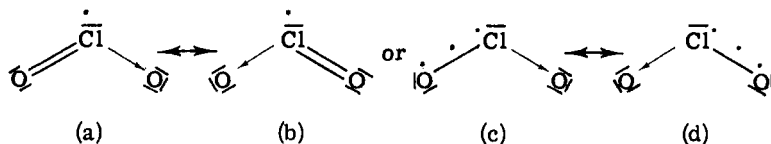
Attempts to fluorinate dichlorine monoxide have so far met with no success; elementary fluorine at -10°C and AgF_2 at room temperature failed to react (59, 122) and no reaction was observed when OF_2 was led through liquid Cl_2O at -100°C (170).

B. CHLORINE DIOXIDE ClO_2

1. Preparation, Structure, and Properties

The best laboratory method for preparing this compound is the action of sulfuric acid on potassium chlorate in the presence of a reducing agent, the most suitable being oxalic acid, since the ClO_2 is then diluted with CO_2 and manipulation becomes relatively free from danger. It is often advantageous to use solutions of chlorine dioxide in carbon tetrachloride; these are made by passing the mixture of ClO_2 and CO_2 coming from the generator into CCl_4 at 0° . Chlorine dioxide is yellow in the gaseous state, red brown as liquid and reddish yellow when solid. The most important physical properties are given in Table II.

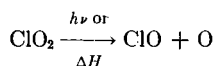
Chlorine dioxide is paramagnetic because it has an odd number of electrons. The bond order calculated from the force constants is 1.5 (188); it has been deduced on theoretical grounds that the unpaired electron is not localized; ClO_2 therefore shows no tendency to dimerize. The electronic structure of ClO_2 may be described in valence-bond terminology by the following formulas, among others.



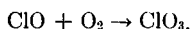
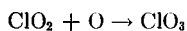
A very high dipole moment would be expected for a structure with three-electron bonds; it is estimated that it would be of the order of 3.4 *D* (43). It follows from the observed dipole moment of 0.78 *D* that structures (a) and (b) must be more important than (c) and (d) (208).

The bond distance $r_{\text{Cl-O}}$ is calculated from the infrared spectrum as 1.49 Å, and the valency angle as 118.5° (82, 138, 203). The same distance has been found from new electron diffraction experiments, though the angle is given as 116.5° (43). From the microwave spectrum (13) the values $r_{\text{Cl-O}} = 1.47$ Å and $\angle \text{OClO} = 117.4^\circ$ were obtained. The paramagnetic resonance spectrum has also been recorded (18).

Chlorine dioxide decomposes at higher temperatures or under the action of light; this is assumed to involve a chain reaction with the initial step

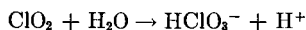
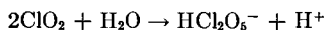


In addition to chlorine and oxygen, which are the end products, Cl_2O_6 is also formed by the steps (25, 179)

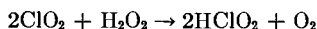


2. Reactions of Chlorine Dioxide

Hydrolysis with aqueous alkali yields chlorite and chlorate as the final products; ClO_2 is therefore usually considered as a mixed anhydride of the two acids. The kinetics of hydrolysis have recently been studied spectrophotometrically, conductometrically and by pH measurements (20). A first or second order reaction predominates, depending on the initial concentration; this is explained in terms of the equations below,



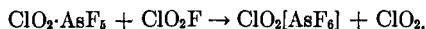
which show ClO_2 to react as a normal acid anhydride. However, secondary disproportionation occurs because of the instability of the acid formed. Chlorine dioxide does not react directly with water, though at low temperatures a solid hydrate is formed; this decomposes at +15°C (191). Reaction of ClO_2 with aqueous hydrogen peroxide according to the equation shown yields appreciable quantities of chlorous acid:



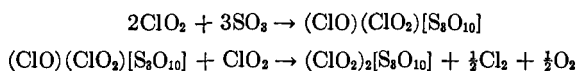
(Yields at 10°C between 26 and 39% HClO_2) (37).

Chlorine dioxide reacts with acceptors to form adducts (160). Antimony pentafluoride at -78°C in C_5F_{12} yields the white nonsublimable compound $\text{ClO}_2\cdot\text{SbF}_5$, which melts at +83°C. In CFCl_3 as solvent at -10°C, ClO_2

and SbCl_5 give $\text{ClO}_2\cdot\text{SbCl}_5$, which decomposes at about 80° with liberation of chlorine and formation of Sb_2O_5 . With AsF_5 at -78° in CFCl_3 , the compound $\text{ClO}_2\cdot\text{AsF}_5$ results; it melts at 80° with decomposition. All these compounds react very violently with water or organic substances. Nothing is known so far about the bonding in these adducts; they may be considered as formally analogous to the nitrogen dioxide addition compounds $\text{NO}_2\cdot\text{AsF}_5$, $\text{NO}_2\cdot\text{SbF}_5$, and $\text{NO}_2\cdot\text{PF}_5$. Elementary fluorine has no reaction on $\text{ClO}_2\cdot\text{AsF}_5$ at $+20^\circ\text{C}$ (59), though the compound is converted to chloryl hexafluoroarsenate by chloryl fluoride (199):



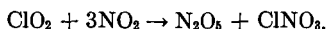
The reaction of ClO_2 with SO_3 was first examined by Lehmann (108). When ClO_2 was passed into liquid SO_3 , products were isolated which contained chlorine, oxygen, and sulfur. The oxidation number of chlorine varied between 4 and 5 according to the quantity of ClO_2 used. It seems that mixtures of chlorosyl-chloryl-trisulfate, $(\text{ClO})(\text{ClO}_2)_2\text{S}_3\text{O}_{10}$, and dichloryl trisulfate, $(\text{ClO}_2)_2\text{S}_3\text{O}_{10}$, must have been formed. Dichloryl trisulfate, m.p. 75.5°C , is obtained when a solution of SO_3 in CFCl_3 is added dropwise at -60° to a solution of ClO_2 in CFCl_3 , so that ClO_2 is always in excess (201). The same compound results when ClO_2 is condensed into chlorosyl-chloryl-trisulfate and the mixture is allowed to warm in the course of 15 hours from -60° to 0°C (201). The reaction between SO_3 and excess of ClO_2 may thus be formulated in two stages:



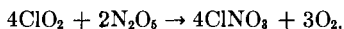
Dichloryl trisulfate may also be obtained from the reaction of SO_3 with KClO_3 or KClO_2 (108).

Formulation of the products as chlorosyl and chloryl compounds is in line with other work by Lehmann (109). When the adduct $\text{N}_2\text{O}_4\cdot 4\text{SO}_3$ is heated a distillate of the composition $\text{N}_2\text{O}_4\cdot 3\text{SO}_3$ results, which is considered to be $(\text{NO})(\text{NO}_2)_2[\text{S}_3\text{O}_{10}]$. The chlorosyl or chloryl sulfates may be converted into the corresponding dinitrosyl or dinitryl compounds by the action of NO or NO_2 (see below under Reactions of Chloryl Compounds, Section II,C,3).

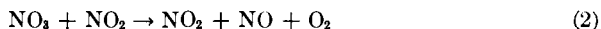
Chlorine nitrate was discovered by Martin and Jacobsen (128) in studying the system $\text{NO}_2/\text{N}_2\text{O}_4/\text{ClO}_2$ at 0° .



Reaction takes place via steps (1), (-1) , (5), and (6) of the scheme given below. This reaction has also been investigated by Schmeisser and Fink (59, 157). The action of ClO_2 with N_2O_5 may be represented approximately by the over-all equation (128):



Chlorine dioxide does not, of course, react directly with N_2O_5 but, as in the case of Cl_2O , with its decomposition products. The reaction scheme proposed for the reaction of ClO_2 with NO_2 or N_2O_5 is (128):



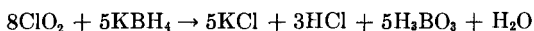
A summary of the reactions leading to formation of ClNO_3 from Cl_2O , ClO_2 and the nitrogen oxides NO_2 and N_2O_5 is given by Martin (126); further literature references are also given.

Reaction between ClO_2 and nitrosyl chloride takes place in the gas phase according to the equation

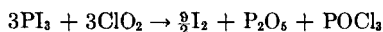


Initially it is extraordinarily slow, but it may be induced by the addition of NO_2 . The reaction is of zero order with respect to chlorine dioxide; its course is believed to involve a chain mechanism initiated by the process $\text{NO}_2 + \text{ClO}_2 \rightarrow \text{NO}_3 + \text{ClO}$ (129, 130).

Chlorine dioxide and chlorite, but not chlorates, are reduced to chloride by potassium borohydride (21).



The oxidation of phosphorus halides by ClO_2 in carbon tetrachloride solution has also been studied (143).



Chlorine dioxide may readily be converted into chloryl fluoride, ClO_2F , by elementary fluorine or other fluorinating agents. These reactions are described in detail in the next section.

C. CHLORYL FLUORIDE, ClO_2F

Chloryl fluoride was first obtained in 1942 by Schmitz and Schumacher (171), by fluorinating chlorine dioxide with elementary fluorine. This method is, however, troublesome because of the extraordinary violence of the reaction and, as a result, no further investigation on ClO_2F appeared

for 10 years. In recent years the formation of ClO_2F has been studied by several workers. Three routes are available, namely fluorination of KClO_3 , ClO_2 , or Cl_2O_6 with elementary fluorine or other fluorinating agents.

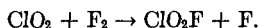
1. Preparation and Formation of ClO_2F

a. Fluorination of KClO_3 . The action of elementary fluorine on KClO_3 represents a method for the formation of chloryl fluoride rather than one for its preparation since it is formed only in small amounts and the main product is perchloryl fluoride (22, 49, 50, 186). These reactions are carried out between -40° and $+30^\circ\text{C}$. Formation of ClO_2F is thought to arise from the combination of fluorine with ClO_2 produced by decomposition of the ClO_3^- anion, and is thus directly related to the formation from ClO_2 and fluorine. The course of the reaction when fluorine acts on potassium chlorate is discussed more fully when perchloryl fluoride is considered. Fluorination of KClO_3 may also be effected with other agents and the yields of ClO_2F are then better. Thus interaction with ClF_3 or BrF_3 leads almost exclusively to ClO_2F because of the higher reaction temperature needed (50, 204).



Fluorsulfonic acid may also be used. It may be thought of as $\text{HF}\cdot\text{SO}_3$, the HF being the actual fluorinating agent, while SO_3 serves to combine with water liberated in the reaction. This method gives a 30% yield of ClO_2F based on the KClO_3 used, in addition to chlorine, chlorine dioxide and oxygen (59).

b. Fluorination of ClO_2 . Chlorine dioxide combines directly with fluorine to form ClO_2F . As already mentioned, chloryl fluoride was first obtained in this way (171). When the reactants are brought together at room temperature only spontaneous decomposition of ClO_2 into chlorine and oxygen is observed. Formation of ClO_2F takes place only if the reactants are brought together at suitable partial pressures which are exactly maintained, or if, after condensing them together, they are warmed slowly from -78°C to $+20^\circ\text{C}$. Reaction is homogeneous and bimolecular; at low ClO_2 concentrations and low pressures the rate controlling step is (7)

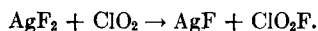


This is followed by the wall reaction $2\text{F} \rightarrow \text{F}_2$. This reaction was developed later by Schumacher (187) into a preparative method. Large quantities of ClO_2F may be prepared by leading fluorine into liquid ClO_2 at -50°C .

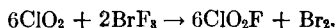
Chloryl fluoride may also be prepared on a larger scale when fluorine is passed into solutions of ClO_2 in indifferent solvents; this eliminates the necessity for working with large quantities of condensed ClO_2 . While in the

case of carbon tetrachloride the relatively high crystallization temperature of the solvent limits the working temperature to a minimum of -20°C , at which only low concentrations are possible, it is feasible with CFCl_3 at -78°C to reach 3 millimole of ClO_2F per ml of solution. Such solutions are excellent for use in studying further reactions of chloryl fluoride (45, 161). By cooling such solutions to -110°C , ClO_2F may be separated and obtained pure after distillation.

The simplest method for preparing chloryl fluoride is certainly to use AgF_2 as the fluorinating agent. When a slow stream of ClO_2 is passed at room temperature through a tube filled with argentic fluoride, quantitative reaction occurs and quite colorless chloryl fluoride may be condensed out in a trap cooled to -78°C (160).



Consumption of argentic fluoride may readily be followed by observing the movement of the boundary between AgF_2 (brown) and AgF (yellow), and in this way excess of ClO_2 can be avoided. Cobalt trifluoride acts in the same way as AgF_2 (160). Chloryl fluoride is also produced when gaseous chlorine dioxide is passed through liquid BrF_3 at $+30^{\circ}\text{C}$ (59, 160).



c. Preparation of ClO_2F from Dichlorine Hexoxide. When dichlorine hexoxide is decomposed thermally in presence of fluorine between 22° and 48°C up to 75% of ClO_2F results (4, 5). From the fact that no formation of ClO_3F can be detected, it may be concluded that neither Cl_2O_6 nor the ClO_3 radical derived from it is capable of reacting with fluorine. It is chlorine dioxide occurring in the decomposition process which unites with fluorine to give ClO_2F . A further product is Cl_2O_7 , in amounts up to 25%. (For the formation of ClO_2F in the thermal decomposition of dichlorine heptoxide in presence of fluorine, see under Dichlorine Heptoxide, Section II,F).

Chloryl fluoride results quantitatively, in addition to nitryl perchlorate, from the action of nitryl fluoride on dichlorine hexoxide at 0°C (see under Dichlorine Hexoxide, Section II,D,2,a). It may also be made from dichlorine hexoxide using bromine trifluoride or pentafluoride as the fluorinating agent (199). Nothing definite can be said about the mechanism of the reaction, which occurs at -40° , at which temperature decomposition of the Cl_2O_6 to ClO_2 is excluded.

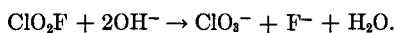
TABLE III
VAPOR PRESSURES OF CHLORYL FLUORIDE (171)

$^{\circ}\text{C}$	-78	-65.5	-55	-45.5	-38	-30.2	-23.8	-17.2	-9.7	-6.3
mm of Hg	8.8	25.2	55.9	103.8	161.4	244	338	459	645	740

2. Reactions of Chloryl Fluoride: Formation of Chloryl Salts

Chloryl fluoride is thermally reasonably stable: decomposition at a measurable rate is first observed in a quartz vessel above 300°C. Glass is only slowly attacked at room temperature, though in presence of the least trace of water reaction is rapid; it is possible that dichlorine hexoxide is produced.

Chloryl fluoride is a true fluoride of chloric acid. Its hydrolysis, which has been investigated by several workers (46, 187, 204, 205), follows essentially the course that would be expected.



Even with careful work, however, the chlorate yields were a few per cent too low, and both chlorite and perchlorate were found to be present; this may be attributed to secondary decomposition of the chloric acid formed initially. Chlorine dioxide was detected as an intermediate product and, when the hydrolysis was effected with only a little water, dichlorine hexoxide was also observed. Decomposition of ClO_2F with ammonia occurs very vigorously, even at -78°C , but the only end products obtained were NH_4Cl and NH_4F (59).

Fluorides capable of forming complexes are converted to an extent depending on their complex forming powers into chloryl salts by the action of chloryl fluoride (45, 161). The form of the vapor pressure curve of mixtures of SiF_4 and ClO_2F below -120°C suggests that an addition compound, probably $\text{SiF}_4 \cdot 2\text{ClO}_2\text{F}$, is formed. A compound isolated by Emeléus (35) by allowing ClO_2F to react with vanadium pentafluoride showed similar instability. While the product isolated at -78° had the composition $\text{VF}_5 \cdot \text{ClO}_2\text{F}$, the composition at -46°C was $\text{VF}_5 \cdot 0.63\text{ClO}_2\text{F}$. On the other hand a compound $\text{ClO}_2\text{F} \cdot \text{BF}_3$ or ClO_2BF_4 , which could be sublimed at 0°C , was formed either by passing BF_3 into liquid chloryl fluoride or by its reaction with solutions of ClO_2F in CFCl_3 . This compound also results directly by the union of chlorine dioxide and fluorine in the presence of BF_3 ; in this case yields are naturally very small since appreciable decomposition of chloryl fluoroborate occurs at room temperature. It is not possible to liberate chloryl fluoride from the compounds by means of NaF , as in the case of NOF from $\text{NO}(\text{BF}_4)$; the necessary reaction temperature cannot be attained because the chloryl compound is too volatile. The great volatility of this compound makes it unlikely that it is a true chloryl fluoroborate, and the formulation as an adduct is more likely. This is also in keeping with the observation that the compound attacks glass, just as ClO_2F itself does. This is probably also true in the case of the reaction product from phosphorus pentafluoride, $\text{PF}_5 \cdot \text{ClO}_2\text{F}$ or $\text{ClO}_2(\text{PF}_6)$.

Marked salt-like character is shown by the compounds $\text{ClO}_2(\text{AsF}_6)$

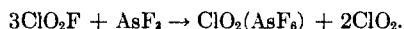
and $\text{ClO}_2(\text{SbF}_6)$, formed by stronger complexing fluorides. The increasing stability of the complexes as we pass to the hexafluoroantimonate is seen in the following table. The two complexes $\text{ClO}_2(\text{BF}_4)$ and $\text{ClO}_2(\text{SbF}_6)$ and

TABLE IV
COMPLEX COMPOUNDS OF ClO_2F WITH FLUORIDES

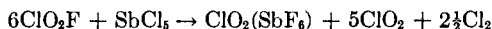
Compound	Reaction temperature (°C)	Temperature of incipient volatility (°C)	Decomposition temperature (°C)
$2\text{ClO}_2\text{F} \cdot \text{SiF}_4$	-150		> -120
$\text{ClO}_2\text{F} \cdot \text{VF}_5$	-78		> -78
$\text{ClO}_2[\text{BF}_4]$	-110	-78	+25
$\text{ClO}_2[\text{PF}_6]$	-78	-35	
$\text{ClO}_2[\text{AsF}_6]$	-78	+50	+150
$(\text{ClO}_2)_2[\text{SnF}_6]$	-70		> +160
$\text{ClO}_2[\text{SbF}_6]$	-10	m.p. +78	> +230

a compound of the composition $\text{TaF}_5 \cdot 0.48\text{ClO}_2\text{F}$ were also obtained by Woolf (204).

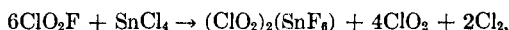
In the reaction of chloryl fluoride with AsF_3 , its fluorinating action is apparent: the AsF_3 is transformed into AsF_5 or $\text{ClO}_2(\text{AsF}_6)$, and chlorine dioxide is also formed, according to the equation (199)



The fluorinating action of ClO_2F naturally shows itself in the reaction with chlorides. Metallic fluorides are first formed and, if these are capable of forming complexes, they then react with further ClO_2F to form chloryl salts (59, 160). This method makes it possible to prepare chloryl salts from insoluble fluorides, such as SnF_4 and TiF_4 . These are insoluble in liquid hydrogen fluoride and cannot therefore be induced to react with ClO_2F . Thus antimony pentachloride reacts with a large excess of chloryl fluoride according to the equation



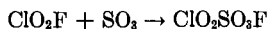
Tin tetrachloride in CFCl_3 solution at -70°C gives dichloryl hexafluorostannate, which decomposes above 160° to SnO_2 , SnF_4 , ClO_2 , and Cl_2 .



Titanium tetrachloride reacts similarly, though reaction at -100°C is so vigorous, in spite of considerable dilution with CFCl_3 , that pure $(\text{ClO}_2)_2\text{TiF}_6$ is not obtained. It is probably contaminated with TiF_4 . Aluminium chloride is converted to AlF_3 , which does not react further with ClO_2F .

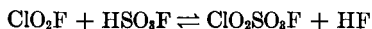
Finally, chloryl fluoride is also able to fluorinate oxides. Corresponding experiments with SiO_2 , Sb_2O_3 , and B_2O_3 at -10°C showed the formation of SiF_4 , $\text{ClO}_2(\text{SbF}_6)$ or $\text{ClO}_2(\text{BF}_4)$, in addition to ClO_2 and Cl_2O_6 resulting from decomposition of unstable chlorine oxides formed initially (45). Reaction of ClO_2F with iodine pentoxide follows a similar course; IF_5 and chlorine oxides are formed at -20°C (199).

Some investigations have been made on the reactions of chloryl fluoride with Lewis acids. Sulfur trioxide in CFCl_3 solution at -10° forms an orange colored chloryl salt of m.p. 27°C , which in the solid state must be $\text{ClO}_2^+\text{SO}_3\text{F}^-$ (161, 204)



This substance may be considered as intermediate between the colorless chloryl salts, e.g., $\text{ClO}_2(\text{SbF}_6)$, and the deep red dichloryl trisulfate, $(\text{ClO}_2)_2[\text{S}_3\text{O}_{10}]$ (108).

Fluorsulfonic acid reacts with chloryl fluoride even at -78°C , and a red color is produced. The equilibrium



is established (160). Chloryl chlorosulfonate, on the other hand, is not stable; interaction of ClO_2F with chlorosulfonic acid at -78°C gives only the decomposition products ClO_2 , chlorine, and SO_2 (160). Hydrogen chloride at -110°C yields HF , ClO_2 , and chlorine (160):

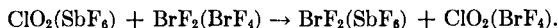


The reaction with anhydrous perchloric acid, in which hydrogen fluoride and dichlorine hexoxide are produced, may be an equilibrium process (45, 122, 162) (see under Cl_2O_6 , Section II,D,2,a). Finally mention may be made of the reaction with anhydrous nitric acid, in which nitryl perchlorate is obtained (160).

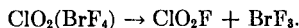


Presumably the unstable compound ClO_2NO_3 is formed initially and decomposes to NO_2 and ClO_3 or Cl_2O_6 . The latter then react to form NO_2ClO_4 . The last reaction may be shown to occur (163, 199). Secondary reactions between NO_2 and ClO_2 are discussed under chlorine dioxide.

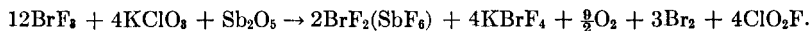
It has not proved possible so far to prepare $\text{ClO}_2(\text{BrF}_4)$. There is no reaction between ClO_2F and BrF_3 either at -78°C or at $+10^\circ\text{C}$. If, however, $\text{ClO}_2(\text{SbF}_6)$ is allowed to interact with BrF_3 the initial reaction occurs as follows (160):



The compound $\text{BrF}_2(\text{SbF}_6)$ is known to be stable, whereas the chloryl compound decomposes at once as shown below.



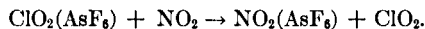
This is in accord with observations on the interaction of KClO_3 with Sb_2O_5 and BrF_3 , which also yields only chloryl fluoride (205).



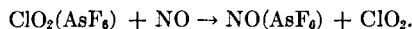
The well known chloryl sulfates which are formed either in the reaction of SO_3 with Cl_2O or ClO_2 or when sulfur oxychlorides or sulfur trioxide reacts with Cl_2O_6 are discussed in the sections dealing with the corresponding chlorine oxides.

3. Reactions of Chloryl Compounds

The chloryl component may be displaced from compounds by means of nitrogen oxides; nitryl or nitrosyl compounds result and the chlorine oxide is set free. Thus nitrogen dioxide reacts with chloryl hexafluoroarsenate according to the equation (160):



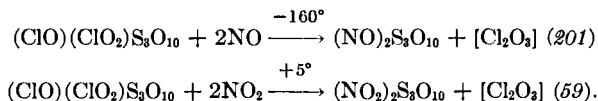
Chlorine nitrate is also formed by secondary reactions between NO_2 and ClO_2 both in this case and in some of the reactions described subsequently. Decomposition with NO follows an analogous course (160):



In this case however a redox reaction between ClO_2 and NO gives NO_2 as a secondary product. This also participates in the reaction so that $\text{NO}(\text{AsF}_6)$ may be isolated only as a mixture with $\text{NO}_2(\text{AsF}_6)$. Decomposition of $\text{ClO}_2(\text{AsF}_6)$ with nitryl chloride at -30°C also leads to $\text{NO}_2(\text{AsF}_6)$ (59)



The following reactions are also of the type discussed above:



In the case of the reaction with NO large quantities of N_2O_3 are also formed.

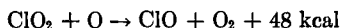
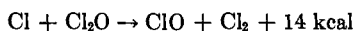
The reactions of "chloryl perchlorate," ClO_2ClO_4 ($= \text{Cl}_2\text{O}_6$), are described under dichlorine hexoxide.

D. DICHLORINE HEXOXIDE Cl_2O_6 1. *Formation and Preparation*

The formation of Cl_2O_6 in the photochemical reaction of chlorine with ozone was studied by Bodenstein and his co-workers (25, 26). Red light, which is absorbed by O_3 , leads to the formation of Cl_2O_6 , whereas light which is absorbed by chlorine only produces decomposition of the ozone. In the thermal reaction of chlorine with ozone the intermediate formation of ClO , ClO_2 , ClO_3 , and ClO_4 has been postulated (5, 27). The mechanism has been discussed recently by Szabo (193), who formulated the reaction leading to dichlorine hexoxide in terms of the equilibrium

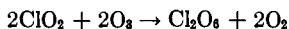


The reaction $\text{ClO} + \text{O}_2 \rightarrow \text{ClO}_3$ is thermoneutral (73). Since ClO is always produced as an intermediate in the decomposition reactions (193)



it is evident that this species occupies a key position in reactions involving both the formation and decomposition of chlorine-oxygen compounds.

Kinetic studies also led to a convenient preparation method from chlorine dioxide and ozone, since Schumacher and Stieger (180) came to the conclusion in discussing their results that the reaction



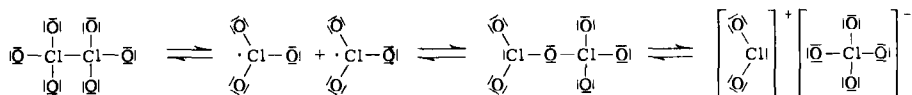
must take place with only a small activation energy. They succeeded in carrying out the reaction on a preparative scale and this method is still used exclusively in the laboratory.

Whereas virtually only ClO_3 is present in the gas phase (74) the liquid oxide consists mainly of the dimer, though the presence of monomer may be detected by magnetic measurements (54). The dissociation energy for the reaction $\text{Cl}_2\text{O}_6 \rightarrow 2\text{ClO}_3$ is only 1.5 kcal.

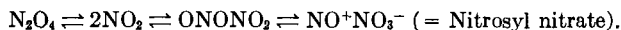
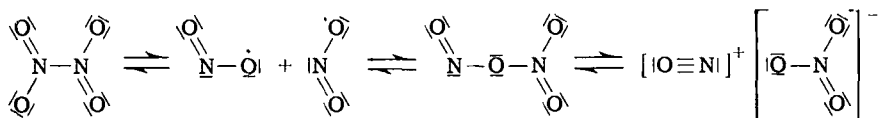
2. *Reactions of Cl_2O_6*

a. Cl_2O_6 Considered as Chloryl Perchlorate. In an extensive experimental study by Schmeisser and his co-workers (162) it was found that Cl_2O_6 is able to react as if it were chloryl perchlorate, $\text{ClO}_2+\text{ClO}_4^-$, as Lehmann (108) also supposed. The first proof of this came from the reaction $\text{ClO}_2\text{F} + \text{HClO}_4 = \text{HF} + \text{ClO}_2\text{ClO}_4$ (see below in this subsection).

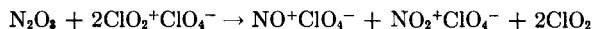
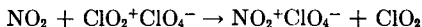
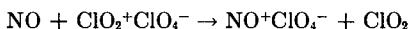
Dichlorine hexoxide is not able to go over directly into this polarized form. It is necessary to assume cleavage, followed by rearrangement:



This scheme for the reactive forms of Cl_2O_6 is completely analogous to those discussed for N_2O_4 (185)

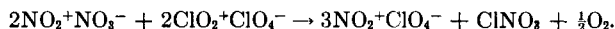


Both NO and NO_2 react with Cl_2O_6 (in carbon tetrachloride solution) at 0°C with displacement of the "chloryl cation" and formation of the corresponding perchlorates, chlorine dioxide being set free. As would be expected N_2O_3 reacts as a mixture of NO and NO_2 (163, 199).

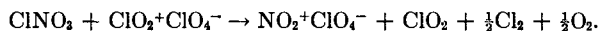


Possible secondary reactions of the nitrogen oxides with ClO_2 leading to ClNO_3 have already been described in connection with the reactions of chlorine dioxide.

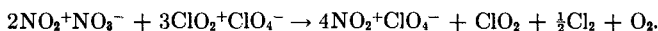
The reaction with N_2O_5 ($= \text{NO}_2\text{NO}_3$) is not quite so straightforward. Nitryl perchlorate is probably formed initially but chloryl nitrate, (ClO_2NO_3), which, at least formally, must be the other product, decomposes at once. This gives rise to secondary reactions in which chlorine nitrate and oxygen are produced (199).



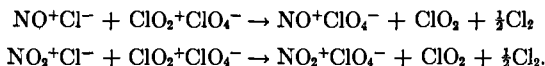
In addition there is a reaction between Cl_2O_6 and chlorine nitrate, the course of which has been elucidated in separate experiments (199).



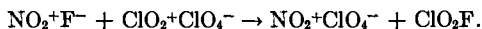
The over-all reaction between N_2O_5 and Cl_2O_6 may then be represented by the equation:



The interpretation of the course of the reaction is supported not only by the well-defined end products mentioned but also by the fact that small amounts of ClNO_3 could be isolated. The chlorides of the nitrogen oxyacids react similarly with Cl_2O_6 in CCl_4 as solvent at -20°C (123, 162).

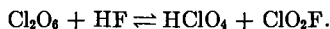


When NO_2F is passed into a solution of Cl_2O_6 in CFCl_3 at 0° a smooth formation of ClO_2F and nitryl perchlorate is observed



The reaction products are unable to interact in the reverse direction (160).

In the double decomposition of Cl_2O_6 with anhydrous hydrogen fluoride in a platinum apparatus at 6°C an equilibrium is set up in which chloryl fluoride and perchloric acid are produced (45, 122, 162).

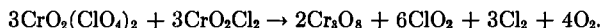


The fact that Cl_2O_6 behaves as chloryl perchlorate is shown not only by the reactions described, but also by experiments in which perchlorates are actually prepared with the help of Cl_2O_6 . These have led to the discovery of a new type of inorganic acyl perchlorate.

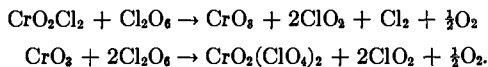
Acyl chlorides undergo a general reaction with dichlorine hexoxide in which they are transformed to acyl perchlorates (123, 162). Chromyl chloride reacts with excess of Cl_2O_6 at the melting point of the latter ($+3.5^\circ\text{C}$) to form the red liquid chromyl perchlorate $\text{CrO}_2(\text{ClO}_4)_2$, which can be distilled in high vacuum at 35°C .



Chromium trioxide is formed as a by-product and is, indeed, the only product containing chromium if CrO_2Cl_2 is used in excess. Chromyl perchlorate reacts with CrO_2Cl_2 to form Cr_3O_8 or CrO_3 , chlorine dioxide, chlorine, and oxygen.

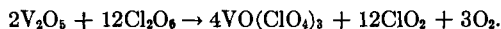


Both this reaction and the formation of CrO_3 in the interaction of CrO_2Cl_2 with Cl_2O_6 , make it likely that the latter reaction takes place via CrO_3 as an intermediate:



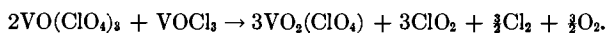
Chromyl perchlorate may also be made by the direct action of Cl_2O_6 on CrO_3 .

Vanadium oxytripерchlorate may be obtained by treating V_2O_5 with a large excess of Cl_2O_6 at 5°C .

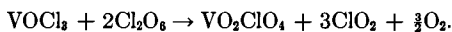


The compound $\text{VO}(\text{ClO}_4)_3$, which crystallizes at $21\text{--}22^\circ\text{C}$, may be distilled

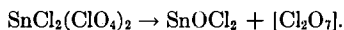
in high vacuum at 33.5°C. It reacts extremely violently with VOCl_3 . Even at temperatures only a little above -180°C sudden formation of ClO_2 , chlorine and oxygen occurs and VO_2ClO_4 remains:



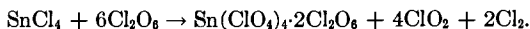
The same compound results from VOCl_3 and Cl_2O_6 at 5°C in CCl_4 as diluent; undiluted VOCl_3 reacts explosively with Cl_2O_6 .



Reaction of Cl_2O_6 with an excess of tin tetrachloride occurs at the melting point of the latter (-33°C) to give a mixture of solids, melting at 40 – 50°C and becoming red. In high vacuum at 50° it is possible to distil red $\text{SnCl}_2(\text{ClO}_4)_2$ from the melt. It crystallizes slowly at room temperature and decomposes to tin oxychloride in CCl_4 solution.



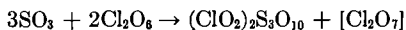
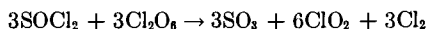
With the reverse proportions of Cl_2O_6 and SnCl_4 very hygroscopic red crystals of the composition $\text{Sn}(\text{ClO}_4)_4 \cdot 2\text{Cl}_2\text{O}_6$ are formed at -30°C .



These react with chlorine nitrate (59) and with NO_2 (123) forming nitryl perchlorate and tin tetranitrate respectively.

In the reaction of Cl_2O_6 with silicon tetrachloride at room temperature products are formed with a lower perchlorate content than that required for $\text{Si}(\text{ClO}_4)_4$. The latter may possibly be formed as the primary product, but it loses Cl_2O_7 and forms $\text{Si}-\text{O}-\text{Si}$ bonds, i.e., tends to form SiO_2 as the end product.

In carbon tetrachloride at -25°C thionyl chloride reacts with Cl_2O_6 , via a primary oxidation of SOCl_2 to SO_3 , to give dichloryl trisulfate, which may also be made directly from SO_3 and Cl_2O_6 (108).

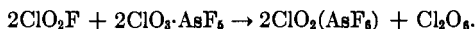


Reaction of SCl_2 with Cl_2O_6 gives the same end products, but SO_2Cl_2 does not react with Cl_2O_6 .

b. Other Reactions of Cl_2O_6 . The oxidizing action of dichlorine hexoxide is apparent in the reaction with iodine or the iodine chlorides ICl and ICl_3 : in each case mixtures of I_2O_5 and ICl_3 result (200).

The ClO_3 radical, which is present in liquid Cl_2O_6 , may be trapped with AsF_5 . At -10°C an adduct with the formula $\text{ClO}_3 \cdot \text{AsF}_5$ is obtained. It is impossible to avoid contamination with $\text{ClO}_2 \cdot \text{AsF}_5$ (ClO_2 being a decom-

position product of Cl_2O_6 , but the melting point of the product (118°C) differs significantly from that of $\text{ClO}_2\cdot\text{AsF}_5$ (78°C). The product cannot be sublimed and reacts explosively with water (199). At -50° it reacts with chloryl fluoride according to the equation (199):

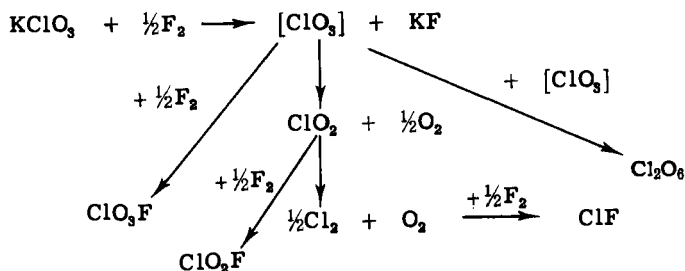


Unlike chlorine dioxide, dichlorine hexoxide is unable to react directly with fluorine. Between 20° and 40°C in the thermal decomposition of the hexoxide in presence of fluorine only ClO_2F , and no ClO_3F , is obtained. The fact that Cl_2O_7 is also formed makes it clear that fluorine reacts only with the decomposition products of Cl_2O_6 . Fluorination of Cl_2O_6 is, however, possible with bromine trifluoride; while chloryl fluoride is produced with this reagent (see under chloryl fluoride, Section II,C,1,b), BrF_3 gives ClO_2F and BrO_2F (see below under bromyl fluoride, Section III,D,1).

E. PERCHLORYL FLUORIDE, ClO_3F

1. Formation, Preparation and Structure of ClO_3F

a. *From Potassium Chlorate and Fluorine.* Perchloryl fluoride was first detected in 1951 by Bode and Klesper as a product of the action of elementary fluorine on potassium chlorate at -40°C (22, 23). These experiments were repeated by Engelbrecht (49, 50). Yields of ClO_3F were about 45%, based on the fluorine used. In this somewhat obscure decomposition ClO_2F , ClF , Cl_2 , Cl_2O_6 , and O_2 are also formed. Engelbrecht discussed the following reaction scheme (50)



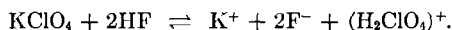
A little later the reaction was reinvestigated by Schumacher (186). Working below -20°C he was able under certain conditions to obtain ClO_3F in yields of 60%; the by-products were Cl_2 , OF_2 , and ClO_2F and its decomposition products.

b. *Electrolysis of Sodium Perchlorate in Anhydrous Hydrogen Fluoride.* Electrochemical fluorination of a 10% solution of NaClO_4 in anhydrous hydrogen fluoride at 0°C and 4-7 volts, using nickel anodes, likewise leads

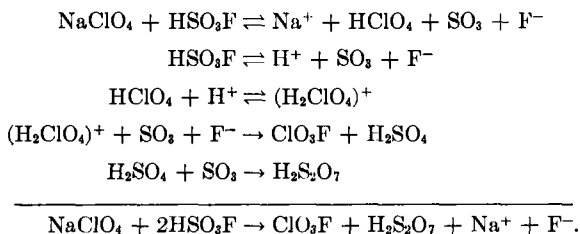
to formation of ClO_3F (50, 164). This electrolytic method has only a limited value since the yields are not particularly high and chlorine oxides and hydrogen are produced, in addition to OF_2 , Cl_2 , or O_2 , and this can lead to explosions (164).

c. From Sodium Perchlorate and Fluorsulfonic Acid. When sodium perchlorate is warmed to 60–70°C with excess of fluorsulfonic acid, ClO_3F is formed in yields up to 73%. After washing with alkali thiosulfate solution and drying with concentrated sulfuric acid it is completely pure. This process was discovered simultaneously and independently by several workers (15, 103, 104) and is applicable on the kilogram scale.

On the basis of Fredenhagen's investigations (62–64), which showed that perchloric acid acts as an ampholyte in liquid hydrogen fluoride and that in dilute solutions of KClO_4 in liquid hydrogen fluoride the equilibrium



predominates, Lang (104) proposed the following reaction scheme. In it, fluorsulfonic acid act simultaneously as a fluorinating and a dehydrating agent:



Alternatively the course of the reaction has been discussed in terms of the perchloryl ion (16, 206):



In addition to sodium perchlorate it is possible to use alkali and alkaline earth perchlorates in general and also perchloric acid. Perchloryl fluoride may also be prepared from perchlorates and antimony pentafluoride in place of fluorsulfonic acid. It is advantageous to use a mixture of the two with 60–70 wt% of SbF_5 and a reaction temperature between 70° and 130°C; yields up to 97% are attained (17, 51).

d. From Dichlorine Heptoxide and Fluorine. Finally, Schumacher (58) described the formation of ClO_3F in the thermal decomposition of Cl_2O_7 at 100° in the presence of fluorine. About 75% of the chlorine oxide is transformed into a mixture of ClO_3F and (less) ClO_2F . This is compatible with the thermal decomposition of Cl_2O_6 in presence of fluorine at 40°C, when Cl_2O_7 but no ClO_3F is formed. A temperature difference of about

60°C can cause very great changes in the separate rate constants and the mean life of excited molecules, so that the kinetics of the above reactions may be quite different.

The *structure* was determined from the infrared spectrum (50, 118, 121). The molecule possesses C_{3v} symmetry; the four peripheral atoms are bound to the central chlorine atom. It was concluded that the Cl-F and Cl-O distances in ClO_3F are smaller than in ClO_2 or ClO_2F , and that correspondingly the bond strength is greater. The same conclusion was reached from a study of the thermal decomposition, which is homogeneous and unimolecular (71).

The dipole moment is $0.023 \pm 0.003D$ and is thus smaller than that of any other polar substance (131). In addition, ClO_3F has the highest known resistance to electrical breakdown of any gas (about 40% higher than for SF_6). It is also not affected by high energy radiation and is thus suitable as an insulator in high voltage systems.

Most of the *physical properties* of ClO_3F are collected in Table V.

TABLE V
PHYSICAL PROPERTIES OF ClO_2F AND ClO_3F

	ClO_2F	ClO_3F
Melting point [°C]	-115 (171) (Crystallization point)	-146 (50) -147.75 (100)
Boiling point [°C]	-6 (171)	-46.7 (50, 89)
Vapor pressure	(see text) (171)	(see text) (100)
Trouton constant	23.2 (171)	
Heat of vaporization (kcal mole ⁻¹)	6.2 (171)	4.61 (23, 89) 4.62 (100)
Heat of formation (kcal)		-5.12 \pm 0.68 (137)
Spectra		Infrared (50, 118, 121) Raman (148) Microwave (119)

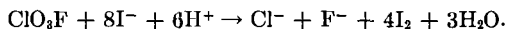
Vapor pressures, densities and critical data have also been determined (52, 89).

$$\begin{aligned}\log p_{\text{mm}} &= 18.90112 - 1443.467/T - 4.09566 \log T \\ D \text{ (gm cm}^{-1}\text{)} &= 2.266 - 1.603 \times 10^{-3}T - 4.080 \times 10^{-6}T^2 \\ T_{\text{crit}} &= 368.33 \pm 0.1^\circ\text{K} \\ p_{\text{crit}} &= 53.0 \text{ atm}\end{aligned}$$

2. Reactions of ClO_3F

Perchloryl fluoride is an extraordinarily stable substance. Hydrolysis (50, 124), which yields fluoride and perchlorate, can be effected only by

concentrated caustic soda in a sealed tube at 200–300°C; only slight reaction occurs with water under the same conditions. In a strongly acid medium ClO_3F is able to oxidize iodide (50, 52):



The oxidizing action is also apparent in reactions with hydrogen-containing compounds. Thus the combustion of H_2 , CH_4 , NH_3 , or H_2S is supported by ClO_3F (120) and its use in flame photometry has been suggested (156).

Reaction with metallic sodium or potassium commences at 300°C, but then proceeds vigorously (50). With ammonia ClO_3F interacts in the gaseous or liquid phase and also in aqueous solution. The product is the ammonium salt of the amide of perchloric acid (50, 124):



This may be isolated as the potassium salts $\text{ClO}_3 \cdot \text{NHK}$ and ClO_3NK_2 or as the barium or silver salt. Both the silver salt ClO_3NHAg and the cesium salt are explosive (50, 124). Perchloryl fluoride and sodium amide do not react (124).

Whereas ClO_2F readily forms adducts or chloryl salts with various electrophilic fluorides, perchloryl fluoride is unable to do so. There is no evidence of compound formation with BF_3 (at -120°C), with AsF_5 (at -78°C) or with PF_5 (at -78° and $+25^\circ\text{C}$). Conductivity measurements on mixtures of BF_3 or PF_5 with ClO_3F also show no measurable change of conductivity compared with pure perchloryl fluoride (105). There is also no reaction between SO_3 and ClO_3F at -75°C (105). There is only a single instance of the formulation of a perchloryl salt. Sprysskow (190) interpreted a product of the composition $2\text{SO}_3 \cdot \text{HClO}_4$ which was obtained by the action of SO_3 on HClO_4 in chloroform, as $(\text{ClO}_3)^+(\text{HS}_2\text{O}_7)^-$.

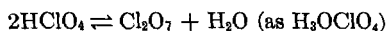
The low reactivity of ClO_3F stems from its structure and electronic configuration. Thus in the first place it is isosteric with the perchlorate anion; the octet of electrons is complete and the molecule is coordinatively saturated. Exchange of O for F in ClO_4^- leads to no essential change in the molecular structure and the high symmetry is retained. Thus the infrared spectrum shows only slight deviations of the O-Cl-F angle from the value for a regular tetrahedral molecule. In keeping with this, the dipole moment is very small and the associated lack of a basic center explains the insolubility in liquid hydrogen fluoride and the lack of reaction with Lewis acids such as PF_5 , BF_3 , and SO_3 .

The analogy to the perchlorate ion is still clearer in reduction reactions. Just as the ClO_4^- ion is reduced only in strongly acid solution, since the symmetry and high stability is lost by the addition of a proton (i.e., by

formation of HClO_4), so reduction of ClO_3F to chloride (e.g., by iodide) takes place only in strongly acid solution.

F. DICHLORINE HEPTOXIDE Cl_2O_7

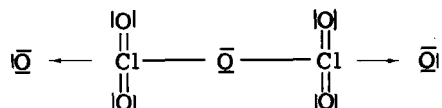
Dichlorine heptoxide is the anhydride of perchloric acid, and may be obtained in a pure state by dehydrating the concentrated acid with phosphorus pentoxide, followed by distillation between -38° and -34°C at 1 mm (209). Just as in the case of Cl_2O , the heptoxide appears to enter into an equilibrium with water. The equilibrium



is indicated both by the fact that hydrated perchlorates of the transition metals result from interaction of anhydrous perchloric acid and transition metal chlorides (81) and also from studies of density for the system $\text{Cl}_2\text{O}_7/\text{H}_2\text{O}$ (149).

Solid Cl_2O_7 is said to undergo a polymorphic transition at $-100 \pm 2^\circ\text{C}$ (209). There is a simple eutectic with a melting point of -94°C in the system $\text{Cl}_2\text{O}_7/\text{CCl}_4$; the compounds are completely miscible above -23°C (209).

The structure of Cl_2O_7 has been discussed by Siebert (188). An approximate value of $N = 1.76$ for the outer ClO_3 groups (where N is bond order or multiplicity) has been obtained on the basis of calculation of the force constants from infrared spectral data. This value is probably somewhat too high as a result of uncertainty in the force constant calculation. It accords well with the assumption of a $5/3$ bond order in the ClO_3 groups, so that the structure shown below is appropriate,



The bonds to the three outer oxygens are made equivalent by resonance, but the Cl-O-Cl group plays no part in this. Chlorine in dichlorine heptoxide thus has a dodecet of electrons. The central $\angle \text{Cl-O-Cl}$ is 128° (14, 61). A dipole moment of $0.72 \pm 0.02D$ has been found (61). The thermal decomposition of Cl_2O_7 in the gaseous state has been studied (36) at temperatures between 100° and 120°C at partial pressures of 1–80 mm with addition of Cl_2 , O_2 and F_2 up to 400 mm in vessels of Pyrex and quartz.

III. Oxy-Compounds of Bromine

A. DIBROMINE MONOXIDE Br_2O

Dibromine monoxide was first isolated by Schwarz and Wiele (182, 183) some time after it had been known in the form of its solution in carbon

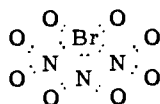
tetrachloride (29, 30). Thermal decomposition of bromine dioxide in high vacuum yields, as Schwarz and Schmeisser also observed, (184), the components bromine and oxygen, a white oxide, and brown-black Br_2O , which may be obtained pure by subliming off bromine at -50°C . The white oxide is richer in oxygen than BrO_2 and Br_2O ; it may be the white oxide BrO_3 .

When slowly warmed at normal pressure dibromine monoxide melts at $-17.5 \pm 0.5^\circ\text{C}$ with partial decomposition; it is completely stable at -40°C . Hydrolysis gives hypobromite, and Br_2O is thus the true anhydride of hypobromous acid (30). In carbon tetrachloride solution dibromine monoxide oxidises iodine to I_2O_5 (183).

B. BROMINE DIOXIDE BrO_2

Bromine dioxide was first prepared by Schwarz and Schmeisser (184) in the glow discharge from a mixture of bromine and oxygen; BrO_2 separates in the discharge tube, which is cooled with liquid air. No ozone is formed if there is not too great an excess of oxygen. The solid yellow BrO_2 decomposes into its elements without melting when rapidly warmed to 0°C ; when slowly warmed in vacuum, however, it gives dibromine monoxide among other products (see above, Section III,A). It is stable below -40°C , but decomposes when dissolved in carbon tetrachloride. The method of preparation in the discharge tube was improved later to give yields of 80% of BrO_2 , based on the bromine used (140). The heat of formation of BrO_2 is -12.5 ± 0.7 kcal (144).

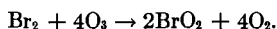
When nitrogen is added to the O_2 - Br_2 mixture streaming through the discharge tube, the compound $\text{BrO}_2 \cdot 3\text{NO}_2$ separates in the discharge tube held at -186° (145). This is stable up to -50°C and may be sublimed in vacuum without decomposition. In its reaction with water and alkalis it behaves as a mixture of BrO_2 and NO_2 . The compound $\text{BrO}_2 \cdot 3\text{NO}_2$ may also be obtained when excess of N_2O_4 is sublimed on to bromine dioxide held at -40°C and the temperature is then raised to -20°C . Excess of N_2O_4 may then be removed at -50°C (145). The structure shown below has been proposed*:



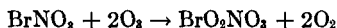
Schmeisser and Jörger (165) recently found that bromine dioxide could be prepared very conveniently by the low-temperature ozonization of bromine. Though reaction between bromine and ozone at room temperatures leads to higher oxides (see Section III,C) it is also possible to obtain BrO_2

* Note added in proof: Latest results show the structure of this compound to be $\text{BrNO}_2 \cdot \text{N}_2\text{O}_5$ (M. Schmeisser and E. Schuster, unpublished).

under suitably controlled conditions. When an O_3 - O_2 mixture, precooled to $-78^\circ C$, is passed into a solution of bromine in a fluorochlorocarbon (e.g., $CFCl_3$, CF_2Cl_2) at $-50^\circ C$, bromine is oxidized quantitatively to BrO_2 , which may be obtained in a state of reasonable purity by distilling off the solvent



This method of low temperature ozonization may also be applied without difficulty to bromine compounds in which bromine is contained either in the cation or the anion. Thus bromine (I) nitrate at $-78^\circ C$ may be smoothly converted to bromyl nitrate (159):



Bromine chloride at $-60^\circ C$ when treated with a stream of ozone gives bromine dioxide quantitatively (90).



The possibility that the bromine chloride breaks down, and that the reaction is simply the ozonization of elementary bromine cannot, however, be excluded. Bromine dioxide mixed with iodine oxides also results if iodine bromide is used (90)



A reaction of the same type occurs when ozone diluted with oxygen is passed into a solution of BrF_5 in liquid bromine at $-5^\circ C$, when bromyl fluoride results (166).



Bromine is initially oxidized to BrO_2 and this is then fluorinated by BrF_5 to BrO_2F (see below, Section III,D,1). Up to the present, apart from the reaction with N_2O_4 , the only reaction of bromine dioxide which has been studied is its fluorination. This is discussed in the Section on BrO_2F .

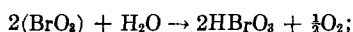
C. HIGHER OXIDES

The action of ozone on bromine at room temperature leads to bromine oxides of various compositions. This thermal reaction was studied in detail as early as 1930 by Lewis, Schumacher and Feitnecht (111-117). The oxides formed had the composition $(Br_3O_8)_n$. Later Pflugmacher, using a greater ozone excess in the same reaction, obtained a compound $(BrO_3)_n$ (146, 147). This led Schumacher to reinvestigate the reaction (6). In a comprehensive investigation he examined the influence of the vessel material on the reaction and its products. Whereas the oxide obtained in quartz vessels had an oxygen-bromine ratio corresponding with the formula $(Br_3O_8)_n$,

oxides with the formula $(\text{Br}_2\text{O}_5)_n$ were formed in Pyrex apparatus. It follows from these results that bromine oxides with a variable bromine:oxygen ratio result from the action of ozone on bromine at room temperature; the ratio of bromine to oxygen is greater than 1:2 and does not exceed 1:3. Which product is formed is determined by the material of the reaction vessel and possibly by the excess of ozone used.

The solid white oxides are stable at room temperature only in presence of ozone or atomic oxygen. The oxide Br_2O_5 dissolves in water to form bromic acid (6) and may therefore be the anhydride. Since, however, all these higher bromine oxides are polymeric it is not possible at present to decide to what extent they are mixtures or single compounds.

An oxide with the approximate composition BrO_3 was obtained by the interaction of Br_2 and O_2 in a glow discharge, using a fifty-fold excess of oxygen and a reaction temperature of -10° to $+20^\circ\text{C}$ (146). BrO_3 is also formed, at least superficially, when BrO_2 is treated with atomic oxygen (146); the oxide produced in addition to dibromine monoxide when BrO_2 decomposes may possibly also be BrO_3 . The " BrO_3 " stable below -70°C dissolves in water to form a colorless solution:

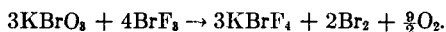


but there is no evidence for the formation of perbromic acid, HBrO_4 .

D. BROMYL FLUORIDE BrO_2F (141, 166, 167)

1. Formation and Preparation

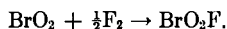
There had been several unsuccessful attempts to prepare oxyfluorides of bromine. Emeléus and Woolf (47), for example, on the basis of the analogy with the preparation of ClO_2F from potassium chlorate and bromine trifluoride, studied the action of BrF_3 on potassium bromate; only KBrF_4 , bromine and oxygen were produced:



When bromate is fluorinated with elementary fluorine at room temperature it is again found that only oxygen and bromine result, together with bromine trifluoride formed by reaction of the latter with fluorine (122).

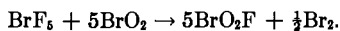
Bromine dioxide is a suitable starting material for the preparation of BrO_2F : the reaction of fluorine with chlorine dioxide led to the first successful preparation of chloryl fluoride (171). Direct reaction with fluorine is not, however, practicable because reaction is exceedingly vigorous even at -78°C , possibly because of spontaneous decomposition of BrO_2 . Explosions occurred on a number of occasions. Liquid chlorine or perfluoropentane, C_5F_{12} , proved to be a suitable diluent; BrO_2 is not soluble and must

be suspended in the diluent, but it was found to be completely stable up to -40°C . When fluorine was passed slowly through a suspension of BrO_2 in C_5F_{12} at -50°C in a quartz flask, light yellow bromyl fluoride was formed.



It was only slightly soluble in perfluoropentane, and could be isolated by distilling off the diluent at -40°C in vacuum. It does not always deposit in a pure form.

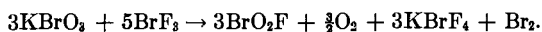
In fluorinating BrO_2 , fluorine may be replaced with advantage by bromine pentafluoride, the lower melting point of which (-61.4°C) gives better reaction conditions. At -55°C bromine dioxide reacts smoothly with liquid BrF_5 to form bromyl fluoride:



After removal of bromine and unused BrF_5 , the BrO_2F may be obtained pure by vacuum sublimation at -25°C .

Since the preparation of BrO_2F on a larger scale was only possible if bromine dioxide, which was available only in relatively small amounts, could be replaced by some other starting material, the fluorination of potassium bromate was reexamined (at the time the convenient method of oxidizing bromine with ozone in CFCl_3 was unknown). At -20° there was no reaction. Fluorsulfonic acid was also not suitable as potassium bromate dissolved in it only with complete decomposition, even at low temperatures.

As mentioned above, potassium bromate and bromine trifluoride at room temperature give only KBrF_4 , bromine and oxygen; in bromine solution, on the other hand, reaction at the melting temperature of the $\text{BrF}_3\text{-Br}_2$ mixture proceeds primarily via bromyl fluoride:

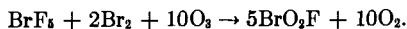


A mixture of BrO_2F and BrF_3 was obtained from which it was difficult to obtain the former in a pure state by fractional distillation.

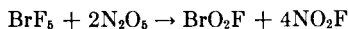
For preparative purposes, on the other hand, bromine pentafluoride may be used. At the melting point of BrF_5 (-61.4°C) the reaction



takes place with oxygen evolution and formation of bromyl fluoride. The conversion of KBrO_3 is 70%. Finally, this process led to the use of elementary bromine as the starting material. In passing a stream of ozone diluted with oxygen through a solution of bromine in BrF_5 at -5°C , BrO_2F is produced smoothly in the reaction

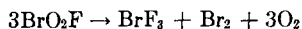


This is a very convenient method for preparing BrO_2F . Bromyl fluoride is also formed together with ClO_2F in the reaction between BrF_5 and dichlorine hexoxide (199) and also in the analogous reaction of BrF_5 with dinitrogen pentoxide (159)

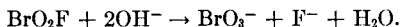


2. Properties and Reactions of BrO_2F

The compound forms colorless crystals, which may be sublimed in vacuum at -25°C . Above its melting point (-9°C) it forms a colorless liquid which gradually becomes yellow at room temperature as the result of incipient decomposition. Vigorous decomposition occurs at $+56^\circ\text{C}$, perhaps according to the equation

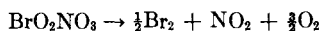


In the liquid state bromyl fluoride attacks glass fairly strongly and becomes reddish brown in color. It is decomposed explosively by water and reacts with organic substances with inflammation. In quartz ampoules BrO_2F may be kept indefinitely at temperatures below the melting point. Hydrolysis by excess of caustic soda solution at as low a temperature as possible is complete and leads to fluoride and bromate:

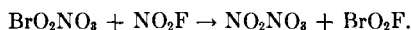


There is a vigorous reaction with boron tribromide above -46°C , the melting point of the latter. However, only B_2O_3 , BF_3 , and Br_2 could be isolated from the products.

Besides BrO_2F the only bromyl compound known at present is bromyl nitrate, which is made from bromine(I) nitrate by ozonization at -78°C in CFCl_3 solution (see also Section III,B) (159). It is an orange colored powder which decomposes thermally according to the equation



and reacts at -78° with nityl fluoride to form bromyl fluoride and dinitrogen pentoxide (159):



No fluorocomplexes could be obtained from BrO_2F and BF_3 , AsF_5 or SbF_5 .

IV. Oxy-Compounds of Iodine

It has so far been impossible to determine with certainty the number of oxides formed by iodine. Diiodine pentoxide, I_2O_5 , is certainly well defined and behaves as the anhydride of iodic acid, but the other two oxides which

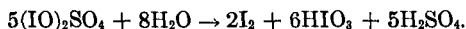
have been isolated, I_2O_4 and I_4O_9 , have not yet been unequivocally characterized, as least as far as their polymeric structures are concerned. Very recently intensive investigations have been commenced to determine their structures by means of spectroscopic studies. Salts of positive univalent iodine, such as I_2SO_4 , may be regarded as derived formally from I_2O , though there is no indication of the existence of such an oxide. The iodine(I) salts will not be dealt with here.

A. DERIVATIVES OF DIIODINE TRIOXIDE I_2O_3

Diiodine trioxide has not yet been isolated in the free state, but it is said to occur as an intermediate in the thermal decomposition of I_2O_5 to iodine and oxygen. When I_2O_5 is heated with fuming sulfuric acid cationic tervalent iodine is stabilized as a salt which is stable at 220°C and one mole of oxygen is liberated (132, 133). One may assume an equilibrium of the type



which is displaced to the right when an acid is added which is strong enough to form a salt with I_2O_3 . In keeping with this iodosyl sulfate, $(\text{IO})_2\text{SO}_4$, is obtained by simply shaking iodine with iodine pentoxide in concentrated sulfuric acid (132, 133). This yellow hygroscopic compound, which is also obtained by heating iodic acid with concentrated H_2SO_4 , has been characterized by some other workers as a mono-hydrate (12) or a hemi-hydrate (34, 55). Hydrolysis occurs in water according to the equation (92)

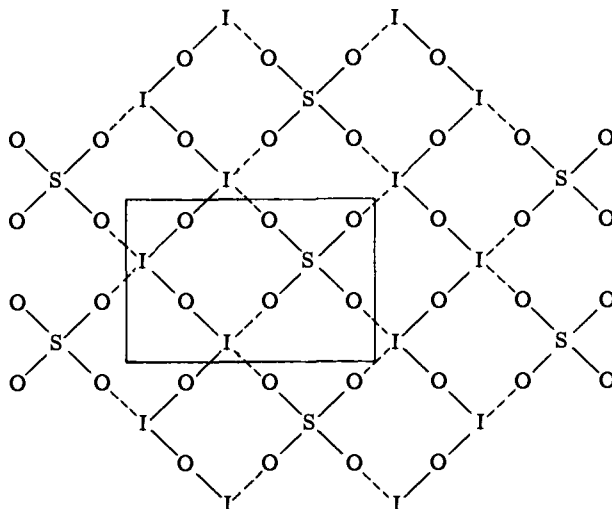


A reaction occurs in essentially the same way when SO_3 reacts with a mixture of iodine and iodine pentoxide. A polysulfate $\text{I}_2\text{O}_5 \cdot 3\text{SO}_3$ results which, by analogy with the monosulfate, may be considered as diiodosyl trisulfate $(\text{IO})_2\text{S}_3\text{O}_{10}$ (110). Direct reaction of SO_3 with I_2O_5 gives $\text{I}_2\text{O}_5 \cdot 2\text{SO}_3$ besides $\text{I}_2\text{O}_5 \cdot 3\text{SO}_3$.

A yellow crystalline compound which is also formed in the reaction of concentrated sulfuric acid with HIO_3 has been formulated as iodine(III) sulfate, $\text{I}_2(\text{SO}_4)_3$ (93). It is possible, however, to formulate this compound as an iodosyl trisulfate, a view which is supported by a method given in the literature (56, 133) for the preparation of the compound by reacting diiodosyl monosulfate with SO_3 . Iodosyl nitrate, IONO_3 , prepared from concentrated or anhydrous nitric acid and iodine (92, 94), has not yet been unambiguously characterized. Iodosyl selenate $(\text{IO})_2\text{SeO}_4$, which is prepared from iodine, iodine pentoxide, and selenic acid, is very similar in its properties to the analogous sulfate, with which it is isomorphous (38).

The structures of iodosyl compounds have been investigated recently

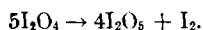
by Dasent and Waddington (38) from a study of infrared and visible spectra of iodosyl sulfate, selenate, and I_2O_4 (see Section IV,B). It was found that all four S-O and Se-O bonds are equivalent and that the tetrahedral symmetry of the sulfate and selenate groups is practically unchanged. The low value of the I-O stretching frequency, on the other hand, suggests a single bond. It was concluded that the structure probably consists of polymeric I-O chains, interspersed with sulfate and selenate groups, as shown in the Fig. 1. It is not possible to say if the SO_4 or SeO_4 groups are ionically or co-



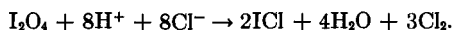
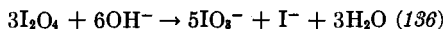
valently bonded, though it is possible that the I---O-S bonds, shown in the figure by dotted lines, are bridging bonds. This interpretation accords with the fact that both iodosyl sulfate (192) and iodosyl selenate (38) are diamagnetic, though one would expect that the IO^+ cation, which is isoelectronic with the oxygen molecule, would be paramagnetic in the ground state (192). A polymeric structure is also in keeping with the insolubility of iodosyl compounds.

B. DIIODINE TETROXIDE I_2O_4

Diiodine tetroxide is prepared by the action of concentrated sulfuric acid on HIO_3 or a solid iodate (12, 136) and is a yellow crystalline powder which is not hygroscopic. Thermal decomposition of I_2O_4 occurs rapidly at 135°C (12) according to the equation

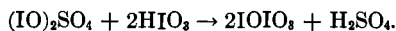


While I_2O_4 forms iodic acid and iodine when heated with water, the following reactions take place in alkaline or acid solution:

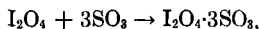


Magnetic measurements (202) show I_2O_4 to be diamagnetic, but this indicates only that it is a polymer $(\text{IO}_2)_n$, where n must be an even number. The infrared investigations of Dasent and Waddington (38) have again given the first insight into the structure of this oxide, and shown it to be similar to that of iodosyl sulfate and selenate. The spectrum can be interpreted without difficulty on the assumption of a network of IO_3 groups and polymeric I-O chains, the two being linked by bonds with some degree of covalent character. On this basis I_2O_4 may be considered as iodosyl iodate, though it must be noted that no discrete IO^+ cations are present and that bonding to iodate occurs which has considerable covalent character.

Chemical evidence for the formulation of I_2O_4 as iodosyl iodate is provided by the hydrolysis of iodosyl sulfate. With excess of water, iodine, and iodic acid are formed (see Section IV,A), but, in moist air, I_2O_4 is formed in larger amounts. This can be interpreted in terms of a reaction between iodic acid formed in the hydrolysis with unchanged iodosyl sulfate, leading to I_2O_4 (38, 92).



A compound $\text{I}_2\text{O}_4 \cdot 3\text{SO}_3$ described by Muir more than 50 years ago (136) has been confirmed by Lehmann (110). This compound, obtained by the action of sulfur trioxide at 100°C according to the equation



may be regarded as iodosyl iodyl trisulfate, $(\text{IO})(\text{IO}_2)(\text{S}_3\text{O}_{10})$. The same compound is formed by the action of ozone on iodine monochloride in a solution of SO_3 in HSO_3F (199). Diiodine tetroxide reacts with iodine pentafluoride to give iodoxy trifluoride (8) (see Section IV,D).

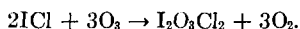
C. TETRAIODINE ENNEAOXIDE I_4O_9

The compound I_4O_9 may be made in two different ways. The first, the heating of concentrated phosphoric acid with HIO_3 , is very similar to the preparation of I_2O_4 from iodic acid and concentrated sulfuric acid (56, 93). The second method is by the reaction of ozone with iodine or compounds of univalent positive iodine. An oxygen-ozone mixture is either passed over heated iodine (12, 57, 95) or into a solution of iodine in chloroform or carbon tetrachloride at room temperature (57, 95, 199).

Ozone will oxidize iodine to I_4O_9 even at -78°C ; thus, when a solution of iodine in CFCl_3 is dropped into a solution of ozone in the same solvent at -78°C and a pre-cooled $\text{O}_2\text{-O}_3$ stream is then passed, I_4O_9 is produced

rapidly and quantitatively (90). The reaction of IBr with ozone to form I_4O_9 and BrO_2 is described under bromine dioxide.

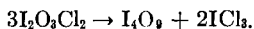
Iodine monochloride also reacts with ozone at -78°C , though, in contrast to IBr, the molecule is not cleaved and a compound $I_2O_3Cl_2$ is formed (90).



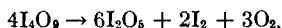
This may be a periodyl compound. Self-dissociation of iodine monochloride, according to the scheme $2ICl \rightleftharpoons I^+ + ICl_2^-$ postulated by Gutmann (79) in which chloride ion transfer occurs, is also probable in fluorochlorohydrocarbons. Attack of the iodide cation would then lead to a salt-like compound $[IO_3]^+[ICl_2]^-$, though this formula has not been verified by structural studies. The compound forms an adduct $I_2O_3Cl_2 \cdot 2C_5H_5N$ (m.p. 85°C) with pyridine and reacts with chlorine nitrate at -78°C according to the equation



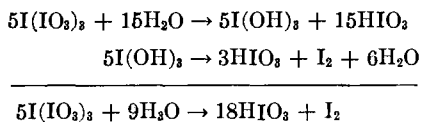
The oxychloride $I_2O_3Cl_2$ decomposes above -30°C to I_4O_9 and ICl_3 (90).



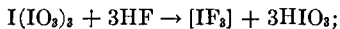
In keeping with this, ICl at 0°C may be ozonized directly to I_4O_9 (199); when ICl_3 is ozonized at 50 – 60°C , I_2O_5 is produced in addition to I_4O_9 (199). The yellow I_4O_9 is hygroscopic and decomposes at 75° (12):



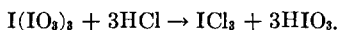
It is commonly regarded as iodine(III) iodate, a formulation which is in keeping with the course of its hydrolysis:



The reaction with anhydrous hydrogen fluoride is completely analogous:



75% of the iodine appears as iodic acid (199). It is very probable that the reaction with hydrogen chloride follows the same scheme. Iodine trichloride results at -78°C , as would be expected from the equation

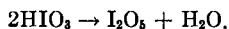


The quantity of ICl_3 is actually much larger than that corresponding with the equation since subsequent reaction of the iodic acid with HCl also gives

iodine chlorides (199). These few reactions all indicate that I_4O_9 should be considered as $I(IO_3)_3$, but this formulation must be regarded as hypothetical as long as the structure has not been investigated.

D. DIIODINE PENTOXIDE I_2O_5

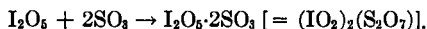
As the anhydride of iodic acid, I_2O_5 may be obtained from it by dehydration at 240–250°C.



Another method of making the pentoxide is the ozonization of ICl_3 at 50–60°. As mentioned in the previous section much I_4O_9 is also produced (199). The oxide is also formed when iodine is passed through a glow discharge with oxygen and nitrogen (air) (145).

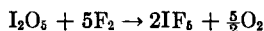
I_2O_5 is a white crystalline compound which decomposes at 300°C to iodine and oxygen. Structural information is given by the infrared spectrum, which shows $O_2I-O-IO_2$ units with an O atom bridging two IO_2 groups (44).

Diiodine pentoxide has oxidizing properties; NO is oxidized to N_2O_4 (and some N_2O_5) (189); C_2H_4 and H_2S are also oxidized (173). Sulfur trioxide forms an adduct at 100° (110, 136, 196):

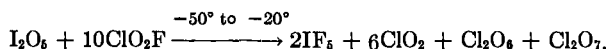
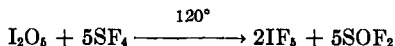
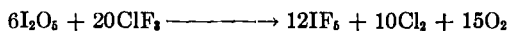
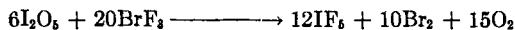


This cannot be sublimed and decomposes at 130°C with loss of SO_3 . Reaction with hydrogen chloride at its boiling point gives ICl_3 (199). I_2O_5 dissolves in liquid hydrogen fluoride; the reactions which occur are discussed under iodyl fluoride (see Section IV,E,1).

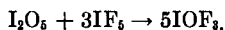
Fluorination of I_2O_5 leads as a rule to IF_5 and the action of elementary fluorine was investigated by Ruff (154):



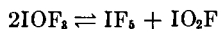
Other fluorinating agents which have been used are BrF_3 (47, 139), ClF_3 (47), SF_4 (135) and ClO_2F (199):



Iodine pentafluoride also reacts with I_2O_5 . After the oxide has been dissolved in boiling IF_5 , iodine oxytrifluoride separates as white needles on cooling to room temperature (8).



Contrary to the results of earlier workers (155), the reaction is not reversible. On warming to 110°C, IOF_3 undergoes a reversible change into IF_5 and iodyl fluoride



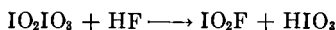
and the latter redissolves on boiling with IF_5 to form IOF_3 (8).

E. IODYL FLUORIDE IO_2F (105, 168)

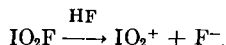
1. Preparation of IO_2F

Iodyl fluoride was first obtained by Aynsley, Nichols and Robinson by heating iodine oxytrifluoride, as described above (8-10). A convenient synthesis is the action of fluorine on a solution of iodic acid or iodine pentoxide in liquid hydrogen fluoride. The mechanism is discussed below.

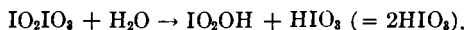
Considerable evolution of heat occurs when HIO_3 or I_2O_5 is dissolved in hydrogen fluoride. If the pentoxide is considered as iodyl iodate, $\text{IO}_2^+\text{IO}_3^-$, then the large heat of solution may be considered as the sum of the heat of solution of iodic acid and the heat of the solvolysis reactions



and



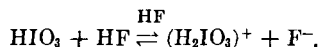
This parallels the hydrolysis



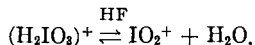
It has been possible to verify experimentally the formation of an equimolar mixture of IO_2F and HIO_3 on decomposing I_2O_5 with hydrogen fluoride.

Exploratory conductivity measurements have been made with solutions of iodic acid in hydrogen fluoride at different concentrations. Addition of HIO_3 to hydrogen fluoride causes a sudden increase in the electrical conductivity, indicating electrolytic dissociation of the iodic acid. This observation is in keeping with work of K. and H. Fredenhagen (62-68) on the liquid hydrogen fluoride solvent system. These authors also carried out conductivity measurements on solutions of inorganic and organic compounds and showed that practically all inorganic acids with the exception of complex fluoro acids function as bases in this solvent.

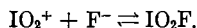
In an earlier section it was shown that perchloric acid, the strongest acid in water, is only an ampholyte in hydrogen fluoride, and has appreciable basic character. Iodic acid is likewise an acid of medium strength in water but functions as a base in hydrogen fluoride:



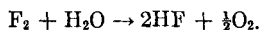
Abstraction of water can also occur:



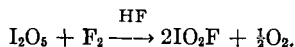
The fact that B_2O_3 is formed on passing boron trifluoride into a solution of HIO_3 in hydrogen fluoride indicates the correctness of the above scheme. At last IO_2^+ and F^- can react:



Fluorine may be successfully used to remove water in preparative reactions in hydrogen fluoride



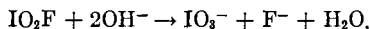
Thus after passing fluorine for several hours through a solution of HIO_3 or I_2O_5 in hydrogen fluoride and distilling off the solvent, iodyl fluoride is obtained in a very pure form after drying in vacuum at 50°C . The over-all reaction may be represented by the following equation:



The colorless crystalline iodyl fluoride is completely stable at room temperature and is not particularly hygroscopic, though in moist air it evolves HF slowly. The decomposition temperature is not sharp; glass is attacked at $210\text{--}230^\circ\text{C}$, iodine being set free.

2. Reactions of IO_2F ; Iodyl Salts

Hydrolysis occurs, as would be expected, according to the equation (8)

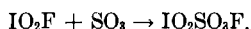


Ammonia, on the other hand, forms, in absence of light, a yellow-white compound of the composition $\text{IO}_2\text{F} \cdot 3\text{NH}_3$; on exposure to light a brownish-black inhomogeneous powder results, in which the ammonia and fluorine contents are lower.

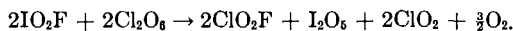
Iodyl fluoride dissolves as a "base" in hydrogen fluoride and iodyl salts may be prepared by neutralization with compounds which function as acids in this system. With fluoroboric acid, obtained by passing BF_3 into the solution, a white crystalline $\text{IO}_2(\text{BF}_4)$ may be isolated. It is very readily soluble in hydrogen fluoride and decomposes again at 45°C into BF_3 and IO_2F . The behavior of AsF_5 or HAsF_6 is completely analogous: $\text{IO}_2(\text{AsF}_6)$ is obtained as a white crystalline powder when the hydrogen fluoride is distilled off. It is not possible to get $\text{IO}_2(\text{AsF}_4)$ with AsF_3 as reduction to iodine takes place. This redox reaction occurs very slowly, however, and the arsenic can be oxidized by passing in fluorine so that $\text{IO}_2(\text{AsF}_6)$ is again obtained. From these clear-cut reactions it is clear that we are dealing with

true iodyl compounds and Aynsley's assumption (11) that the arsenic compound is $(\text{AsF}_4)^+(\text{IO}_2\text{F}_2)^-$ becomes less probable. If BF_3 , SiCl_4 , AsF_5 , or SO_3 are passed directly over solid IO_2F no reaction results (11). A compound $\text{IO}_2\text{F} \cdot 0.8\text{SbF}_5$ was also obtained by Aynsley (11).

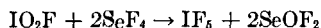
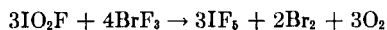
Iodyl fluoride functions in the hydrogen fluoride solvent system only as a weak base and no reaction could be detected with perchloric acid, which functions as an ampholyte. When IO_2F is heated under reflux with excess of sulfur trioxide the reaction is exactly like that of chloryl fluoride.



Iodyl fluoride reacts with N_2O_5 or anhydrous nitric acid to form I_2O_5 , and behaves similarly with dichlorine hexoxide, though chloryl fluoride is also formed (199).



Strong fluorinating agents convert iodyl fluoride into iodine pentafluoride (11).



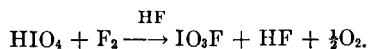
With 100% hydrogen peroxide reduction to elementary iodine occurs. Iodyl sulfates are considered under iodine oxides.

Conversely, IO_2F is also able to take up a fluoride ion. As early as 1899 Weinland, Lauenstein, and Köppen (197, 198) obtained compounds of the type MIO_2F_2 ($\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$) by evaporating solutions of the alkali iodate in 40% hydrofluoric acid. Investigation of the structure of the potassium salt KIO_2F_2 showed the presence of IO_2F_2^- groups (83). Further reactions in which IO_2F reacts by taking up fluoride ions are not yet known.

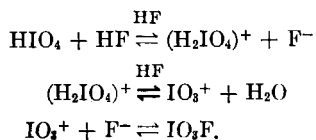
F. PERIODYL FLUORIDE IO_3F (105, 168)

1. Preparation of IO_3F

The analogous method to that used in preparing iodyl fluoride may be used to make this compound, *meta*- or *ortho*-periodic acid being decomposed by fluorine in anhydrous hydrogen fluoride:



The mechanism discussed for the formation of IO_2F may be applied directly to this reaction, which can then be formulated as follows:

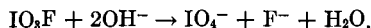


The water produced in the equilibrium reaction is taken up by fluorine. The preparation, like that of IO_2F is carried out in platinum apparatus. Since periodic acid is catalytically broken down to iodic acid and oxygen, the periodyl fluoride isolated is contaminated with IO_2F .

Periodyl fluoride is a white crystalline compound which is more stable to hydrolysis than IO_2F . It may be stored in glass vessels without decomposition. It decomposes at about 100°C to IO_2F and oxygen. Periodyl fluoride is soluble in hydrogen fluoride and in anhydrous hydrogen cyanide without decomposition.

2. Reactions of IO_3F

Periodyl fluoride dissolves slowly in caustic soda solution to form sodium periodate and sodium fluoride.

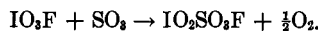


Ammonia gives periodyl amide, which may be isolated as an ammoniate



The amide shows remarkable thermal stability; it starts to turn brown at 185°C and decomposes spontaneously at 210°C . It decomposes in water to periodate and ammonia. This parallels the reaction of ammonia with ClO_3F (50), though in that case the ammonium salt $\text{ClO}_3\text{NH} \cdot \text{NH}_4$ is formed because of the acid character of the amide of perchloric acid. This salt is stable in aqueous solution.

The tendency to form complexes containing the periodyl cation, IO_3^+ , is appreciably less than that for IO_2F , just as it is for ClO_3F compared with ClO_2F . Nevertheless, neutralization reactions may be carried out in hydrogen fluoride with IO_3F acting as a base. Thus, with HBF_4 , $\text{IO}_3(\text{BF}_4)$ may be obtained as a colorless crystalline powder; in moist air it deliquesces to a brown mass. Reaction with HAsF_6 leads to a solvated product of composition $\text{IO}_3(\text{AsF}_6) \cdot 10\text{HAsF}_6$. Thermal degradation leads first of all to a product with 4HAsF_6 , but above 90°C decomposition occurs with loss of oxygen. Reaction with SO_3 at -10°C in CFCl_3 gives iodyl fluorosulfanate, with evolution of oxygen:



Both AsF_3 and 100% H_2O_2 reduce IO_3F to elementary iodine.

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THE CHEMISTRY OF GALLIUM

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I. Introduction

Gallium has several unique properties which have stimulated interest in its chemistry ever since 1875 when its discovery by Lecoq de Boisbaudran (17) confirmed so eloquently his own predictions and those of Mendeleef for eka-aluminium. The chemistry of gallium was reviewed by Gmelin (96) in 1936 and in the following year by Einecke (63) but since that time only one extensive review has appeared (22), though the number of papers being published annually on this element now exceeds the total number of papers included in Gmelin's volume. Several general articles have appeared dealing with certain aspects of the history, occurrence, extraction, purification, analysis, physical and chemical properties, toxicology, or uses of the element (10, 18, 23, 32, 65, 233, 276, 285).

During the last decade there have been five main areas of interest in the chemistry of gallium:

- (a) the existence of lower valency states in which the oxidation number of the metal is +1 or +2,
- (b) the structure and semiconducting properties of binary compounds of gallium with phosphorus, arsenic, and antimony, in group V and sulfur, selenium, and tellurium in group VI,

- (c) the crystal chemistry of the oxides, hydroxides, and related compounds,
- (d) the structure and catalytic activity of the trihalides and their molecular addition compounds,
- (e) the preparation and reactions of hydrides and organometallic compounds of gallium.

These topics will be dealt with in successive sections of this review which also refers to recent work on the salts and coordination complexes of gallium.

The physical constants of gallium which are of interest to chemists are summarized in Table I. The atomic radius and first ionization potential of

TABLE I
PHYSICAL PROPERTIES OF GALLIUM (264, 276)

Atomic number	31	Melting point (°C)	29.75°
Atomic weight	69.72	Boiling point (°C)	~2227 ^a
Atomic radius (Å)	1.245	d_4^{20} (solid) (gm/ml)	5.907
Ionic radius (Å)	0.62	$d_4^{29.8}$ (liquid) (gm/ml)	6.0948
Ionization potential (ev)	6.00	Atomic volume (29°) (ml)	11.81
Std. electrode potential, (volts)	0.52	Atomic volume (30°) (ml)	11.44

^a This figure is obtained by an extrapolation of 1000° from vapor pressures below 1 mm!

gallium are almost identical with those of aluminium and the two elements frequently resemble each other in chemical properties. Both are amphoteric, but gallium is less electropositive as indicated by its lower electrode potential. Differences in the chemistry of the two elements can be related to the presence of a filled set of 3*d* orbitals in gallium.

The unusual physical properties of metallic gallium arise from its unique crystal structure which consists of Ga₂ units arranged in deformed sets of hexagonal rings (20, 188). Each gallium atom has one nearest neighbor at 2.442 Å. The orthorhombic unit cell has 4Ga₂ units lying symmetrically in the *a-c* plane at angles of 17° to the *c*-axis, the spacing of these molecular planes being *b*/2. This rather open structure collapses to a more nearly close-packed arrangement in the liquid state, and melting is accompanied by a contraction of 3.1% in atomic volume and by a considerable increase in electrical conductivity (222, 223, 228). Here gallium resembles its neighbor germanium and also antimony and bismuth. The element has a very low m.p. and an extraordinary low vapor pressure (less than 1 mm at 1300°). These factors combine to give gallium the longest liquid range of any known substance and form the basis of its (very limited) use in high temperature thermometers (285). An alloy of gallium, indium, and tin, melting at 5° and having excellent wetting properties and a vapor pressure of <10⁻⁷ mm at 500° has been suggested as a high-vacuum seal (198).

II. Lower Valencies (Oxidation States I and II)

Compounds in which the valency of gallium is less than +3 have been known since the earliest experiments of de Boisbaudran (96), but it is only in the last decade that structural studies have elucidated the variety of ways in which gallium achieves these lower oxidation states. It is now recognized that gallium forms a range of stable univalent compounds, many of which also contain an equal number of gallium atoms in the +3 oxidation state, thus leading to a formal over-all oxidation state equivalent to $\text{Ga}^{(III)}$. The +2 state can also be achieved by the presence of Ga—Ga bonds in the structure and unstable gaseous compounds are known in which gallium is in a lower valency state.

A. UNSTABLE GASEOUS MOLECULES

Gallium monochloride is formed at 1100° either by the dissociation of the trichloride or by the reaction of gallium metal with chlorine (191).



Other diatomic halides are formed similarly. Faint absorption bands were also observed (209) when the arc spectrum of gallium was studied in the presence of hydrogen and these have been assigned to the compound GaH. The interatomic distances and energies of dissociation of these molecules into atoms are recorded in Table II.

TABLE II
DIATOMIC MOLECULES CONTAINING $\text{Ga}^{(I)}$

Molecule	GaH	GaF	GaCl	GaBr	GaI
r (Å)	~1.66	1.775	2.202	2.353	2.575
$\Delta H_{\text{dissoc.}}$ (kcal/mole)	~78	143	115	—	—
Reference	196	8	6, 191	6	6

It has been suggested (196) that these diatomic molecules are essentially ionic, like those of the gaseous alkali metal halides, but the binding energies calculated from thermochemical cycles do not agree well with those calculated on the basis of pure ionic attraction using the latest experimental values for the internuclear distances. Moreover, the radius of the Ga^+ ion calculated from the observed internuclear distances and the radii of the gaseous halides ions (231) decreases from 0.74 Å, to 0.56 Å, the mean value of 0.63 Å being almost identical with the accepted value for Ga^{3+} . The univalent ion would be expected to be considerably larger than this and a value of 1.17 Å has been suggested on the basis of a semiempirical theory

(308). On a covalent model, however, the calculated radius for gallium increases with increasing atomic number of the halogen atom from 1.06 Å to 1.241 Å, which is close to the accepted value of 1.245 Å for the covalent radius of gallium. A covalent model is also consistent with the quadrupole coupling constants of these molecules which have been interpreted in terms of partial *sp* hybridization (6).

Flame reactions provide another source of unstable species containing univalent gallium. Typical reactions are the following (33):



The value for the heat of dissociation of GaOH according to Eq. (4) is 102 ± 5 kcal/mole (33). Similarly, from the partial pressure of gallium in oxyacetylene or oxyhydrogen flames of known temperature, the dissociation energy of the molecule GaO was found to be 115.6 ± 3 kcal/mole (127).

B. CHALCOGENIDES

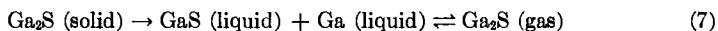
Compounds of univalent gallium have been reported for all elements of group VI except polonium, but little is known of their structure. Gallium(I) oxide can be prepared by reduction of the sesquioxide with gallium at 700° and is purified by vacuum sublimation at 500° (96):



The dark brown, diamagnetic powder is stable in dry air, but undergoes surface oxidation at higher temperatures. Above 800° it disproportionates according to the reverse of Eq. (5). More recently (84) Ga₂O has been made by the reaction of gallium with carbon dioxide at 10 mm pressure and 850°:



Gallium(I) sulfide, like the oxide, cannot be prepared directly from the elements but is obtained by thermal decomposition of higher sulfides (96). Thus, when gallium(II) sulfide is heated at 1100° for several hours in a stream of nitrogen, gallium(I) sulfide sublimes quantitatively as green hexagonal prisms or yellow-green plates (263) [see Eq. (9) below]. The compound is a phase of variable composition Ga₂S_{0.8-1.1} and has a hexagonal lattice similar to that of gallium(II) sulfide (see below). Above 950° pure gallium(I) sulfide decomposes to a liquid mixture of gallium(II) sulfide and metallic gallium which becomes homogeneous above 1150°:



In this temperature range the gas above the mixture is monomeric Ga₂S

and the vapor pressure of the system is given by the relation $\log p_{\text{mm}} = 7.93 - 9098/T$. From this the "b.p." is 1530° , the heat of vaporization 39.6 kcal/mole and the entropy change 21.8 e.u. (263).

Gallium(I) selenide and the previously unknown gallium(I) telluride can apparently be made by melting the elements together in evacuated quartz tubes for prolonged periods; their X-ray powder diagrams have been recorded and indexed (177).

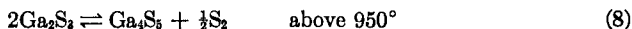
The divalent compounds GaS, GaSe, and GaTe, can all be prepared by direct reaction of the elements at high temperatures. They have recently been investigated as semiconductor materials, their intrinsic energy gaps being about three times that of germanium. By contrast, gallium(II) oxide has not yet been prepared as a stable solid though bands have been ascribed to the gaseous, diatomic species GaO (141). Some physical properties are summarized in Table III. Crystal structure determinations (128,

TABLE III
PHYSICAL PROPERTIES OF GaS, GaSe, AND GaTe

	m.p.	color	d_4^{25}	unit cell size (Å)	ΔE (kcal/mole)		Reference
					elec.	optic.	
GaS	$970 \pm 3^\circ$	yellow	3.75	a 3.578, c 15.47	—	—	(128, 263)
GaSe	$960 \pm 10^\circ$	red brown	5.03	a 3.735, c 15.887	46.3	47.1	(69, 241, 248, 274)
GaTe	$824 \pm 2^\circ$	grey	—	a 23.76, b 4.068 c 10.46, β 45.4°	41.5	38.2	(69, 241, 249)

248, 249) have shown that the +2 oxidation state in these compounds results from a layer lattice arrangement in which the characteristic feature is the occurrence of Ga_2^{4+} units, i.e., $-\text{SGaGaS}$, $\text{SGaGaS}-$. This immediately explains the diamagnetism of the compounds. Within each layer each gallium is tetrahedrally surrounded by three sulfur atoms and one gallium atom to which it is covalently bound, and the neighboring multiple layers are held by van der Waals attraction. Interatomic distances are Ga—Ga 2.46 Å, Ga—S 2.34 Å. The selenide and telluride have similar structures. It is interesting to note that none of the chalcogenides of gallium(II) crystallize in the TlS-type structure in which half the thallium atoms are univalent and half tervalent, i.e., $\text{Tl}^+[\text{Tl}^{\text{III}}\text{S}_2]^-$. The Tl^{III} are tetrahedrally surrounded by sulfur and the tetrahedra are linked into infinite chains by sharing edges (69).

Gallium monosulfide and sesquisulfide both disproportionate at high temperatures to give a solid phase of variable composition between $\text{Ga}_4\text{S}_{4.8}$ and $\text{Ga}_4\text{S}_{5.2}$:



The compound Ga_4S_6 , which is stable up to 1200° and has a density of 3.82 ± 0.01 gm/ml, can also be formed directly from the elements (263).

C. HALIDES

Evidence for univalent halides in the solid state is fragmentary. The monochloride disproportionates readily into a higher halide and gallium; e.g., at 820° gallium metal rapidly volatilizes in a stream of hydrogen chloride gas to give a brown-black sublimate analyzing as $\text{GaCl}_{0.94}$ in which small drops of gallium metal can be seen (83). The gallium-iodine phase diagram (44) shows that the limiting composition of the halide phase in contact with molten gallium is $\text{GaI}_{1.19}$. When this is repeatedly extracted with dry benzene a residue of composition $\text{GaI}_{1.06}$ is obtained; the X-ray powder diagram shows this to be a distinct phase rather than a mixture and the extrapolated m.p. of the mono-iodide was found to be 271° . Other indications of unstable oxidation states below +2 come from anodic oxidation of gallium in glacial acetic acid (52) or anhydrous ammonia (51) and from the solubility of gallium in molten dihalides (43, 46, 47, 78, 275).

Very recently, complexes of gallium(I) chloride and bromide have been reported (24). They were prepared by allowing volatile ligands (L) such as dioxane, morpholine, or acetylacetone, to diffuse into a benzene solution of gallium dihalide in a closed system; disproportionation occurred into gallium trihalide, which remained in solution, and insoluble complexes of formula L_2GaX . The X-ray crystal structure of $[\text{Ga}(\text{diox})_2]\text{Cl}$ shows it to contain discrete chloride ions and a disposition of the four oxygen atoms around the gallous ion which is in the form of a distorted trigonal pyramid (24).

Gallium forms stable dihalides with chlorine, bromine, and iodine and it has now been established conclusively that this oxidation number arises from the existence of equal numbers of gallium atoms in the +1 and +3 oxidation states. Pure gallium dichloride is best prepared (120) by heating the trichloride with slightly less than the stoichiometric amount of gallium and then volatilizing the excess of trichloride from the molten mixture. The last traces of impurity can be removed by fractional freezing to a constant m.p. of 172.4° . A variation of this method (78, 187), which employs a slight excess of gallium, is less satisfactory. The dichloride has also been prepared by heating gallium in a stream of dry hydrogen chloride (153) or by reacting it with the stoichiometric amount of mercurous chloride in a sealed tube (34). The X-ray crystal structure of the dichloride (82), the Raman spectrum (303), electrical conductivity of the fused compound (120), and its

chemical reactions in benzene solution (3, 34) all indicate that it is correctly formulated as gallous tetrachlorogallate, $\text{Ga}^+[\text{GaCl}_4]^-$. The compound is thus an unusual example of the stabilization of an unfamiliar oxidation state by coordination since the ion which is stabilized (Ga^+) is not the one which is coordinated, $[\text{Cl} \rightarrow \text{GaCl}_3]^-$. There are four $\text{Ga}^+[\text{GaCl}_4]^-$ units in the orthorhombic cell, space group $Pnna$, $a = 7.29$, $b = 9.72$, $c = 9.50$ Å. Each gallous ion is surrounded by an irregular dodecahedron of 8 chlorine atoms from six different GaCl_4^- tetrahedra (82). The Ga—Cl distance within each tetrahedron is 2.19 Å and the crystal radius of the Ga^+ ion is 1.33 Å (82). This is somewhat larger than expected (cf. p. 93) and is possibly due to anion-anion contact. The Raman spectrum of the fused compound (303) showed four fundamentals, as expected for a regular tetrahedral species, and these corresponded closely with the known spectrum of the tetrachlorogallate ion (305): 115 cm^{-1} (ν_2 , strong, sharp, depolarized); 153 cm^{-1} (ν_4 , weak, diffuse, depolarized); 346 cm^{-1} (ν_1 , very strong, sharp, polarized); 380 cm^{-1} (ν_3 , very weak, diffuse, depolarized).

Fused gallium dichloride is a typical molten salt and the variation of its electrical conductivity ($\kappa\text{ ohm}^{-1}\text{cm}^{-1}$) and dynamic viscosity ($\eta\text{ cp}$) with temperature and the corresponding activation energies E_κ , E_η are characteristic of a compound in which the cation is smaller than the anion (120).

$$\begin{aligned}\log \kappa &= 1.180 - 784/T; & E_\kappa &= 3.59\text{ kcal/mole} \\ \log \eta &= 1.768 + 1022/T; & E_\eta &= 4.68\text{ kcal/mole}\end{aligned}$$

The temperature variation of the density and surface tension have also been determined (120): $d_4^t = 2.4206 - 1.36 \times 10^{-3}(t - 170)\text{ gm/ml}$; $\gamma = 56.6 - 0.18(t - 170)\text{ dyne/cm}$. Above about 200° gallium dichloride disproportionates reversibly to gallium and the trichloride and above 400° the vapor density indicates considerable quantities of monomeric GaCl_2 molecules (187).

Gallium dichloride is readily soluble in benzene (187), a saturated solution at room temperature containing 4.60 gm/100 gm solvent (153). The Raman spectrum of the solution confirms the ionic nature of the solute (195) and a crystalline phase $[\text{Ga} \cdot \text{C}_6\text{H}_6]^+[\text{GaCl}_4]^-$ can be separated from the solution (238). Gallous tetrachloroaluminate GaAlCl_4 (45), forms a similar complex (238). Further proof of the two oxidation states of gallium in the dichloride comes from the reaction of a benzene solution with hydrogen sulfide: Ga^I was precipitated as the sulfide and gallium trichloride remained in solution (34).

The strongly reducing nature of the dichloride, which was observed by the earliest workers (231) has been repeatedly confirmed and it has been shown that carbon tetrachloride is reduced to carbon (187). Limited stabilization of the gallous ion has been achieved by coordination, and a wide

variety of complexes of the form $[\text{GaL}_4]^+[\text{GaCl}_4]^-$ have been prepared with oxygen, sulfur, selenium, nitrogen, and arsenic donors where L_4 represents four monodentate ligands, two bidentate ligands, or one quadridentate ligand (3, 24). Such complexes are usually white or pale cream though the adducts with 2,2'-dipyridyl and dithizone were red. Molecular-weight determinations, electrical conductivity, and diamagnetism confirm the general ionic formulation but the problem of the detailed stereochemistry of the $[\text{GaL}_4]^+$ cations has not yet been settled. The gallous ion in such complexes has five pairs of electrons and is therefore isoelectronic with phosphorus, sulfur, and chlorine in their compounds PF_5 , SF_4 , and ClF_3 , all of which are based on trigonal bipyramidal symmetry. If, however, the $4s^2$ electrons are stereochemically inert, then presumably either planar or tetrahedral symmetries are possible though these would involve the use of unusual hybrids. The stereochemistry of the complex $[\text{Ga}(\text{diox})_2]\text{Cl}$ has already been mentioned on p. 96.

Gallium dibromide is very similar in its structure and properties to the dichloride. It is best prepared pure by heating the tribromide in a sealed, evacuated tube at 180° with slightly less than the theoretical weight of gallium, after which excess of the tribromide is volatilized away and the compound fractionally crystallized from the melt to a constant melting point of 166.7° (124, 304). Reaction of gallium with mercuric bromide also affords gallium dibromide and when this reaction is carried out in the presence of benzene, the solvate $\text{Ga}_2\text{Br}_4 \cdot \text{C}_6\text{H}_6$ is obtained (34).

Crystalline gallium dibromide (304) like the dichloride (171) is diamagnetic, and the Raman spectrum of the fused compound showed only the four fundamental modes expected for the tetrahedral GaBr_4^- ion (304): 79 cm^{-1} (ν_2 , strong, sharp, depolarized); 107 cm^{-1} (ν_4 , strong, sharp, depolarized); 209 cm^{-1} (ν_1 , very strong, sharp, strongly polarized); 288 cm^{-1} (ν_3 , weak, diffuse, depolarized). The electrical conductivity ($\kappa\text{ ohm}^{-1}\text{cm}^{-1}$) viscosity, ($\eta\text{ cp}$) and density are given by the equations:

$$\log \kappa = 1.142 - (865/T)$$

$$\log \eta = 1.793 + (1158/T)$$

$$d = 3.4656 - 1.69 \times 10^{-3} (t - 170).$$

These data, together with the activation energies ($E_\kappa = 3.96$, $E_\eta = 5.30\text{ kcal/mole}$) show that the compound is a completely dissociated molten salt in which the cation is small compared with the anion (120, 304).

Gallium dibromide apparently has two crystalline modifications, α and β , melting at 153° and 165° (43). As mentioned on p. 96 the fused compound dissolves metallic gallium to some extent but complete reduction to the monobromide could not be effected, the limiting composition being 31.4 mole % GaBr at 170° . In the presence of aluminium tribromide,

however, complete reduction to monovalent gallium occurred and the compound $\text{Ga}^+[\text{AlBr}_4]^-$ (m.p. 159°) was found to be dimorphic, each modification being isomorphous with the corresponding form of $\text{Ga}^+[\text{GaBr}_4]^-$ (43). A variety of complexes $[\text{GaL}_4]^+[\text{GaBr}_4]^-$ analogous to the chlorogallates has also been described (3, 24).

Gallium di-iodide (m.p. 211°) can be prepared by direct reaction of the correct amounts of gallium and iodine (44) or by the reaction of gallium with mercuric iodide in a sealed tube (34). It is diamagnetic (44), and in the absence of further data can be presumed to have the structure $\text{Ga}^+\text{GaI}_4^-$. When heated at 250° the di-iodide loses gallium tri-iodide by disproportionation, leaving a residue of limiting composition close to the monoiodide (see p. 96).

III. Binary Compounds of Gallium(III) with Group V Elements

The compounds which gallium forms with nitrogen, phosphorus, arsenic, and antimony are isoelectronic with the Group IV elements and there has been considerable interest, particularly in the physical properties of these compounds, since 1952 when Welker first showed that they had semiconducting properties analogous to those of silicon and germanium (287).

Gallium nitride is the only member of the group which cannot be prepared by direct reaction of the elements. It was first made (155) by the reaction of gallium with ammonia at 900° – 1000° and has also been prepared by the decomposition of $(\text{NH}_4)_3\text{GaF}_6$ at 600° (131). Crystalline gallium nitride is formed when the adduct $\text{GaCl}_3 \cdot \text{NH}_3$ is pyrolyzed at 1000° (219). The compound is grey or yellow (131, 155, 192, 229), diamagnetic (131), and crystallizes in the Würtzite (ZnS) structure (156). Its physical properties are summarized in Table IV and the heat of formation $-\Delta H_f^\circ$ is 24.9 ± 0.9 kcal/mole (131).

Gallium nitride is not hydrolyzed by hot water or by acids such as dilute or concentrated hydrofluoric, hydrochloric, or nitric (155, 229). Aquaregia is also without effect but the compound dissolves slowly in hot concentrated sulfuric acid (155). With hot concentrated aqueous alkali, ammonia is evolved (229). There is no reaction with hydrogen at 800° but oxygen slowly reacts with gallium nitride at 900° over a period of days to give nitrogen and the sesquioxide Ga_2O_3 (155). The reaction proceeds with ignition in the presence of paraffin (131).

Although gallium nitride cannot be formed directly from gallium and nitrogen, the compound Li_3Ga reacts with nitrogen at 600° to give the ternary nitride, Li_3GaN_2 (158). This light-grey powder, d 3.35, can also be prepared by heating lithium nitride and gallium in nitrogen at 730° or by heating a mixture of lithium nitride and gallium nitride. Lithium gallium nitride is very similar to lithium aluminium nitride, Li_3AlN_2 : both crystal-

TABLE IV
PHYSICAL PROPERTIES OF III-V COMPOUNDS

Property	GaN	GaP	GaAs	GaSb
m.p.	$d > 1250^\circ$ (156, 229)	1350° (258)	1238° ^a (19, 176)	712° ^b (9, 95)
Crystal structure	Würtzite (156, 157) $a = 3.180$, $c = 5.166$ Å $c/a = 1.625$ ^c	zinc blende $a_0 = 5.4505$ Å (90) 5.436 Å (74)	zinc blende $a_0 = 5.6534$ Å (90, 210) 5.6560 Å (175)	zinc blende $a_0 = 6.0954$ Å (90, 175) 6.1342 Å (15)
Refractive index	—	3.37 (75), 2.9 (258)	3.4 (212), 3.2 (258)	3.9 (213), 3.7 (258)
κ ohm ⁻¹ cm ⁻¹	10^{-9} – 10^{-7} (229) 2.5×10^{-9} (159)	10^{-2} – 10^{+2} (75)	10^{-6} – 10^{+3} (134) (0.17–1.0) $\times 10^3$ (175)	12 (56), 6–13 (257) 10–12 (190)
ΔE ev (optical)	3.25 (163)	2.24 ^d (74)	1.25 (50), 1.35 ^e (212)	0.68 (212), 0.71 ^f (50)
ΔE ev (electrical)	—	—	1.320 (175)	0.7–0.8 ^g

^a Also 1280° (50).

^b Also 702° (288), 703° (176), 705.9° (101), 725° (161).

^c Also $a = 3.160$ Å, $c = 5.125$ Å, $c/a = 1.622$ (192).

^d $\Delta E = 2.4 - 5.4 \times 10^{-4}T$ (211).

^e $\Delta E = 1.53 - 5.0 \times 10^{-4}T$ (211).

^f $\Delta E = (0.695-0.704) - 2.9 \times 10^{-4}T$ (232).

^g 0.71 (175, 190), 0.775 (15), 0.78 (55), 0.80 (190), 0.82 (212, 288).

lize in the antiferite structure and are readily hydrolyzed by water or dilute acids (158). Ternary phosphides and arsenides can also be prepared by heating mixtures of the binary compounds at 450–650°. Lithium gallium phosphide, Li_3GaP_2 , resembles the nitride in having the antiferite structure but the arsenide, Li_3GaAs_2 , has a tetragonal unit cell with the axial ratio $c/a = 1.016$ (160).

Gallium phosphide, arsenide, and antimonide can all be prepared by direct reaction of the elements; this is normally done in sealed silica tubes (19, 210) or in a graphite crucible under hydrogen (9, 190, 257). Phase diagrams indicate the stoichiometry GaAs and GaSb (176). Similar data are hard to obtain in the gallium–phosphorus system because gallium phosphide has a vapor pressure of more than 13.5 atm at its melting point (73)—cf. 0.89 atm for gallium arsenide (73).

The physical properties of these three compounds are compared with those of the nitride in Table IV. All three adopt the zinc blende crystal structure and are more highly conducting than gallium nitride. Whereas the group IV semiconductors silicon and germanium are purely covalent, the III-V compounds have some ionic character and provide a wider range of basic semiconductor parameters such as energy gaps and mobilities. Estimates of the precise extent of heteropolarity vary widely as is to be expected, but, independently of the method used to determine ionic character (221, 301), there is general agreement that this diminishes in the sequence $\text{GaP} > \text{GaAs} > \text{GaSb}$. The energy gap ΔE decreases in the same order (see Table IV). In general, the m.p. and energy gap of III-V compounds are higher than those of the isoelectronic Group IV elements, despite the similarity in bond distances.

Gallium phosphide forms orange, transparent crystals and is potentially useful for very high temperature work particularly where high frequency performance is not required. Gallium arsenide forms good *pn*-junctions and has been used to study photovoltaic effects. It is one of the most promising semiconductors for high frequency and high temperature work. Gallium antimonide is the most studied compound of the group because of its low melting point. It is normally a *p*-type semiconductor but *n*-type samples have been prepared by doping with tellurium.

Further flexibility is introduced by the possibility of alloying these various compounds. There is normally a complete range of solid solutions with other III-V compounds (306, 307), and properties tend to vary approximately linearly with composition (14, 175). By contrast, germanium ($a_0 = 5.658 \text{ \AA}$) is less than 2% soluble in gallium arsenide ($a_0 = 5.656 \text{ \AA}$) despite the near identity of their lattice parameters (151).

The chemical properties of this group of compounds have been less studied. There is no reaction with water or dilute alkali but dilute hydro-

chloric acid yields small quantities of arsine or stibine (161). Ternary compounds such as Li_3GaP_2 and Li_3GaAs_2 can be formed by direct reaction of lithium phosphide or arsenide with gallium phosphide or arsenide (160).

IV. Binary and Ternary Oxides and Hydroxides

The precipitation of the hydrous oxide of gallium from aqueous solutions and its dissolution in excess of alkali has been a subject of continuing interest (144, 150, 270, 284). For example precipitation from an 0.007*M* solution of gallium trichloride begins at pH 3.15 and is complete at pH 6, after which redissolution begins and is complete at pH 9.5 (183). The solubility product $[\text{Ga}^{3+}][\text{OH}^-]^3$ is $10^{-36.5}$ and may be compared with those of aluminium and indium hydroxides which are $10^{-33.8}$ and $10^{-33.9}$ (183). In the presence of sulfate ions the hydrous oxide begins to precipitate after approximately one OH^- per mole of gallium has been added, but aqueous solutions of the chloride, bromide, or nitrate can be treated with up to three OH^- per mole of gallium without precipitation though addition of more hydroxyl ions causes the solutions to flocculate sharply. Diffusion current data show that this unusual behavior is due to the formation of $\text{Ga}^{3+}\text{—OH}^-$ aggregates rather than to peptization (203) and detailed isopiestic studies on perchlorate solutions suggest that the degree of polarization of the oxygen-bridged cationic gallium aggregates increases from 1.3 at a mole ratio $\text{OH}^-/\text{Ga}^{3+}$ of 0.5, to 84 at a mole ratio of 2.0 (215). Further work using Rayleigh turbidities and refractive index increments indicates that Sillen's core-link hypothesis applies to these aggregates (239).

When freshly precipitated gallium hydroxide is dissolved in saturated aqueous lithium hydroxide and the solution evaporated, the compound $[\text{Li}(\text{H}_2\text{O})_4][\text{Ga}(\text{OH})_4]$ crystallizes. This readily loses water over sulfuric acid at room temperature, and again at 100° to give compounds which can be formulated as $[\text{Li}(\text{H}_2\text{O})_2][\text{Ga}(\text{OH})_4]$ and $\text{Li}[\text{GaO}(\text{OH})_2]$. Further heating results in irreversible dehydration to LiGaO_2 (145). Sodium hydroxide yields $\text{Na}[\text{Ga}(\text{OH})_4]$ and NaGaO_2 and potassium hydroxide yields $\text{K}[\text{Ga}(\text{OH})_4]$, $\text{KGaO}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, and $\text{KGaO}_2 \cdot \text{H}_2\text{O}$. By contrast, calcium and strontium hydroxides tend to give six-coordinate complexes of the form $\text{M}_3\text{Ga}(\text{OH})_6$ (145). The phase diagram of the system $\text{Ga}_2\text{O}_3\text{—Na}_2\text{O—H}_2\text{O}$ has also been studied and various hydrated gallates established (89). (See also ref. 79).

Gallia, like alumina, exists in a variety of structural forms and these have been extensively investigated by electron diffraction and X-ray crystallographic methods. Forms designated α , β , γ , δ , and ϵ have been distinguished, the stable form between room temperature and the m.p. being $\beta\text{-Ga}_2\text{O}_3$ which is isomorphous with $\theta\text{-Al}_2\text{O}_3$ (79, 174, 235). The low-temperature thermodynamic properties of $\beta\text{-Ga}_2\text{O}_3$ have been tabulated (1, 167) and its m.p. is 1725° (139). The hydrous oxide, $\text{GaO} \cdot \text{OH}$, has the

same structure as diaspore, $\beta\text{-AlO}\cdot\text{OH}$ (16), and undergoes dehydration to $\beta\text{-Ga}_2\text{O}_3$ at 300° (185, 235). A metastable phase $\text{Ga}(\text{OH})_3$ and possibly also $\text{Ga}_2\text{O}(\text{OH})_4$ have also been recognized (185). Treatment of the first of these compounds with calcium hydride removes only one mole of water and this has been taken to indicate that its structure is $\text{GaO}\cdot\text{OH}\cdot\text{H}_2\text{O}$ rather than $\text{Ga}(\text{OH})_3$ (5).

The close similarity in ionic radii between gallium and aluminium which leads to the similarity in oxide and hydrous oxide phases just mentioned, also ensures that the two series of compounds exhibit extensive solid solution. Thus, below 810° , the compound GaAlO_3 and a series of solid solutions extending almost to pure alumina and gallia are stable. When water is added, these phases are stable only above a transition temperature in the region of $300\text{--}400^\circ$ (depending on composition). Below this temperature a complete series of diaspore-type structures extends from $\text{AlO}\cdot\text{OH}$ to $\text{GaO}\cdot\text{OH}$ and below about 275° a series of boehmite-type structures extends from $\text{AlO}\cdot\text{OH}$ to a composition in which 30% of the aluminium ions have been replaced by gallium (139, 236). Similarly gallium analogs of the aluminosilicates and aluminogermanates have been prepared (7). For example, fully substituted or partly substituted counterparts have been prepared of sodium feldspar, ($\text{NaAlSi}_3\text{O}_8$), calcium feldspar, orthoclase (KAlSi_3O_8), leucite (KAlSi_2O_6), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), and mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) (86, 97, 189). Both silicon and aluminium can be completely removed without change in structure from gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) by replacing aluminium by gallium and (Si + Ca) by (Ga + Ln) to give $\text{CaLnGa}_2\text{O}_7$ where Ln is a lanthanide element (59).

Similar isomorphous substitutions in the sesquioxide (Ga_2O_3) itself lead to perovskite lattices such as LaGaO_3 , CeGaO_3 , NdGaO_3 (165, 234) and, as expected, substitution can also occur in spinel-type lattices, e.g., half the aluminium ions in chrysoberyl can be replaced to give BeAlGaO_4 (93).

A variation on the III-V theme discussed in the preceding section concerns the replacement of pairs of silicon atoms in silica by gallium and a group V element. Thus GaPO_4 exists in forms corresponding to a low-temperature quartz, a metastable, low-temperature cristobalite and a high-cristobalite with transition temperatures at 933° and 616° respectively (205, 217, 251). The compound GaAsO_4 exists only in the low-temperature quartz form and with the compound GaSbO_4 , where the increased cation radius requires 6:3 rather than 4:2 coordination, a disordered rutile (TiO_2 -type) structure is adopted (21, 251).

V. Compounds with Sulfur, Selenium, and Tellurium

The sesqui-sulfide, -selenide, and -telluride of gallium can all be prepared by direct reaction of the elements at high temperature. The compounds are isomorphous with zinc sulfide (132) and this, rather than iso-

morphism of zinc sulfide with gallium arsenide, is now thought to be the reason for specific enrichment of gallium in sphalerite minerals (99).

Gallium sulfide has three crystal modifications (128, 132):

$\gamma\text{Ga}_2\text{S}_3$ (zinc blende) $a_0 = 5.171 \pm 0.004 \text{ \AA}$, stable at low temperatures; the gallium atoms randomly occupy 2/3 of the tetrahedral sites in the sulfide cubic close-packed lattice.

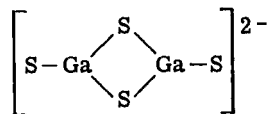
$\beta\text{Ga}_2\text{S}_3$ (Würtzite) $a = 3.678 \pm 0.005$, $c = 6.016$, $c/a = 1.636$; the gallium atoms randomly occupy 2/3 of the tetrahedral sites in the sulphide hexagonal close-packed lattice; $\gamma \rightleftharpoons \beta$ transition $550^\circ\text{--}600^\circ$.

$\alpha\text{Ga}_2\text{S}_3$ (Würtzite superlattice with unit cell containing $6\text{Ga}_2\text{S}_3$); $a = 6.370$; $c = 18.05 \text{ \AA}$, $c/a = 2.833$.

Gallium selenide and telluride exist only in the zinc blende structure with two-thirds of the cation sites occupied by gallium atoms. Unit cell dimensions are: Ga_2Se_3 $a_0 = 5.430 \pm 0.005 \text{ \AA}$ (99) [or 5.418 \AA (132)]; Ga_2Te_3 $a_0 = 5.887 \pm 0.003 \text{ \AA}$ (99) [or 5.874 \AA (132)]. In all cases bond distances are close to those expected.

All three compounds are semiconductors, though their use is somewhat restricted by their ready hydrolysis. Activation energies are intermediate between those of the isoelectronic II-VI and III-V compounds (98), typical values for the energy gap ΔE between bands being: Ga_2S_3 2.85 eV (164); Ga_2Se_3 1.9 eV (164); Ga_2Te_3 1.0–1.55 eV (136, 137, 138, 164). The energy gap decreases with decreasing ionic character (cf. Ga_2O_3 4.4 eV) and the above values are thus less than those of the corresponding aluminium chalcogenides but greater than those of the indium analogs (164). Ternary compounds such as CuGaS_2 , AgGaS_2 , and the corresponding selenium and tellurium compounds which all adopt the chalcopyrite structure (130) have also been investigated as semiconductors (4, 71, 94). The compounds CdGa_2S_4 , HgGa_2S_4 , CdGa_2Se_4 , HgGa_2Se_4 , and CdGa_2Te_4 have been prepared by direct reaction of the component binary chalcogenides and all adopt a chalcopyrite structure in which the appropriate number of cation sites is left vacant (129). The corresponding reaction between cuprous oxide and gallium oxide leads to the compound CuGaO_2 , but this, being more ionic than the chalcogenides, crystallizes in the NaHF_2 -type structure with octahedral, rather than tetrahedral coordination (133).

An interesting series of alkali metal thiogallates $\text{M}_2\text{Ga}_2\text{S}_4$ has been prepared (146) in which the anion is considered to have the structure:



The lithium and sodium compounds are prepared by heating an equimolar mixture of alkali metal carbonates and gallium sesquioxide to 900° in a stream of hydrogen sulfide whereas the potassium, rubidium, and cesium salts are prepared by heating the carbonate and oxide in molten sulfur and then leaching with water to leave the insoluble thiogallate. The five compounds are yellow or light brown, have m.p.'s in the range 952 – 1020° , are stable in air or water, but are decomposed by strong acids with liberation of hydrogen sulfide (146).

VI. Gallium Trihalides and Their Adducts

Current interest in the trihalides of gallium centers on their structure and catalytic activity, and on the stoichiometry, structure and stability of their coordination complexes. Gallium fluoride differs markedly from the other halides and in this it resembles the fluorides of aluminium and indium. For example, the m.p.'s of the fluorides are several hundred degrees above those of the chlorides, though this difference decreases from 1097° for aluminium and 872° for gallium to 584° for indium.

A. GALLIUM(III) FLUORIDE

Gallium trifluoride can be prepared by dissolving gallium hydroxide in 40% hydrofluoric acid and adding this to a saturated solution of ammonium fluoride. The complex $(\text{NH}_4)_3\text{GaF}_6$ so obtained is heated to 630° in a current of fluorine to yield the trifluoride (135). More recently it has been made by direct reaction of hydrogen fluoride and gallium at 440° (25). This method is to be preferred since samples prepared from the hexafluorogallate are invariably contaminated with nitride derivatives. When the hexafluorogallate is heated at 220° in a stream of nitrogen the compound NH_4GaF_4 is obtained. This has tetragonal crystal symmetry with $a = 3.71 \text{ \AA}$, $b = 6.39 \text{ \AA}$ and is isostructural with several tetrafluoroaluminates (25). Gallium trifluoride is isostructural with ferric fluoride and the rhombohedral unit cell has $a = 5.20 \text{ \AA}$, $\beta = 57.5^{\circ}$ (25). The density is 4.47 and the compound is said to have a m.p. greater than 1000° and to sublime readily at 950° (135). An electron diffraction study of the gas at high temperature indicates the presence of GaF_3 molecules in which the Ga–F distance is 1.88 \AA and the F–F distance 3.25 \AA ; dimeric molecules, Ga_2F_6 , if present, have a concentration of less than 1% (2).

The hexafluorogallate mentioned in the preceding paragraph presumably contains 6-coordinate gallium and there is strong presumptive evidence for sixfold coordination in the following complexes: Li_3GaF_6 , Na_3GaF_6 , $\text{K}_2\text{GaF}_6 \cdot \text{H}_2\text{O}$, $\text{RbGaF}_4 \cdot 2\text{H}_2\text{O}$, $\text{CsGaF}_4 \cdot 2\text{H}_2\text{O}$, (224), as well as in $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$ and $\text{GaF}_3 \cdot 3\text{NH}_3$ (169). A series of complexes $[\text{M}(\text{H}_2\text{O})_6][\text{GaF}_6 \cdot \text{H}_2\text{O}]$ ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}$) has also been described and

also $\text{Ba}_3[\text{GaF}_6]_2 \cdot \text{H}_2\text{O}$, $3\text{SrF}_2 \cdot \text{GaF}_3 \cdot 3\text{H}_2\text{O}$, $\text{Ag}_3\text{GaF}_6 \cdot 10\text{H}_2\text{O}$, and $\text{Tl}_2[\text{GaF}_5 \cdot \text{H}_2\text{O}]$ (225).

The trihydrate of gallium trifluoride is formed by dissolving gallium or its nitrate or oxide in 40% hydrofluoric acid and evaporating the solution (169, 271). The triammine cannot be formed from the trifluoride directly but is prepared via the trihydrate (169). The affinity of the gallium ion for fluoride ions has been measured spectrophotometrically and has been found to be greater than that of chromium for fluoride. At 25° and an ionic strength of 0.5 the quotient $[\text{GaF}^{2+}][\text{H}^+]/([\text{Ga}^{3+}][\text{HF}])$ is 120 compared with 26 for the corresponding Cr^{3+} system (300).

B. GALLIUM(III) CHLORIDE, BROMIDE, AND IODIDE

Gallium trichloride is readily prepared in quantitative yield by the reaction of either chlorine or hydrogen chloride gas on heated gallium metal (96, 113, 154). Chlorination may also be effected by heavy metal chlorides such as AgCl , HgCl_2 , or PbCl_2 ; in these reactions, which have potential use for preparing chlorine-36 labeled gallium trichloride, an equilibrium is established and reasonable yields can only be obtained by volatilizing the chloride from the reaction zone (37). Gallium trichloride is normally purified by vacuum sublimation, though zone refining has also been suggested (218, 230).

The Raman spectrum of gallium trichloride has been interpreted in terms of bridged dimeric molecules Ga_2Cl_6 (87) and this is also consistent with the very low electrical conductivity of the melt (119). When the compound solidifies, however, the conductivity increases ninefold to a value comparable with that of a fully ionized salt near its m.p. It is concluded that the m.p. of gallium trichloride is the transition temperature between an ionic solid and a covalent liquid (119). A similar phenomenon has been observed for gallium tribromide (119) aluminium trichloride (13), and phosphorus pentachloride (256).

Some physical properties of gallium trichloride are given in Table V. The low m.p. is particularly noteworthy. The vapor density of the gas shows it to be dimeric with a degree of dissociation of 0.4% at the m.p. and 2% at the b.p. (72). The complexes of gallium trichloride are discussed in Sections VI C, D, and E.

Gallium tribromide is readily prepared by the reaction of heated gallium with a bromine-nitrogen gas mixture (72, 170) and detailed experimental procedures have been described (123). The compound can also be prepared from gallium and hydrogen bromide (26).

Like the trichloride, solid gallium tribromide has an appreciable electrical conductivity which decreases by a factor of 23 when the compound is fused (119). Other properties of the tribromide are summarized in Table

TABLE V
PHYSICAL PROPERTIES OF GALLIUM TRIHALIDES

Property	GaCl ₃		GaBr ₃		GaI ₃	
m.p.	77.75 ± 0.05°	(115)	122.3 ± 0.05°	(119)	211.5 ± 0.1°, 214°	(44, 119)
b.p.	201.2°	(72)	279°	(72)	346°	(72)
<i>p</i> (mm)	10.4 (at 78°)	(72, 187)	4.7 (at 125°)	(72)	19.2 (at 215°)	(72)
<i>d</i> ₄ ²⁵ (solid)	2.47	(170)	3.69	(170)	4.15	(170)
<i>d</i> ₄ ^t (liquid)	2.0531-0.00209(<i>t</i> - 78)	(115)	3.1076-0.00247(<i>t</i> - 125)	(121)	3.591-0.00224(<i>t</i> - 215)	(170)
<i>η</i> (cp)	1.816 (at 78°)	(115)	2.780 (at 125°)	(121)	—	—
<i>E</i> _{<i>η</i>} (kcal/mole)	3.64	(115)	3.94	(121)	—	—
<i>γ</i> (dyne/cm)	27.3 - 0.105(<i>t</i> - 78)	(115)	34.8 - 0.15(<i>t</i> - 125)	(121)	—	—
<i>κ</i> (ohm ⁻¹ cm ⁻¹)	1.86 × 10 ⁻⁶ (at 78°)	(119)	7.2 × 10 ⁻⁷ (at 125°)	(119)	1.18 × 10 ⁻⁴ (at 212°)	(119)
<i>ΔH</i> _{vap} (kcal/mole)	11.8, 12.3	(72, 187)	14.3	(72)	18.1	(72)
<i>ΔH</i> _{fus} (kcal/mole)	5.2	(187)	—	—	<i>ΔH</i> _{subl} 23.0	(259)
<i>ΔH</i> _{dimer} (kcal/mole)	21.0 (per Ga ₂ Cl ₆)	(72)	18.5 (per Ga ₂ Br ₆)	(72)	11.0 (per Ga ₂ I ₆)	(72)
<i>ΔH</i> ^o _f (kcal/mole)	125 ± 1	(168)	92.4 ± 0.3	(168)	(~61)	(168)

V from which it is seen that there are trends to increasing m.p., density, and viscosity and to decreasing volatility, heat of dimerization, and heat of formation with increasing atomic weight of the halogen.

Gallium tri-iodide is prepared by direct reaction of the elements in a sealed tube (96, 119). It is important to avoid excess of iodine since this cannot easily be removed by vacuum sublimation of the compound (44). The trends noted in Table V for the chloride and bromide continue for the iodide. In addition the degree of dissociation of the saturated vapor into monomeric GaX_3 units at the m.p. is 0.4% for the chloride, 14% for the bromide and 96% for the iodide. The corresponding figures at the respective b.p. are 2%, 30%, and 87% (73). The virtually complete dissociation of the tri-iodide into monomeric molecules is confirmed by electron diffraction on the gas which indicates the predominance of planar GaI_3 units (26) as in GaF_3 (2). Structural deductions have also been made from nuclear quadrupole measurements on crystals of the trihalides of gallium (35).

C. ADDITION COMPOUNDS OF THE TRIHALIDES

A discussion of the molecular addition compounds of the gallium trihalides must include reference to their stoichiometry, structure, and stability. All these aspects have been studied extensively during the last decade, and a fairly complete picture is now beginning to emerge. The known complexes of gallium trichloride are listed in Table VI from which it is seen that 1:1 complexes predominate though some compounds are well established in which there are two moles of ligand, and alkyl chlorides, in addition to forming 1:1 complexes, apparently form complexes in which one more of ligand is associated with two GaCl_3 units. Intercalation compounds of gallium trichloride in graphite have also been described (237) but these nonstoichiometric adducts are of a different type and will not be considered further. Fewer complexes of gallium tribromide have been described (see Table VII) and the coordination chemistry of the tri-iodide is almost completely unexplored.

The general properties of complexes with organic ligands will be mentioned first, and this will be followed by a discussion of the complexes with inorganic ligands. Aspects which relate specifically to the electrochemistry or thermochemistry of these systems will be deferred until Sections D and E.

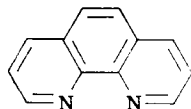
Gallium trichloride resembles aluminium chloride in forming no compound with anhydrous hydrogen chloride. However, in the presence of an aromatic hydrocarbon such as toluene a compound is formed having the structure $[\text{PhMeH}^+][\text{GaCl}_4^-]$ (28). Ethers can also be used to solvate the proton (299).

Organic nitrogen-containing ligands, as expected, form strong com-

TABLE VI
COMPLEXES OF GALLIUM TRICHLORIDE

Complex	m.p.	Reference	Complex	m.p.	Reference
$\text{GaCl}_3 \cdot \text{MePhHCl}$	—	(28)	$\text{GaCl}_3 \cdot \text{MeCl}$	48°	(27, 261)
$\text{GaCl}_3 \cdot \text{Me}_3\text{N}$	>200°	(283)	$2\text{GaCl}_3 \cdot \text{MeCl}$	—	(27)
$\text{GaCl}_3 \cdot 2\text{Me}_3\text{N}$	$d > -48^\circ$	(283)	$\text{GaCl}_3 \cdot \text{EtCl}$	—	(302)
$\text{GaCl}_3 \cdot \text{C}_6\text{H}_5\text{N}$	126°	(108, 116, 148)	$2\text{GaCl}_3 \cdot \text{EtCl}$	(-29° calc)	(302)
$\text{GaCl}_3 \cdot 2\text{C}_6\text{H}_5\text{N}$	113°	(108, 116, 148)	$\text{GaCl}_3 \cdot \text{Pr}^i\text{Cl}$	—	(302)
$\text{GaCl}_3 \cdot \text{C}_6\text{H}_{10}\text{NH}$	134°	(108, 117)	$2\text{GaCl}_3 \cdot \text{Pr}^i\text{Cl}$	—	(302)
$\text{GaCl}_3 \cdot 2\text{C}_6\text{H}_{10}\text{NH}$	112°	(108, 117)	$\text{GaCl}_3 \cdot \text{Ph}_3\text{CCl}$	—	(102)
$\text{GaCl}_3 \cdot 3\text{phen}^a$	—	(147)	$\text{GaCl}_3 \cdot \text{NH}_3^b$	124°	(81, 172)
$\text{GaCl}_3 \cdot \text{PhCN}$	125°	(280)	$\text{GaCl}_3 \cdot \text{NOCl}$	—	(214)
$\text{GaCl}_3 \cdot \text{PrCN}$	—	(280)	$\text{GaCl}_3 \cdot \text{PCl}_3$	28° incongr.	(111)
$\text{GaCl}_3 \cdot \text{PhNO}_2$	64°	(68)	$\text{GaCl}_3 \cdot \text{PCl}_5$	368-371°	(140a)
$\text{GaCl}_3 \cdot p\text{-MeC}_6\text{H}_4\text{NO}_2$	95°	(280)	$\text{GaCl}_3 \cdot \text{POCl}_3$	118.5°	(88, 104, 114)
$\text{GaCl}_3 \cdot \text{Me}_2\text{O}$	3.0°	(282, 283)	$\text{GaCl}_3 \cdot \text{AsCl}_3$	incongr.	(110)
$\text{GaCl}_3 \cdot \text{Et}_2\text{O}$	16.2°	(102, 105)	$\text{GaCl}_3 \cdot \text{AsCl}_3 \cdot \text{Cl}_2$	5°	(173)
$\text{GaCl}_3 \cdot 2\text{Et}_2\text{O}$	9°	(102, 105)	$\text{GaCl}_3 \cdot \text{LiCl}$	—	(81)
$\text{GaCl}_3 \cdot \text{Et}_2\text{OHCl}$	—	(299)	$\text{GaCl}_3 \cdot \text{KCl}$	259°	(81)
$\text{GaCl}_3 \cdot \text{Me}_2\text{CO}$	42.2°(d)	(106)	$\text{GaCl}_3 \cdot \text{CsCl}$	385°	(81)
$\text{GaCl}_3 \cdot \text{MeCOCl}$	86°(d)	(42, 106, 113)	$\text{GaCl}_3 \cdot \text{NH}_4\text{Cl}$	304°	(81)
$\text{GaCl}_3 \cdot \text{PhCOCl}$	46.5°	(113, 280)	$\text{GaCl}_3 \cdot \text{GaCl}$	172.4°	(82, 120, 303)

^a phen = *o*-phenanthroline, i.e.,

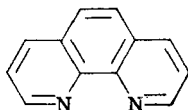


^b Also at ratios of 3, 5, 6, 7, and 14 moles of NH_3 per mole of GaCl_3 (172).

TABLE VII
 COMPLEXES OF GALLIUM TRIBROMIDE

Complex	m.p.	References	Complex	m.p.	References
$\text{GaBr}_3 \cdot \text{NMe}_3$	$>200^\circ$	(283)	$\text{GaBr}_3 \cdot \text{NH}_3^b$	—	(172)
$\text{GaBr}_3 \cdot 2\text{NMe}_3$	$d > -48^\circ$	(283)	$\text{GaBr}_3 \cdot \text{POCl}_3$	115°	(125)
$\text{GaBr}_3 \cdot \text{C}_6\text{H}_5\text{N}$	126°	(108, 122)	$\text{GaBr}_3 \cdot \text{POBr}_3$	154°	(121)
$\text{GaBr}_3 \cdot 3\text{C}_6\text{H}_5\text{N}$	$90-100^\circ$	(148)	$\text{GaBr}_3 \cdot \text{KBr}$	—	(149)
$\text{GaBr}_3 \cdot \text{C}_6\text{H}_5\text{NH}$	139°	(122)	$\text{GaBr}_3 \cdot \text{CsBr}$	—	(149)
$\text{GaBr}_3 \cdot 3\text{phen}^a$	—	(147)	$\text{GaBr}_3 \cdot \text{Et}_4\text{NBr}$	—	(149)
$\text{GaBr}_3 \cdot \text{Me}_2\text{O}$	8.5°	(283)	$\text{GaBr}_3 \cdot \text{GaBr}$	166.7°	(120, 304)

^a phen = *o*-phenanthroline, i.e.,



^b Also at ratios of 5, 7, 9, and 14 moles of NH_3 per mole of GaBr_3 (172).

plexes. The 1:1 complexes of trimethylamine with gallium trichloride and tribromide are chalky powders stable in anhydrous conditions to 200° (283). Complexes with two moles of trimethylamine also form at low temperatures but these dissociate at temperatures above -48° to give the 1:1 compound and trimethylamine (283). Conductimetric behavior of these systems in nonaqueous solvents have been investigated. Thus addition of a ligand such as dimethylamine, dimethyl ether, or ammonia to a solution of gallium trichloride or tribromide in nitrobenzene rapidly increased the conductivity of the system, and this was followed by a slow increase over a period of up to two days before an equilibrium value was attained (282). Detailed interpretation is further complicated by the fact that gallium trichloride and nitrobenzene themselves form a complex, m.p. 64° , which can dissociate ionically, the specific conductivity of the fused compound being $5.8 \times 10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$ at 75° (68).

Pyridine and piperidine also form 1:1 and 2:1 adducts with gallium trichloride, (108, 116, 117, 148), but only 1:1 complexes with the tribromide. The complexes with two moles of ligand are both relatively unstable and evolve 1 mole of ligand when warmed under vacuum. Evidence for the compounds $\text{GaBr}_3 \cdot 3\text{C}_6\text{H}_5\text{N}$ and $\text{GaI}_3 \cdot 3\text{C}_6\text{H}_5\text{N}$ in which the gallium is presumably six-coordinate has also been adduced (48). The tris(*ortho*-phenanthroline) complex appears to be of a different type and has been formulated as a six-coordinate trisbidentate complex of the Ga_3^+ cation, $[\text{Gaphen}_3^{3+}][\text{Cl}^-]_3$ (147).

Little is known about the complexes of gallium trichloride with benzonitrile and butyronitrile though the dipole moment of the former in benzene solution has been found to be 8.65 *D* (280). The corresponding value for

p-nitrotoluene-gallium trichloride is 9.16 *D* (280). A cryoscopic study of the nitrobenzene-gallium trichloride system in benzene revealed an unstable incongruently melting compound $\text{GaCl}_3 \cdot 2\text{PhNO}_2$ but the stable adduct is again the 1:1 complex (68).

Ethers readily complex with the gallium trihalides, and there seems to be less tendency than with the aluminium analogues for thermal elimination of alkyl halides. Gallium trichloride and tribromide form 1:1 complexes with dimethyl ether which melt below room temperature (283). Vapor pressure-composition curves at -82° show only the 1:1 complex but in nitrobenzene solution there is some indication of the attachment of a second mole of ligand (283). This behavior contrasts with that of diethyl ether since the phase diagram of this ligand with gallium trichloride shows two well defined complexes melting at 16.2° and 9° (105). The bis(diethyl ether) complex reverts to the 1:1 complex in vacuo at room temperature. Vapor pressure data on some of these complexes are as follows (110, 283):

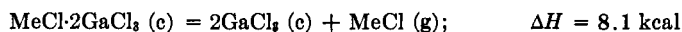
$\text{GaCl}_3 \cdot \text{Me}_2\text{O}$	$\log p_{\text{mm}} = 6.52 - 1956/T$	$\Delta H_{\text{vap}} = 8.95 \text{ kcal/mole}$	
			$p(43^\circ) = 2.1 \text{ mm}$
$\text{GaBr}_3 \cdot \text{Me}_2\text{O}$	$\log p_{\text{mm}} = 4.61 - 1205/T$	$\Delta H_{\text{vap}} = 5.51 \text{ kcal/mole}$	
			$p(26^\circ) = 3.4 \text{ mm}$
$\text{GaCl}_3 \cdot \text{Et}_2\text{O}$	$\log p_{\text{mm}} = 9.56 - 2780/T$	$\Delta H_{\text{vap}} = 12.72 \text{ kcal/mole}$	
			$p(26^\circ) = 1.8 \text{ mm}$

The relatively high vapor pressure and low heat of vaporization of the bromide complex is noteworthy.

The only reported ketone complex of a gallium trihalide is gallium trichloride-acetone which has been established by phase studies; it melts with some decomposition at 42.2° (106). This contrasts with the many known complexes of aluminium halides with ketones and reflects the limited study which has been afforded to the gallium systems rather than their instability.

Acetyl and benzoyl chlorides form 1:1 adducts with gallium trichloride and the chemical (113) electrical (113) and infrared spectroscopic (42) evidence suggests that the structure is predominantly of the form $[\text{RCO}^+]\text{[GaCl}_4^-]$. In benzene solution the dipole moment of the compound $\text{GaCl}_3 \cdot \text{PhCOCl}$ is 6.85 *D* (280). Phase studies indicate the absence of adducts at stoichiometric ratios other than the 1:1 (113).

Alkyl halides form weak complexes with gallium trichloride at low temperatures (27, 302). In addition to the 1:1 complexes, solvates of the type $\text{RCl} \cdot \text{Ga}_2\text{Cl}_6$ were also observed though their structure has not been established. The heat of dissociation of the complex $\text{EtCl} \cdot 2\text{GaCl}_3$ was found to be 0.74 kcal/mole (302) and dissociation pressure measurements on the corresponding system with methyl chloride led to the following heats (261):



The 1:1 complex is therefore moderately stable. The slow rate of halogen exchange between gallium trichloride and methyl bromide at -80° suggests that the 1:1 complexes are not ionized as $\text{R}^+\text{GaCl}_4^-$ but should be formulated as covalent adducts $\text{RX} \rightarrow \text{GaX}_3$ (27). The solutions are unstable and evolve hydrogen halide below room temperature, the rate increasing with increasing chain length of the alkyl group (302). Isomerization of Pr^nCl to Pr^iCl has also been noted. Other compounds such as $\text{GaBr}_3 \cdot \text{EtBr}$ have been postulated to explain kinetic results but have not been isolated (261). The compound $\text{Ph}_3\text{C}^+\text{GaCl}_4^-$ has been prepared as a yellow solid by mixing benzene solutions of gallium trichloride and triphenylmethyl chloride (102).

Ammonia forms a variety of compounds with the gallium halides of empirical formula $\text{GaX}_3 \cdot n\text{NH}_3$ though their structure is unknown (172). It is not clear that all are simple adducts or solvates, and solvolysis may well have occurred at the higher mole ratios. Values of n are 1, 3, 5, 6, 7, and 14 for gallium trichloride, 1, 5, 7, 9, and 14 for the tribromide, and 1, 5, 6, 7, 9, 13, and 20 for the tri-iodide. The heat of addition per mole of ammonia as determined from vapor pressure isotherms decreases with increase in n : for gallium trichloride the decrease is from 32.9 kcal/mole NH_3 for the monoammine to 12.6 kcal/mole NH_3 for the 14-ammine; for the tribromide the decrease is from 30.3 kcal to 13.0 kcal/mole NH_3 ; and for the tri-iodide from 26.9 kcal to 11.4 kcal/mole NH_3 (172). The compound $\text{GaCl}_3 \cdot \text{NH}_3$ has m.p. 124° ; d_{25}^{25} 2.189 (221); b.p. 438° ; ΔH_{vap} 17.7 kcal/mole and $\log p_{\text{mm}} (\text{liq}) = 7.333 - 3877/T$ (81).

The reaction of nitrosyl chloride with either gallium metal or gallium trichloride yields the compound $\text{GaCl}_3 \cdot \text{NOCl}$ (214). Phosphorus trichloride and arsenic trichloride (110) form incongruently melting compounds with gallium trichloride and Raman spectra have shown in the former case that the fused compound is merely a solution of the dimeric gallium trichloride in the liquid ligand (111). Consistent with this the compound has negligible conductivity and a low heat of formation (111). By contrast, a congruently melting compound in the system $\text{GaCl}_3\text{—AsCl}_3$ can be prepared by adding one mole of chlorine gas; colorless, hygroscopic crystals of the 1:1:1 compound are formed m.p. 5° and it is suggested, on the basis of conductivity measurements, that the structure is $\text{AsCl}_4^+\text{GaCl}_4^-$ (173). The high-melting complex $\text{GaCl}_3 \cdot \text{PCl}_5$ is apparently much more stable (140a).

Phase studies of the systems of phosphorus oxychloride with gallium trichloride (114) and tribromide (125) and of phosphorus oxybromide with gallium tribromide (121) have established well-defined congruently melting

1:1 compounds. Similarity in m.p. of $\text{GaCl}_3 \cdot \text{POCl}_3$ and $\text{GaBr}_3 \cdot \text{POCl}_3$, and of the adducts of the trihalides with pyridine and piperidine is noteworthy. A Raman investigation of the compound $\text{GaCl}_3 \cdot \text{POCl}_3$ established that oxygen is the donor atom (88), rather than chlorine (121).

Complexes with alkali metal halides and ammonium halides have the general formula $\text{M}^+\text{GaCl}_4^-$ and have been prepared by a variety of methods (81, 149). These include direct reaction of the univalent halide and the gallium trihalide in a sealed tube (81), reaction in a nonaqueous solvent such as arsenic tribromide (149), or reaction in aqueous hydrochloric acid solution (81), though in this last procedure the product was never very pure. That the tetrachlorogallates can be regarded as typical donor-acceptor adducts is seen by the ease with which the chloride ion in the complex is displaced by a strong ligand. Thus gallium trichloride is extracted by ether from lithium tetrachlorogallate and the potassium salt reacts with gaseous ammonia at elevated temperatures to give volatile amines such as $\text{GaCl}_3 \cdot 3\text{NH}_3$ (81).

The particular case where gallium monohalide is the ligand is of interest since this is effectively the structure of gallium dihalides $\text{Ga}^+\text{GaCl}_4^-$ and $\text{Ga}^+\text{GaBr}_4^-$. (See Section II,C.)

D. ELECTRICAL CONDUCTIVITY AND RELATED PROPERTIES

The quantitative treatment of electrochemical data requires a knowledge of the viscosity (η cp) and density (d gm cm⁻³) of a fused system in addition to its specific conductivity (κ ohm⁻¹ cm⁻¹). The underlying theory has been developed (103) and indicates that the degree of ionic dissociation ($\alpha\%$) of a molten complex is given approximately by the expression

$$\alpha \simeq M\kappa\eta/d = \mu\eta$$

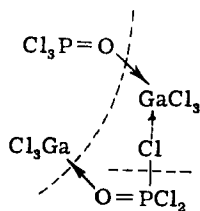
where M is the molecular weight and μ the molar conductivity ($M\kappa/d$). It follows that complexes which do not dissociate into kinetically free ions will have zero conductivity and those which are completely dissociated into ions will have values of conductivity, viscosity, and density which give a value of approximately 100. Some information on these properties for the complexes of gallium trihalides is assembled in Table VIII. Choice of a comparison temperature is difficult and various suggestions have been made in the literature but for the data in Table VIII the melting point of each complex has been arbitrarily chosen as the comparison temperature. (The surface tension γ dyne cm⁻¹ is also included in Table VIII for convenience.)

It is clear from Table VIII that the trihalides themselves have a very low electrical conductivity and this is consistent with their structure as covalent dimeric molecules in the fused state; the degree of ionic dissociation based on these measurements is only 4–6 ppm (115, 119). By contrast

the dihalides are completely dissociated ionic complexes and the value of $\mu\eta$ approximates to 100%. The fact that values of $\mu\eta$ somewhat above 100 are obtained can be understood in terms of a detailed analysis of the conduction mechanism for these salts, in which the cation is much smaller than the anion (120). Complexes of the gallium trihalides fall between these two extremes, typical values ranging from $\frac{1}{2}$ –7%. In this, the complexes resemble those of boron trifluoride and other donor-acceptor systems (103).

The activation energies for conduction and viscous flow fall in the range 3–12 kcal/mole, which is typical of ionizing systems and for each compound the activation energy for conduction is approximately the same as for viscous flow, the mean value for E_η/E_μ being 1.08 (118). This is consistent with the assumption made in developing the theory that ionic mobility in these systems is viscosity-controlled.

Little positive information is available as to the precise nature of the ionic species in these melts, except for the dihalides themselves, which have been shown to ionize as $\text{Ga}^+\text{GaCl}_4^-$ and $\text{Ga}^+\text{GaBr}_4^-$ (see Section II,C). The Raman spectrum of fused $\text{GaCl}_3 \cdot \text{POCl}_3$ has been interpreted in terms of the covalent adduct $\text{Cl}_3\text{PO} \rightarrow \text{GaCl}_3$ and this is undoubtedly the predominant species in the melt (88). However, the conductivity data in Table VIII suggest that in addition there is about $\frac{1}{2}\%$ of free ions and it is unlikely that the Raman lines from these species will be detectable in the presence of 99.5% of the undissociated complex, particularly as the positions of several of the lines from both structures will be similar. It is possible that a small equilibrium concentration of ions such as POCl_2^+ and GaCl_4^- could be formed in this system by a ligand-switch rearrangement of the type illustrated in the figure, though there is no direct evidence for this:



The absence of gaseous products when the molten 1:1 and 2:1 adducts of gallium trichloride with pyridine and piperidine are electrolyzed eliminates the possibility that the complexes ionize as $\text{H}^+[\text{C}_5\text{H}_4\text{N} \rightarrow \text{GaCl}_3]^-$, $[\text{C}_5\text{H}_5\text{NH}]^+[\text{C}_5\text{HN} \rightarrow \text{GaCl}_3]^-$, etc. Such a formulation would also imply that the adduct with two moles of ligand would be more stable than the 1:1 complex whereas the reverse is true. This contrasts with the adducts of boron trifluoride where the 2:1 complexes are always more stable than the 1:1 and suggests that the gallium complexes have a different structure. An

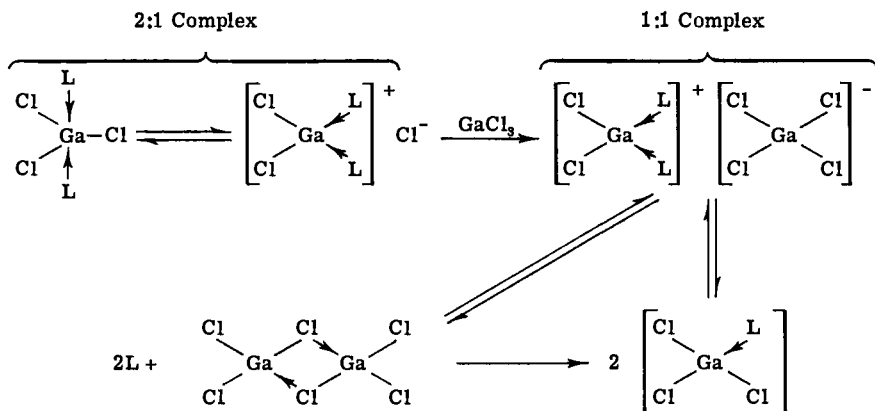
TABLE VIII
PHYSICAL PROPERTIES OF GALLIUM HALIDES AND THEIR COMPLEXES

Complex	m.p.	γ (dyne-cm ⁻¹)	$10^3 \cdot \kappa$ (ohm ⁻¹ cm ⁻¹)	η (cp)	d (gm-cm ⁻³)	$\mu\eta$ ($\simeq \alpha\%$)	References
Ga ₂ Cl ₆ ^a	77.75°	27.3	1.86×10^{-3}	1.823	2.0536	5.8×10^{-4}	(115)
Ga ₂ Br ₆ ^a	122.5°	35.1	0.76×10^{-3}	2.867	3.1137	4.0×10^{-4}	(121)
Ga[GaCl ₄]	172.4°	56.2	264.2	3.355	2.4173	103.3	(120)
Ga[GaBr ₄]	166.7°	—	149.2	6.918	3.4712	136.3	(120)
GaCl ₃ ·POCl ₃	118.5°	32.1	1.261	1.947	1.8304	0.442	(114)
GaCl ₃ ·py	126°	38.1	2.725	2.408	1.5552	1.077	(116)
GaCl ₃ ·2py	113°	50	9.67	2.911	1.368	6.88	(116)
GaCl ₃ ·pip	134°	34.1	1.97	4.713	1.4856	1.63	(117)
GaCl ₃ ·2pip	112°	27.3	0.620	7.571	1.3253	1.23	(117)
GaCl ₃ ·Et ₂ O	16.2°	48.5	0.810	5.77	1.8990	0.604	(105, 110)
GaBr ₃ ·POBr ₃	154°	—	1.0 ^b	4.921 ^b	2.8839	1.0	(121)
GaBr ₃ ·py	126°	42.7	1.242	7.090	2.2291	1.531	(122)
GaBr ₃ ·pip	139°	43.8	1.503	6.844	2.1052	1.931	(122)

^aThe conductivities for these compounds are taken from ref. 119.

^b At 161.2°.

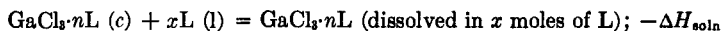
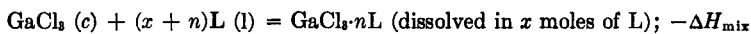
obvious possibility is that the 2:1 complexes in this case are 5-coordinate and that there is an ionization equilibrium as follows (118):



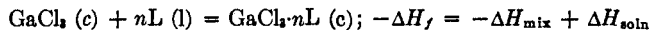
The 2:1 complex ionizes by rearrangement of the gallium from trigonal bipyramidal to tetrahedral configuration with elimination of a chloride ion and this ion can donate to a further GaCl_3 unit to give the ionic 1:1 complex. This interprets the ionization of the 2:1 complex and the greater stability of the 1:1 compound. The direct formation of the 1:1 complex from Ga_2Cl_6 and 2 moles of ligand would involve a replacement of bridged chlorine donors by either one or two moles of ligand to give the ionic and covalent form of the 1:1 complex respectively. On this basis the ionization equilibrium of the 1:1 complex itself (shown as the vertical equilibrium on the right hand side of the diagram) involves a ligand replacement reaction of precisely the same kind as that proposed for the complex $\text{GaCl}_3 \cdot \text{POCl}_3$.

E. THERMOCHEMISTRY OF GALLIUM TRIHALIDE ADDUCTS

The energy involved in donor-acceptor reactions and the heat of formation of crystalline molecular addition compounds can be measured directly in those cases where one of the compounds is a liquid and the other is a solid or a liquid. The method has so far only been applied systematically to complexes of gallium trichloride (102) but could be extended with advantage since data obtained in this way, in conjunction with heats of sublimation, lead directly to the gas-phase heat of interaction of donors and acceptors. The reaction sequence uses excess of the ligand as the calorimetric liquid:



hence,



It is clearly immaterial whether the solution of the complex is ionized, dissociated, or solvated, provided only that in both reactions the same final state is achieved.

The results are summarized in Table IX and may be illustrated by the case of phosphorus oxychloride (104). When crystalline gallium trichloride reacts with excess of liquid phosphorus oxychloride the heat of mixing, $-\Delta H_{\text{mix}}$, is 11.01 kcal per mole of GaCl_3 . Then the crystalline 1:1 complex $\text{GaCl}_3 \cdot \text{POCl}_3$ is dissolved in an excess of the same liquid, the heat of solution, $-\Delta H_{\text{soln}}$, is 0.85 kcal/mole. By difference, the heat of formation of the crystalline complex from crystalline acceptor and liquid ligand, $-\Delta H_f$, is 10.17 kcal/mole. By measuring the heat of sublimation of the complex (15 kcal/mole) and using the known heat of vaporization of phosphorus oxychloride (8.4 kcal/mole), and heats of sublimation and dimerization of gallium trichloride (8.5, 10.5 kcal/mole) the heat of the gas-phase reaction, $-\Delta H_f(\text{g})$, was found to be:



Since phosphorus oxychloride is an oxygen-atom donor in this complex (88) this implies that the $\text{O} \rightarrow \text{Ga}$ bond in the complex is some 12 kcal stronger than the $\text{Cl} \rightarrow \text{Ga}$ bond in the bridged dimer Ga_2Cl_6 (104).

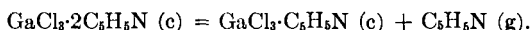
The ligands PCl_3 and AsCl_3 form incongruently melting complexes with gallium trichloride and, consistent with this, both complexes have very low heats of formation, 3.4 and 1.4 kcal/mole respectively (109, 110, 111). Gallium trichloride-acetyl chloride (106) also has a low heat of formation (4.1 kcal/mole) and the difference between this value and that for the corresponding acetone complex (15.3 kcal/mole) reflects the fact that the negative inductive effect of the chlorine atom has reduced the electron availability at the carbonyl oxygen to a point where the oxygen is no longer the donor atom, the structure of the complex being (42) $\text{MeCO}^+[\text{Cl} \rightarrow \text{GaCl}_3]^-$. In this case, the over-all heat of reaction not only involves the energy involved in forming the $\text{Cl} \rightarrow \text{Ga}$ bond and the reorganization energy of the gallium atom, but also the energy required to cleave acetyl chloride into MeCO^+ and Cl^- ions and the coulomb attraction of the resultant ionic species MeCO^+ and GaCl_4^- .

Table IX also indicates that nitrogen donors (pyridine, piperidine) evolve 2-3 times as much heat as oxygen donors (phosphorus oxychloride, acetone, ether) and this difference persists, though slightly less marked, for the gas-phase reactions. Thus the heats of formation of the gaseous complexes from gaseous ligand and monomeric gaseous GaCl_3 are: $\text{GaCl}_3 \cdot \text{POCl}_3 (\text{g}) 22.6 \pm 1$, $\text{GaCl}_3 \cdot \text{Et}_2\text{O} (\text{g}) 22.3 \pm 1$, $\text{GaCl}_3 \cdot \text{C}_5\text{H}_5\text{N} (\text{g})$

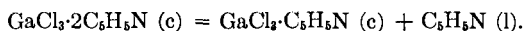
TABLE IX
HEAT OF FORMATION OF GALLIUM HALIDE COMPLEXES

Complex (c or l)	$-\Delta H_f(\text{kcal})$	Reference	Complex (c or l)	$-\Delta H_f(\text{kcal})$	Reference
$\text{GaCl}_3 \cdot \text{POCl}_3$ (c)	10.17 ± 0.01	(104)	$\text{GaCl}_3 \cdot \text{Me}_2\text{CO}$ (c)	15.3 ± 0.9	(106)
$\text{GaCl}_3 \cdot \text{PCl}_3$ (c + l)	3.40 ± 0.03	(111)	$\text{GaCl}_3 \cdot \text{MeCOCl}$ (c)	4.1 ± 0.1	(106)
$\text{GaCl}_3 \cdot \text{C}_5\text{H}_5\text{N}$ (c)	29.8 ± 0.1	(108)	$\text{GaCl}_3 \cdot \text{Et}_2\text{O}$ (l)	9.34 ± 0.08	(109)
$\text{GaCl}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$ (c)	41.5 ± 0.1	(108)	$\text{GaCl}_3 \cdot 2\text{Et}_2\text{O}$ (l)	15.48 ± 0.09	(109)
$\text{GaCl}_3 \cdot \text{C}_5\text{H}_{10}\text{NH}$ (c)	33.7 ± 2.7	(108)	$\text{GaCl}_3 \cdot \text{AsCl}_3$ (c + l)	1.4 ± 0.2	(110)
$\text{GaCl}_3 \cdot 2\text{C}_5\text{H}_{10}\text{NH}$ (c)	52.1 ± 2.0	(108)	$\text{GaBr}_3 \cdot \text{C}_5\text{H}_5\text{N}$ (c)	34.5 ± 0.4	(108)

35.2 ± 2 , and $\text{GaCl}_3 \cdot \text{C}_5\text{H}_{10}\text{NH}$ 38.1 ± 2 kcal/mole. As expected, piperidine is a stronger donor than pyridine in both the condensed and gas-phase reactions, and those cases where both 1:1 and 2:1 complexes are formed (pyridine, piperidine, ether) the second mole of ligand evolves much less heat on addition than the first. Equilibrium vapor-pressure measurements afford a useful check on the calorimetric data here (108) for the solid 2:1 pyridine complex dissociates on heating to the solid 1:1 complex and pyridine vapor:



From the dissociation pressure equation $\log p_{\text{mm}} = 15.973 - 4670/T$, the heat of dissociation is -21.3 kcal/mole, and this, coupled with the heat of vaporization of pyridine (9.7 kcal/mole) leads to a value of $-\Delta H = -11.6$ kcal/mole for the dissociation reaction



This compares with the calorimetric value $-\Delta H = 11.7$ kcal/mole for the reverse (formation) reaction deduced from Table IX.

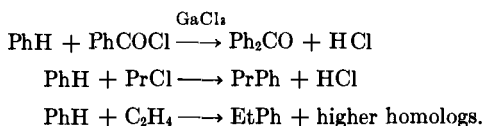
The final entry in Table IX refers to the complex $\text{GaBr}_3 \cdot \text{C}_5\text{H}_5\text{N}$. The heat of formation of this crystalline complex from crystalline gallium bromide and liquid pyridine is 34.5 kcal/mole which is significantly greater than the value of 29.8 for the corresponding chloride complex. This difference appears to persist for the gas-phase reaction ($\sim 38.3 \pm 2$ kcal/mole) and affords an example of the sequence $\text{I} > \text{Br} > \text{Cl} > \text{F}$ for the heats of formation of boron, aluminium, and gallium halide complexes (107, 108). This order is determined mainly by the extent of π bonding in the monomeric trihalides which in turn influences the energy of reorganization of the electron acceptor from planar to tetrahedral. (Key references to the rather extensive literature on this point, particularly for boron halide complexes will be found in refs. 107, 108, 184.) The reorganization energies for boron and aluminium halides have been calculated by a simple molecular-orbital theory (48), and, on the reasonable assumption that the trends persist with the gallium halides, the reorganization energy of GaCl_3 can be taken to be 33 kcal/mole and that of GaBr_3 30 kcal/mole (118). This leads to the following values for the bond dissociation energies:

Complex	$D(\text{N} \rightarrow \text{GaX}_3)$ (kcal/mole)	Complex	$D(\text{O} \rightarrow \text{GaCl}_3)$ (kcal/mole)
$\text{GaCl}_3 \cdot \text{C}_5\text{H}_5\text{N}$	68.2	$\text{GaCl}_3 \cdot \text{POCl}_3$	55.6
$\text{GaBr}_3 \cdot \text{C}_5\text{H}_5\text{N}$	68.3	$\text{GaCl}_3 \cdot \text{Et}_2\text{O}$	55.3
$\text{GaCl}_3 \cdot \text{C}_5\text{H}_{10}\text{NH}$	71.1		
mean	69.2	mean	55.5

Since the $\text{Cl} \rightarrow \text{Ga}$ bond is some 12 kcal weaker than the $\text{O} \rightarrow \text{Ga}$ bond (see above) it appears that the bond dissociation energy $D(\text{Cl} \rightarrow \text{GaCl}_3)$ is approximately 43 kcal/mole.

F. CATALYTIC PROPERTIES

The early work of Ulich (279, 281) established that gallium trichloride could be used instead of aluminium chloride in the Friedel-Crafts synthesis of ketones and hydrocarbons. Three reactions were studied:



The gallium catalyst, which formed a homogeneous reaction phase, was found to promote more rapid reaction and to be less easily deactivated than the aluminium catalyst.

In a more detailed study of the metal chloride catalyzed acetylation of aromatic hydrocarbons with benzoyl chloride, the relative rates at 25° were found to be SbCl_5 1300, FeCl_3 570, GaCl_3 500, AlCl_3 1, SnCl_4 0.0029, BCl_3 0.00062 (152). The similarity in isomer distribution from the benzoylation of toluene argues for a common reaction intermediate, presumably PhCO^+ . However, a carbonium ion mechanism is less likely for the alkylation of aromatic hydrocarbons with alkyl halides except in the case of readily ionizable tertiary halides (29).

A detailed kinetic study of the alkylation of benzene and toluene with ethyl bromide in the presence of gallium tribromide has shown that the reaction is zero order with respect both to the aromatic hydrocarbon (used as solvent) and to the ethyl bromide, and was second order with respect to gallium tribromide (261). Toluene reacted some $2\frac{1}{2}$ times as rapidly as benzene, suggesting that an aromatic complex is involved in the rate-determining step. It is considered that, in this reaction, gallium tribromide is a weaker catalyst than aluminium tribromide and that the second mole of trihalide is required to facilitate the transfer of the alkyl group from the bromide to the aromatic nucleus. The relative rates of reaction when ethyl bromide is replaced by a series of alkyl bromides was also studied (262) as were the *o*-, *m*-, and *p*-isomer distributions and partial rate factors (30).

Solid gallium trihalides have been used to catalyze the gas-phase addition of hydrogen chloride to olefins; e.g., the reaction with ethylene at -20°, which is particularly well adapted to the manufacture of ethyl chloride (213).

A continuous process for the dimerization of propylene at 200 atm and 200–350° has been developed using, among other catalysts, trimethyl-

gallium or triphenylgallium (310). Similarly, ethylene is polymerized under a variety of temperature and pressure conditions in the presence of trimethyl or triethyl gallium (49, 309). In the analogous polymerization of vinyl ethers in inert solvents at room temperature, gallium trichloride is claimed to be a superior catalyst (126).

Gallium trichloride has also been found more effective than other metal halides in the Lewis acid catalyzed decomposition of benzazide to phenylisocyanate, and a kinetic investigation of the reaction indicates the initial rapid formation of the 1:1 complex which then decomposed slowly with first-order kinetics (41):



The strength of catalytic activity decreased in the sequence



Another unusual catalytic effect which gallium trichloride has in common with many other electron-pair acceptors is the ability to enhance greatly the reducing power of sodium borohydride towards a variety of organic compounds (31), e.g., ethyl benzoate was rapidly reduced to benzyl alcohol in 90% yield at 75°.

VII. Other Salts and Complexes of Gallium(III)

The compounds discussed in the preceding sections have almost all been prepared and investigated either in nonaqueous solvents or in the absence of any solvent at all. Aqueous systems have also been extensively studied and the results are briefly reviewed in the present section.

Progressive dehydration of the salt $\text{Ga}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ leads to three new hydrates, viz., 15, 14, and $7\text{H}_2\text{O}$, in contrast to aluminium sulfate which forms hydrates containing 18, 16, 10, and 6 moles of water (278). A large variety of other hydrated salts such as the phosphate, chlorate, bromate, iodate, and double sulfates have been described (207, 208, 269) as well as the hydrated perchlorate (76, 193). Earlier work on such compounds was reviewed in 1942 (64).

A series of dithiocarbamates, $(\text{R}_2\text{MCS}_2)_3\text{Ga}$, and xanthates, $(\text{ROCS}_2)_3\text{Ga}$, have been prepared (53). The crystal structure of the guanidinium salt $[\text{C}(\text{NH}_2)_3]\text{Ga}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (85) and the corresponding selenate (216) have been reported in connection with a study of ferroelectric domains.

The analytical chemistry of gallium ferrocyanide, $\text{Ga}_4[\text{Fe}(\text{CN})_6]_3$ has been studied (11, 66, 272, 273) and the complex tetracyanonickelate, $\text{Ga}_2[\text{Ni}(\text{CN})_4]_3 \cdot 6\text{H}_2\text{O}$, has been prepared as a bluish-grey precipitate from gallium sulfate and potassium tetracyanonickelate (162).

A variety of organic chelating reagents has been investigated mainly

from the point of view of analytical chemistry. These include substituted quinolines (182, 183, 199, 200, 204, 219, 226), ethylenediaminetetra-acetic acid (242), 1,2-diaminocyclohexanetetra-acetic acid (250), acetylacetone (36, 140, 143, 179), pyrocatechol (12, 240), sodium 3,4-dihydroxyazobenzene-4'-sulfonate (180), trihydroxyglutaric acid (67) and tartaric acid (229, 245, 277). In addition, several tris(malonato) complexes have been prepared, e.g., $M_3Ga[CH_2(CO_2)_2]_3 \cdot 3H_2O$ ($M = Na, K$) (60, 61), and $Tl_3Ga[CH_2(CO_2)_2]_3 \cdot H_2O$ (265).

It has been shown, further, that gallium has a much stronger tendency to complex with ligands such as tartrate (245) and oxalate (181, 183, 244) than has aluminium, and the species $[Ga(C_2O_4)]^+$, $[Ga(C_2O_4)_2]^-$, and $[Ga(C_2O_4)_3]^{3-}$ have been identified by emf, conductimetric, polarographic, and optical density measurements. Despite this, the tris-bidentate complexes are still too labile in aqueous solution to be resolvable into optically active diastereoisomers and an earlier claim (206) to have resolved the trisoxalatogallium(III) anion, $[Ga(C_2O_4)_3]^{3-}$, has been refuted (62, 201). Gallium acetylacetonate, m.p. 195–196° has also defied attempts to resolve it (202).

Preliminary experiments on the potential use of liquid gallium as an electrode in polarography have not been encouraging (91, 100, 243).

The use of radioactive Ga-72 in the diagnosis and treatment of bone cancer has been investigated using organic salts such as gallium citrate and lactate (56–58). Gallium metal itself is only mildly toxic (197).

VIII. Gallium Hydrides and Organogallium Compounds

It is doubtful whether uncoordinated gallium hydride has ever been prepared as a stable compound and there is no evidence for its existence as digallane Ga_2H_6 . Earlier claims (290–292) to have prepared digallane by the disproportionation of dimethylgallium hydride in the presence of trimethylamine or triethylamine have been disputed (254) and a careful series of experiments designed to liberate free gallium hydride, always resulted in decomposition to gallium and hydrogen (254). Likewise the preparation of an ill-defined salt-like hydride by the action of atomic hydrogen on gallium metal (220) appears questionable (255). Apparently a polymeric form of gallium hydride $(GaH_3)_x$ can be prepared by the reaction of gallium trichloride with lithium gallium hydride in ether (297) but the compound has not been fully characterized.

By contrast, complexes of gallane (GaH_3) are well characterized and some are moderately stable. Lithium gallium hydride was first prepared in 1947 during the pioneering researches on lithium aluminium hydride (70); gallium chloride [or bromide (142, 295)] was reacted with an excess of lithium hydride in ether below room temperature and, after filtration to

remove lithium chloride, the ether was removed by evaporation. The compound decomposes slowly at room temperature and more rapidly at 150° to give lithium hydride, gallium, and hydrogen (70, 294). It is a milder reducing agent than either lithium borohydride, or lithium aluminium hydride (247, 294). Silver gallium hydride (289) and thallium gallium hydride (296) have also been prepared at very low temperatures but decompose at -75° and -90° respectively.

The most stable adduct of gallane so far prepared is trimethylamine-gallane, $\text{Me}_3\text{N}\cdot\text{GaH}_3$, which is obtained by reaction of trimethylamine hydrochloride and lithium gallium hydride, (112, 252). It melts at 70.5° and its infrared (112) and Raman (252) spectra have been analyzed in some detail by comparison with the spectra of trimethylamine-trideutero-gallane, m.p. 68.1° (112). Adducts with diethyl ether (295), dimethyl sulfide (254), and several tertiary amines (112) have also been prepared. The etherate reacts with hydrazoic acid below room temperature to give crystals of gallium triazide $\text{Ga}(\text{N}_3)_3$ (293).

Trimethylgallium (178), triethylgallium (54), and triphenylgallium (92), are known and their chemistry has recently been reviewed (40). Trimethylgallium has been prepared by the reaction of dimethyl-zinc vapor on gallium trichloride (178) but is most conveniently synthesized by reacting dimethylmercury with gallium metal (38, 292). It melts at -15.7° boils at 55.8°, has a density at 15° of 1.151 (194), and is monomeric in the gas phase (178). Vapor pressure measurements lead to the following results (194):

$$\log_{10} p_{\text{mm}} (\text{solid}) = 10.5664 - 2362.2/T$$

$$\log_{10} p_{\text{mm}} (\text{liquid}) = 32.9398 - 2833.4/T - 8.5201 \log T$$

$$\Delta H_{\text{subl}} 10.81 \text{ kcal}, \Delta H_{\text{vap}} (\text{m.p.}) 8.60 \text{ kcal}, \Delta H_{\text{fus}} 2.21 \text{ kcal},$$

$$\Delta H_{\text{vap}} (\text{b.p.}) 7.39 \text{ kcal}, \text{ Trouton const. } 22.5 \text{ e.u.}$$

The heat of formation of liquid trimethylgallium was found to be 17.6 ± 3 kcal/mole by bomb calorimetry (194) and 14.5 ± 8 kcal/mole by reaction calorimetry with iodine in benzene (80); the former figure is probably the more accurate and leads to a mean bond dissociation energy, $D(\text{Ga}-\text{C})$, of 57.7 kcal. This is somewhat smaller than the value of 62.9 kcal for $D(\text{Al}-\text{C})$ found for trimethylaluminium and this parallels the trend found for bond dissociation energies of 4-coordinate complexes of gallium (Section VI,E) and aluminium (118).

Less is known about the physical properties of triethyl- and triphenylgallium though the former was the first organogallium compound to be prepared (54). Triethylgallium is a somewhat viscous liquid m.p. -82.3°, d_4^{30} 1.058 (54), and $\log_{10} p_{\text{mm}} = 8.224 - 2222/T$; the extrapolated b.p.

is 142.8° , ΔH_{vap} 10.2 kcal/mole and Trouton constant 24.5 (186). The rather high Trouton constant may be related to the fact that, though the vapor is monomeric (186), the liquid is somewhat viscous and the compound is associated approximately into dimers in benzene and cyclohexane solution (268). Triphenylgallium, m.p. 166° , like the trialkyl compounds, is readily prepared from the corresponding organomercury compound (92). Its solubility in a variety of solvents has been studied at 20° and varies from 4.15 gm/liter in heptane to 289 gm/liter in chloroform (266). The compound is monomeric in benzene, cyclohexane, and dioxane (268).

Trimethyl- and triethyl-gallium are moderately good electron-pair acceptors and early work established the existence of such compounds as $\text{Me}_3\text{Ga}\cdot\text{NH}_3$ (178), $\text{Me}_3\text{Ga}\cdot\text{NEt}_3$ (290), $\text{Me}_3\text{Ga}\cdot\text{Et}_2\text{O}$ (178), $\text{Et}_3\text{Ga}\cdot\text{NH}_3$ (54), and $\text{Et}_3\text{Ga}\cdot\text{Et}_2\text{O}$ (54). Knowledge of such adducts has been greatly extended by the elegant work of Coates (38, 39) who pointed out that, because it is monomeric, trimethylgallium is a convenient acceptor with which to assess the relative donor properties of the elements of groups V and VI. Trimethylgallium is a stronger acceptor than trimethylboron but is weaker than trimethylaluminium. Despite this, weak donors which will coordinate to trimethylgallium sometimes do not form adducts with trimethylaluminium because of the 20 kcal energy required to break the dimer, Me_2Al_2 , into monomeric Me_3Al . The physical properties of the gallium adducts are summarized in Table X. The compounds are all volatile liquids or low melting solids and the high values of the Trouton constants can be ascribed to the tendency for dipole association in the liquid phase and to the extensive dissociation which frequently occurs in the gas phase. The gas-phase heat of dissociation of the complexes (in kcal/mole) decreases in the sequence (40) $\text{NMe}_3, 21 > \text{PMe}_3, 18 > \text{AsMe}_3, 10 > \text{SbMe}_3$ very small. The sequence is less regular for group VI ligands, being 9.5 kcal/mole for the dimethyl ether adduct, 10 kcal/mole for the selenium compound and about 8 kcal/mole for the sulfur and tellurium analogs; the free energies of dissociation follow the sequence $\text{O} > \text{Se} > \text{S} = \text{Te}$ (38).

The dipole moments of triethyl- and triphenyl-gallium have been studied in various solvents. There was zero dipole moment in heptane; the values in benzene were 0.67 and 0.4 D , and in dioxane 2.11 and 2.14 D (267). When compared with dipole moments of other organometallic group III acceptors the relative order was $\text{B} < \text{Al} > \text{Ga} > \text{In} > \text{Tl}$ (267), which agrees with conclusions drawn from dissociation-pressure measurements (38).

The thermal decomposition of trimethylgallium-ammonia leads to the formation of the dimeric compound $(\text{Me}_2\text{Ga}\cdot\text{NH}_2)_2$ and similar compounds can be formed from the coordination compounds with methylamine and dimethylamine (38). Reaction of trimethylgallium with methanol,

TABLE X
COMPLEXES OF TRIMETHYLGALLIUM

Compound	m.p.	b.p. (calc)	$\log_{10} p_{\text{mm}}$	ΔH_{vap} (kcal/mole)	Trouton constant	Reference
$\text{Me}_3\text{Ga}\cdot\text{NH}_3$	32°	179°	7.190 - 1947/ T	8.9	19.7	(38)
$\text{Me}_3\text{Ga}\cdot\text{NH}_2\text{Me}$	38°	169°	9.119 - 2760/ T	12.6	28.6	(38)
$\text{Me}_3\text{Ga}\cdot\text{NHMe}_2$	33.6°	170°	8.596 - 2532/ T	11.6	26.2	(38)
$\text{Me}_3\text{Ga}\cdot\text{NMe}_3$	96.2°	164°	7.974 - 2226/ T	10.19	23.3	(292)
$\text{Me}_3\text{Ga}\cdot\text{PMe}_3$	56.7°	173°	8.851 - 2662/ T	12.2	27.3	(38)
$\text{Me}_3\text{Ga}\cdot\text{AsMe}_3$	23.7°	121°	9.114 - 2458/ T	11.2	28.5	(38)
$\text{Me}_3\text{Ga}\cdot\text{SbMe}_3$	2.2°	95°	8.591 - 2105/ T	9.6	26.1	(38)
$\text{Me}_3\text{Ga}\cdot\text{OMe}_2$	—	100°	8.453 - 2078/ T	9.5	25.5	(38)
$\text{Me}_3\text{Ga}\cdot\text{SMe}_2$	—	116°	9.516 - 2580/ T	11.8	30.4	(38)
$\text{Me}_3\text{Ga}\cdot\text{SeMe}_2$	-42°	111°	10.118 - 2783/ T	12.7	33.0	(38)
$\text{Me}_3\text{Ga}\cdot\text{TeMe}_2$	-32°	122°	9.172 - 2488/ T	11.4	28.8	(38)
$\text{Me}_3\text{Ga}\cdot\text{NCMe}$	25.2°	120°	8.840 - 2342/ T	10.7	27.3	(39)
$\text{Me}_3\text{Ga}\cdot\text{OCMe}_2$	—	104°	9.896 - 2648/ T	12.1	32.1	(39)
$\text{Me}_3\text{Ga}\cdot\text{NEt}_3$	96°	167°	9.493 - 2909/ T	13.3	30.2	(292)

methanethiol, methaneselenol, and acetic acid also results in elimination of methane to give dimeric products such as $(\text{Me}_2\text{Ga}\cdot\text{SMe})_2$ (39). These, and similar compounds, presumably contain 4-membered heterocyclic rings of alternate gallium and donor atoms and their properties have been studied in some detail. For example, in some cases the ring can be split reversibly by a ligand such as trimethylamine to give adducts of the type $\text{MeSGaMe}_2\cdot\text{NMe}_3$ and a wide range of analogous compounds has been prepared by this method and their properties intercompared (38, 39).

Other reactions of gallium trialkyls include their conversion by halogens or hydrogen halides to gallium trihalides and mixed alkylgallium halides (40, 292). Many of these form adducts with group V ligands e.g., $\text{Me}_2\text{GaCl}\cdot\text{NH}_3$ m.p. 54° (178), $\text{Me}_2\text{GaCl}\cdot\text{NMe}_3$ m.p. 112.5° , $\text{Me}_2\text{GaCl}\cdot\text{PMe}_3$ m.p. 93.5° , $\text{Me}_2\text{GaBr}\cdot\text{NMe}_3$ m.p. 136° , and $\text{Me}_2\text{GaI}\cdot\text{NMe}_3$ m.p. 128° (40). Dimethylgallium chloride also forms a diammoniate, m.p. 112° (178), which has recently been shown to have the structure $[\text{Me}_2\text{Ga}\cdot 2\text{NH}_3]^+\text{Cl}^-$ (253).

Lithium aluminium hydride reacts with trimethylgallium over a period of 24 hr at room temperature to give dimethylalane, Me_2AlH , and another product presumed to be $\text{Li}^+[\text{GaH}_3\text{Me}]^-$ (286), which could be considered as a derivative of gallane. Diborane, on the other hand, reacts rapidly with trimethylgallium at room temperature to give methyldiborane, MeB_2H_5 , together with gallium metal and hydrogen (246). This is a further illustration of the instability of uncoordinated gallium hydride discussed earlier in this section. When the preceding reaction is carried out at -45° a compound analyzing as dimethylgallium borohydride is formed as a liquid m.p. 1.5° , b.p. (extrap.) 92° ; this is stable at -80° but decomposes slowly at room temperature (246). The gas-phase molecular weight corresponds to the monomer and the compound clearly merits further examination since, if it has the bridged structure $\text{Me}_2\text{GaH}_2\text{BH}_2$ it would be the first authenticated example of this structural type.

Trimethyl- and triethyl-gallium are both violently hydrolyzed by water to give compounds R_2GaOH (54, 178). The reaction can be controlled by hydrolyzing the etherate in the presence of a limited amount of water (166). In this way, the apparently trimeric compound $(\text{Me}_2\text{GaOH})_3$ was obtained m.p. 87° , d 1.75, dipole moment 1.8 D , molecular weight 331 (trimer requires 350) (166). The detailed X-ray analysis of this compound, however, showed that, at least in the crystalline state, it was a cyclic tetramer $(\text{Me}_2\text{GaOH})_4$ (260). In this form the compound has a center of inversion and should therefore have zero dipole moment and it is possible that the compound is trimeric in solution and tetrameric in the solid. It will be recalled that compounds of the type $(\text{Me}_2\text{GaOMe})_2$ were cyclic dimers (see top of this page).

In summary it can be said that organogallium compounds are highly

reactive; they are violently hydrolyzed by water, and the lower trialkyls are spontaneously inflammable. However, they are less reactive than their aluminium analogs and the acceptor power of gallium alkyls towards a variety of ligands is less than that of aluminium. In this, the organogallium compounds parallel the trends in acceptor properties discussed in Section VI,E for the trihalides of gallium and aluminium (118).

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CHEMICAL EFFECTS OF NUCLEAR ACTIVATION IN GASES AND LIQUIDS

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I. Introduction

The first experiment on the chemical effects of nuclear activation was done by Szilard and Chalmers (295), who studied the behavior of radioactive iodine atoms formed in neutron irradiated liquid ethyl iodide. The observation that some of the radioactive iodine could be extracted into water was interpreted by assuming that part of the binding energy of the neutron in the iodine nucleus appeared as recoil from gamma quantum emission, leading to rupture of the bonds between the iodine atom and the rest of the molecule (4).

Subsequent studies of the chemical behavior of atoms activated by nuclear processes have provided information as to the secondary reactions of atoms which have freed themselves from their parent molecules, as well as to the primary processes of bond rupture.

As the subject developed several types of nuclear transformation in addition to the (n,γ) reaction were used to induce nuclear activation. In earlier work the subject was viewed primarily as an investigation of the chemical consequences of nuclear events. More recently it has been realized that nuclear activation is a useful and often unique tool for examining cer-

tain kinds of reaction mechanism. In the nuclear process a daughter atom is simultaneously energized and made radioactive. The property of radioactivity allows the energized atom to be directly identified in the reaction products. Nuclear activation permits study of the chemical behavior of atoms in energetic situations which are rather unusual from the chemical point of view. For example, recoil from nuclear emission of gamma radiation in the case of the (n,γ) reaction can give radioactive atoms with kinetic energies of the order of several hundreds of electron volts. On the whole, chemistry has been severely limited in the field of high-energy interactions. Thermal activation only permits limited data to be acquired on high-energy reactions. Collision efficiencies will start from zero as the activation energy for a given reaction is passed, rise with increasing energy of the reactants, and then fall from a maximum value as atomic velocities become too great for stable products to be formed. In thermal reactions the first part of this curve is observed, and collision efficiencies are strongly dependent on activation energies, so that as a result only reactions with minimum activation energies are attained. Nuclear activation offers a possibility of examining reaction modes over a wider range of reactant energies (129).

In some instances an atom undergoing nuclear activation can be located at a known point in a molecule. It is then possible to study the chemical effects of supplying localized momentum impulses, ionization, or electronic excitation within the molecule. In addition, atoms with positive charges of several units can be produced by nuclear activation, and the reactions of such charged atoms with various molecular species or the consequences of charge neutralization can be studied.

The ways in which energy of nuclear origin passes into forms of chemical interest are not clearly understood for all the nuclear processes which have been employed. In some cases lack of detailed knowledge of the physical processes has limited interpretation of the observed chemical phenomena. Furthermore, a particular nuclear process may lead to energy appearing in more than one chemically significant form. It should be pointed out, however, that many studies of the kinetics of reactions initiated by means other than nuclear activation suffer from a similar lack of exact data as to the energy and physical state of the atom at the time of reaction.

Extensive research has been done in the field in recent years. A number of reviews of the subject have appeared (10, 14, 23, 31, 57, 60, 62, 63, 73, 94, 101, 107, 114, 172, 187, 188, 214, 217, 223, 227, 235, 257, 268, 291-293, 319, 320, 322, 324, 328) and several symposia have been held.

A. ORIGIN OF CHEMICALLY SIGNIFICANT ENERGY FROM NUCLEAR PROCESSES

As a result of a nuclear reaction or of radioactive decay from a higher to

a lower nuclear level, the atom in which the nuclear transformation has occurred may acquire kinetic energy, may become ionized, or may come to possess considerable energy of excitation of the electron shells.

1. Kinetic Energy

Kinetic energy may be imparted to an atom as a consequence of conservation of momentum during emission of quanta or particles by the nucleus.

For the case of quantum emission, formulas have been developed which give the total recoil energy as a function of the nuclear mass and the total amount of energy radiated (10, 23, 172). The most commonly employed reaction resulting in gamma quantum emission has been the (n,γ) reaction with thermal neutrons, in which the binding energy of the neutron is shared between the emitted quanta and the recoiling nucleus. Binding energies lie in the range ~ 5 –10 Mev (5) and recoil energies have values of ~ 200 –1500 ev.

In the case of the (n,γ) reaction several quanta are usually emitted in succession, and these gamma cascades have been extensively investigated (11, 12, 70, 108–112, 133, 147, 148, 159, 206, 211, 212, 288). Multiple gamma quantum emission is important for studies of the chemical behavior of atoms activated by the n,γ reaction because of the possibility of mutual cancellation of the individual recoils giving significantly reduced net recoil momentum in a fraction of the nuclear transformations. In part of the events in which the activated atom is found to be retained in its parent molecule after the nuclear transformation, the excited atom may have failed to rupture its bonds due to extensive momentum cancellation in the gamma cascade.

In order to examine this possibility procedures have been developed for estimating the probability that after a gamma cascade the recoiling atom would possess a net recoil momentum less than that calculated to be necessary for bond rupture. In the first papers on the subject by Cobble and Boyd (59) and McCallum and Maddock (176), the arbitrary assumption was made that the total energy available for radiation, taken as the binding energy of the neutron, was divided between 2, 3, 4, or 6 quanta of equal energy. If the additional assumptions are made that the recoil momenta can be vectorially combined and that quantum emission is isotropic, the problem can be treated as a random walk in momentum space. A distribution is found for the probability that after a given number of steps of equal length, randomly orientated with respect to each other, the final point will lie within a given radius of the starting point, the radial distance being taken as the net momentum necessary for bond rupture. Appropriate integration of these equations then yields the probability of bond rupture.

The random walk problem has been treated by Rayleigh (238) and Chandrasekhar (49). The equations have been given in integrated form suitable for radiochemical calculation (31), and an expression has been derived by Schweinler (265) for the average energy of recoil after emission of n quanta of equal energy. Since the quanta emitted in the cascades are usually of markedly unequal energies, a useful extension to the theory has been the development by O'Connor (224), Zvara (343), and Gordus *et al.* (138) of general solutions to a random walk with steps of unequal lengths.

A fairly well studied gamma spectrum is that of the reaction $\text{Cl}^{35}(n,\gamma)\text{Cl}^{36}$, and attempts have been made to calculate a continuous probability distribution for the kinetic energy of atoms recoiling from this reaction (101, 138, 343). The procedure has been to reduce the range of gamma cascades included in the calculations by omitting cascades of low probability, or by including only lines which can be consolidated into a complete cascade corresponding to the neutron binding energy. Probability distributions for the individual cascades are evaluated from the random walk procedure, and the curve of distribution of recoil energies is then constructed by adding the probabilities for individual cascades according to the frequency of their occurrence.

If the time interval between emission of the n th and the $(n + 1)$ th quanta in a cascade is sufficient for the recoiling atom to have moved a distance comparable to that separating it from the rest of the molecule, then bond rupture may occur. In this case the net recoil momentum from the first n quanta alone is effective. Some knowledge of the duration of excited nuclear states is thus necessary for application of the stochastic treatment.

Considerable difficulty has been experienced in evaluating the half-lives of the excited states involved in (n,γ) cascades (9). Most half-lives lie in the range 10^{-13} – 10^{-17} sec. The duration of a radiative transition is related to the nuclear radius, the multipolarity order of the emitted radiation, and the energy of the emitted quantum (87, 208, 307). Formulas have been given for calculating multipolarities (208), involving the change in total nuclear angular momentum I_n and the change in nuclear parity, Π , accompanying the radiative transition. The ground angular momentum of the target nucleus in the (n,γ) reaction will be known, and neutron capture will change this by $\Delta I_n = \pm \frac{1}{2}$. Angular momenta and parity values for the state corresponding to excitation of the nucleus by the full binding energy, and for various nuclear levels corresponding to observed transitions, have been determined for a number of cases and listed (112). Calculations based on these data show that the majority of hard transitions involve dipole radiation with half lives in the range 10^{-14} – 10^{-16} sec and for this range vector addition of recoil momenta will remain valid (59, 343).

Such hard transitions will impart the greater part of the recoil energy to the atom. On the other hand, magnetic dipole transitions of quantum energy less than about 1 Mev have lifetimes greater than 10^{-14} sec and quanta of this energy will often be present in the cascade (112).

In general gamma cascades from (n, γ) reactions are so far known in only a few cases in sufficient detail to justify full calculations of recoil energy spectra. But as studies proceed it can be expected that energy spectra will be evaluated for a number of isotopes commonly encountered in chemical studies.

Kinetic energy may also be imparted to an atom when a positive charge, acquired as a result of a nuclear process, is neutralized by transfer of electrons from neighboring atoms. Magee and Gurnee (195) have treated the case of HBr^{++} , in which the positive charge has been acquired from an Auger cascade initiated by $\text{Br}^{80m} \rightarrow \text{Br}^{80} + h\nu$, and have found that during discharge of HBr^{++} , for example, the available maximum of 51 ev will not usually be imparted to the ion pair as kinetic energy after the first neutralization act. About 10–20 ev will usually appear as kinetic energy and the remainder as energy of electronic excitation.

In the case of (n, γ) reactions with thermal neutrons the source of kinetic energy is the binding energy of the neutron. When the nucleus is struck by a fast neutron or charged particle, part of the energy of the incident particle will be transferred as kinetic energy to the struck nucleus. In this case it is possible to achieve kinetic energies of recoil in the range 10^3 – 10^6 ev. Formulas have been developed for calculating recoil energies for reactions with monoenergetic fast particles (73, 172, 265), and Schweinler (265) has discussed the case of irradiation in the spectrum of fast neutrons found in a nuclear reactor.

Formulas have also been developed for calculation of the recoil energy from alpha or proton emission in radioactive decay (10, 23, 172). In this case energies of tens to hundreds of kev may be attained.

The case of recoil from beta emission has been treated by Libby (172), assuming no angular correlation between beta particle and neutrino. Edwards and Davies (73) have discussed the case in which such a correlation exists. In the absence of correlation the recoil energy spectrum has a broadly rounded peak and extends up to a maximum value of $548(E_{\beta\text{max}}/M_e) + 536[(E_{\beta\text{max}})^2/M_e]$ ev, where M_e is the mass of the emitting atom, and the maximum beta particle energy, $E_{\beta\text{max}}$, is in Mev. For a 0.5 Mev beta emitter of mass 50 the maximum recoil energy will thus be about 8.2 ev. If the beta particle and neutrino tend to be emitted in the same hemisphere the recoil energy spectrum will tend to be fairly sharply peaked towards the higher energies. If emission in opposite hemispheres is preferred the spectrum declines slowly from a maximum at zero recoil energy.

Extensive work has been done to establish the nature of the correlation between beta and neutrino emission (14, 121, 140, 141, 152, 270, 277) and Konopinski has reviewed the subject (154a).

Baulch and Duncan (14) have calculated the energy spectrum of recoils from beta emission by C^{14} for different assumed beta-neutrino interactions.

Recoil from nuclear fission gives fragments with recoil energies totaling ~ 170 Mev in the case of U^{235} .

2. Ionization

An important process leading to loss of electrons is internal conversion of gamma quanta in isomeric transitions or (n, γ) reactions. An Auger or vacancy cascade following upon loss of a K or L shell electron can result in a charge of several units at the periphery of the atom (28, 64, 71, 231, 275, 337). Electron capture by the nucleus leading to a vacancy in an inner shell can also initiate an Auger process.

Measurements of the charge acquired by halogen atoms as a result of (n, γ) reactions and isomeric transition have been made by Wexler and Davies and their collaborators (308, 312, 314, 315, 340). In later work charge spectrometry has been developed in order to investigate the relative probabilities of loss of one, two, three, or more electrons following the nuclear event. This technique, which has been described by Snell, Pleasonton, and Carlson (275, 280), involves a source volume containing the gas in which the nuclear event is to occur, a magnetic analyzer, and an electron-multiplier detector. The gas must be at a sufficiently low pressure to give a very small probability of charge transfer during collision.

In the case of nuclear processes that give rise to loss of an inner shell electron it is found by charge spectrometry that the Auger cascade leads to a charge spectrogram with relatively low probabilities at charge +1, rising to a maximum at about 8 charge units, and then falling again towards higher charge numbers. To avoid complications of charge sharing between fragments of a molecule decomposed by the charging process, charge acquisition from nuclear processes is best studied in monatomic gases. The isomeric transition $Xe^{131m} \rightarrow Xe^{131}$ has been studied by Snell *et al.* (233, 280). In this case the Auger cascade gives a most probable charge value of +8 units, this charge being acquired in about 20% of events.

When a change in charge, ΔZ , occurs on the nucleus of an atom undergoing radioactive decay, there is a change in the nuclear field strength causing expansion of the extranuclear shells when $\Delta Z < 0$ and contraction when $\Delta Z > 0$. If the rearrangement of the electron shells is slow by comparison with the nuclear process then considerable electronic excitation can occur (13, 46, 86, 106, 153, 199, 264, 267, 327, 336, 337) and ionization may result. Ionization from this cause has been termed "shake-off" (275).

Charge spectrograms have been obtained by Snell, Pleasonton, and Carlson for β^- emission (45, 46, 232, 275, 276, 278, 280, 282) and have been found to differ markedly in shape from those obtained when the charging process is initiated by loss of an inner electron. For β^- (or β^+) emission there is usually no electron loss so that charge +1 (or -1) dominates in the charge spectrum, followed by a distribution resulting from loss of outer electrons, dropping off sharply towards higher charge values. For example, in the decay $\text{Kr}^{85} \rightarrow \text{Rb}^{85} + \beta^-$ a charge of +1 is found in 79% of cases, +2 in 11%, and at +6 the probability has dropped to 0.7% (46). In the case of the transitions studied by Carlson *et al.* (46) there is a good agreement with the predicted extents of ionization given on theoretical grounds by Winther (327) and Green (106). Charge spectrometry has also been used to study the charging process consequent upon electron capture (279) and in mixed decay schemes (282).

From the comparison of charge spectra given above it seems that isomeric transition with an Auger cascade should have violent chemical consequences for any molecule in which it occurs, whereas the effects of "shake-off" should be much milder.

Emission of charged particles from the nucleus may cause ionization of the electron shells by processes other than shake-off. There is a finite probability that the emitted particle may interact directly with one of the extranuclear electrons. The direct ejection of an electron by a beta particle passing through the shells has been studied theoretically by a number of workers. Migdal (199), Feinberg (86) and Winther (327) conclude that the probability of direct ejection of an electron by a beta particle is two or three orders of magnitude less than the probability of ionization by shake-off. Grard (105), however, suggests that the coulombic interaction between beta particle and extranuclear electron may be more important for heavy elements.

Ejection of an electron in alpha particle emission is more probable than in beta emission. The charge on atoms of Ra D recoiling after alpha emission by Ra C has been measured and found to be +2 (181), and a similar charge is found in the decay $\text{Rn} \rightarrow \text{Ra A} + \alpha$ (213).

Wolfsberg and Perlman (337) have suggested that the Auger cascade should not necessarily be treated as a process involving two electrons, one of which undergoes a transition to a vacant orbital of lower energy while the other is raised to the continuum. Some of the outer electrons have velocities small compared with those of Auger electrons ejected from inner shells, so that the effective nuclear charge is suddenly changed and the outer electrons may experience a shake-off similar to that induced by emission of a charged particle from the nucleus. This polyelectronic treatment predicts a larger charge from the Auger effect than that expected on a 2-electron

basis. Snell and Pleasonton have obtained charge spectrograms of Cl^{37} resulting from electron capture in A^{37} (275, 277) and find a 10% probability for Cl^{5+} , 1.8% for Cl^{6+} , and 0.4% for Cl^{7+} . The usual 2-electron Auger mechanisms predict a maximum charge of +5, so that Snell and Pleasonton's figures may perhaps be interpreted as supporting the polyelectronic process. However, increase of multiplicative steps by Coster-Kronig transitions between subshells must also be taken into account (280).

In the case of atoms recoiling with energies in the multi-keV range auto-ionization may occur. It was pointed out by Bohr (20, 21), Knipp and Teller (149) and Lamb (158) that electrons whose peripheral velocity was less than that of the recoiling nucleus should be shed. This results in $\sim 10^3 \times m$ eV as the upper limit of the energy range in which such ionization will not occur (172), where m is the mass of the recoil in a.m.u. Ionization by this means will therefore only be of importance in cases of highly energetic recoils from heavy particle emission, fission, or nuclear reactions with fast incident particles. In the case of the most probable mode of fission of U^{235} the lighter fragment has a recoil velocity of $\sim 1.5 \times 10^9$ cm/sec and this will cause ~ 10 – 20 electrons to be stripped off by auto-ionization (73).

Starodubtsev and Romanov (283) have given a general review of the mechanisms whereby ionization of electron shells may be produced by nuclear transformation.

3. *Electronic Excitation*

As mentioned in Section I,A,2 electronic excitation can be expected to occur in those processes in which a change of nuclear charge takes place more rapidly than the readjustment of the electron shells. In some cases the electron cloud will contract adiabatically to the configuration corresponding to the new charge, but sometimes excited states will result in which the energy of excitation has been derived from the particle emission.

Serber and Snyder (267) conclude that for the case of nonadiabatic emission average, the energy of electronic excitation is given approximately by $E_{\text{exc}} = 24.47Z^{1/3}(Z' - Z)^2$ eV, where Z , Z' are the nuclear charges before and after the emission. For a C^{14} atom beta particle emission thus imparts an energy of 59 eV to the electron shells, and considerably more energy will be supplied in the case of the heavier elements.

The theoretical treatments of Migdal (199), Winther (327) and Green (106) allow calculations to be made of the distribution of energy of electronic excitation resulting from particle emission. This distribution has been calculated for the cases $\text{H}^3 \rightarrow (\text{He}^3)^+$ and $\text{He}^6 \rightarrow (\text{Li}^6)^+$, using the sudden perturbation method of Migdal and Winther. The distributions show a rapid decline of probability with increase of excitation energy, 67–70% of the daughter ions being formed in the ground state (313).

However, 25% of the $(\text{He}^3)^+$ ions have 20.5 ev of excitation energy, while 17% of the Li^+ possess about 60 ev. Kołos (153) has compared the results of calculations of the probability of formation of ground state daughter ions from the He^6 beta decay using self-consistent field wave functions with those obtained by previous authors using one-electron hydrogen-like orbitals.

Baulch *et al.* (15) have discussed methods of assessing the electronegativities of atoms in excited states after nuclear decay. Pauling-Mulliken methods are used to calculate the electronegativities. Heats of formation of excited molecules and the fractional charges on constituent atoms are thus estimated. The method has been applied to the formation of $\text{Bi}(\text{CH}_3)_4^+$ from $\text{Pb}(\text{CH}_3)_4$ by beta decay, and it has been found that an enhanced charge should be present on the Bi atom in the 4-methyl compound by comparison with $\text{Bi}(\text{CH}_3)_3$, which may account for the ease of hydrolysis of the gaseous products of beta decay of lead tetramethyl.

Electronic excitation may also occur during neutralization of the charge acquired as a result of nuclear transformation. Magee and Gurnee (195) have pointed out that such excitation may occur, due to crossover of the potential energy curves for an ion-molecule pair with curves for excited states of one member of the ion-pair which results from charge transfer. As mentioned in Section I,A,2, during the reaction $\text{HBr}^{+4} + \text{HBr} \rightarrow \text{HBr}^{+3} + \text{HBr}^{+1}$ as much as 30–40 ev may be available for excitation of the electrons of the products.

4. Summary

To sum up the present section it can be seen that nuclear activation can supply kinetic energy, charge, and energy of electronic excitation to marked atoms within limits which are wide from the chemical point of view. Kinetic energies can vary in the range of a few ev for beta emission to many hundreds of kev for reactions with fast incident particles. Electron loss can be a relatively mild process involving perhaps only a 10% probability of producing a charge of +2 units in the case of shake-off, or it can be a violent process readily causing loss of 8–20 electrons in the case of internal conversion or nuclear fission. Electronic excitation from nonadiabatic particle emission may considerably exceed the first and second ionization potentials of the atom.

One of the greatest drawbacks to the use of nuclear activation in chemical studies is the occurrence of more than one mode of energization in a single nuclear process. Thus, for example, a marked atom from an (n,γ) reaction will have recoil energy, but there is also a considerable probability of charge acquisition by internal conversion of some of the softer quanta in the gamma cascade (134, 210). Neutralization of the charge of this atom

during its recoil may in turn cause excitation of its extranuclear electrons. As a second example, an atom may emit soft gamma rays during an isomeric transition. The energy of recoil from the quantum emission may be too small to be chemically significant. Nevertheless conversion of the quanta may lead via a vacancy cascade to a charge of several units on the periphery of the atom, and neutralization of this charge may then impart a kinetic energy four or five times greater than the energy of chemical bonds in the vicinity.

The studies reviewed in subsequent parts of this article show that despite the complicated nature of nuclear activation the chemical consequences of this process can often be successfully related to the energetics of the nuclear event.

B. LOSS OF ENERGY OF ATOMS ACTIVATED IN NUCLEAR PROCESSES

Kinetic energy is lost from a recoiling ion by elastic or inelastic collisions with atoms or molecules of the environment (18, 72), or by interaction of the ion with electrons of the medium in which recoil occurs.

For ions whose velocity is much greater than the velocity v_e of the outermost electrons of a struck atom, excitation and ionization by interaction with electrons of the medium account for practically all the energy loss. At recoil velocities considerably smaller than v_e elastic and inelastic collisions with the struck atom as a whole become increasingly predominant.

Seitz (266) has suggested that the limiting kinetic energy, E_{\min} , for excitation of electrons of the medium by a recoiling atom of mass m is given approximately by $(m/m_e)I_{\text{exc}}$, where m_e is the mass of an electron and I_{exc} is the lowest electronic excitation level, corresponding to the lower limit of the main optical absorption band. For insulators $I_{\text{exc}} \approx 4\text{--}5$ ev, so that for an atom of mass 50, for example, $E_{\min} \approx 46$ kev. Loss of energy by interaction with electrons of the medium will thus only be important for ions recoiling from reactions with fast particles, from alpha, proton, or neutron emission, or from nuclear fission. In calculations of the amounts of energy delivered up to the medium by excitation or ionization, the approximation is often made that for $E_{\text{recoil}} > E_{\min}$ the recoil loses energy only by electronic events, and for $E_{\text{recoil}} < E_{\min}$ all energy is lost by elastic collisions (18).

The theory of energy loss from a recoiling atom or ion by elastic collisions has been well established (87, 97, 172, 230, 306).

In the intermediate range, for which $v_{\text{recoil}} \approx v_e$, the recoiling atom will go through many cycles of electron capture and loss as it slows down. The considerable amount of work which has been done on the exchange process for gaseous ions of hydrogen and helium has been reviewed by Allison (3). The total number of collisions in which the neutral atom is formed is a

function of the stopping power of the medium (which depends on the energy of the moving ion) and the energy-dependent cross-section for completion of the electron capture and loss cycle. As an example, an H atom in slowing down from 300 kev to 9 kev in hydrogen gas goes through ~ 2000 charge-changing cycles. Measurements have been made of the equilibrium fractions of -1 , 0 , and $+1$ states in hydrogen or helium beams passing through various gases (3). The equilibrium fractions are a function of the recoil energy and the nature of the medium. In the energy region above ~ 100 kev in hydrogen gas the H^+ state predominates, but at energies below ~ 10 kev the neutral atom is present to about 90%, the H^+ state having dropped to a little below 10%. This finding has important implications for chemical studies with H^3 atoms activated by the reactions $Li^6(n,\alpha)H^3$ [$E_{\text{recoil}} = 2.730$ Mev] or $He^3(n,p)H^3$ [$E_{\text{recoil}} = 0.192$ Mev]. When the tritium atom has cooled to energies at which it can react to form stable chemical bonds it would seem from the above picture that it should exist predominantly as the neutral atom (67, 77). Rowland *et al.* (247) have pointed out, however, that there is a possible positive ion contribution when H^3 recoils through a medium containing molecules of ionization potential greater than the first ionization potential of hydrogen.

The data on equilibrium fractions do not as yet extend down to the few ev range in systems of chemical interest. Fite *et al.* (89, 90) have measured the cross-sections for the transfer reactions $p + H \rightarrow H + p$ and $p + H_2 \rightarrow H + H_2^+$. The cross-section for neutralization of the proton in atomic hydrogen has been measured down to 100 ev. As the energy declines from 10 kev to 100 ev the cross-section rises by a factor of approximately 5. The neutralization in molecular hydrogen has been studied from 10 kev down to 400 ev and in this range the cross-section declines by a factor of 8. Simons *et al.* (215) have found a large cross-section for neutralization of H^+ in the 2–150 ev range in organic gases, but not in helium or argon. This finding emphasizes the current lack of data from which we can derive the equilibrium fractions of the charge states of hydrogen atoms recoiling through gases or liquids containing various compounds. The situation is no better for recoiling species other than hydrogen.

Some light is thrown on the way in which the cross-sections for positive charge neutralization vary with ion velocity by the resonance rule (197, 209), which states that maximum cross-section occurs when $\Delta E/h \approx v/a$, where ΔE is the net energy defect, v is the relative velocity of the interacting particles, and a is the range over which interaction occurs. Wolfgang *et al.* (77) have used this rule and the energies of charge transfer processes in methane to suggest that in the terminal part of a recoil track neutralization probability for $(H^3)^+$ will become maximal, whereas ionization probability for H^3 will decline.

Energy of electronic excitation from nuclear transformation may be lost from an atom before it can affect its chemical behavior. Baulch and Duncan (13, 15) have discussed the conditions favoring isothermal decay, in which energy of electronic excitation is lost before the bond between the atom and the remainder of the molecule is affected, and adiabatic decay in which the chemical behavior of the daughter is not that of the atom in its ground state. Evidence quoted by these authors from pre-dissociation spectra of I_2 , S_2 , AlH , CaH , InH , and TlH at high argon pressures or in a magnetic field (95, 113, 154, 299, 300, 304) indicates that in these cases dissociation is induced by collision and that metastable states can have lives as long as 10^{-6} sec. These experiments support the conclusion that the lifetime depends on the stability of the excited state itself and on whether chemical reaction is induced before de-excitation can occur.

II. Primary Processes Leading to Bond Rupture

A. GENERAL CONSIDERATIONS

The earliest experiments on the chemical effects of nuclear activation were concerned with the way in which the activated atom ruptured its bonds with the molecule in which it was located before the nuclear event, and this problem has remained an important aspect of the subject. It would be very desirable to know accurately the fraction of events in which the atom failed to rupture its bonds as a result of possessing too small an energy of activation, or too small a degree of ionization. If this fraction were then subtracted from the fraction of labeled daughter atoms found in the parent molecule at the end of the experiment, we would know the number of events in which the activated atom had freed itself from its initial bonds and, after a period of freedom, had recombined to form the parent type molecule. Such information is required to evaluate the relative probability of recombination processes.

In order to measure the probability of primary bond rupture we need to arrange experimental conditions so that the chances of recombination to reform the parent type molecule are minimal. In the case of nuclear processes giving very small recoil energies (e.g., internal conversion of soft gamma quanta, as in $Br^{80m} \rightarrow Br^{80} + h\nu$) the cage of solvent molecules around the nuclear transformation site in a liquid may favor recombination, and experiments should then be done in the gas phase. Where kinetic energies are sufficiently large to separate primary fragments in a liquid system, the probability of recombination of the fragments can be reduced by working with very low concentrations of the parent molecule in an "inert" diluent. By an inert diluent is meant a substance with which the

activated atom will not combine to form a species impossible to separate from the parent molecule before radioactivity measurements. Sometimes it may be useful in gas or liquid systems to add a trapping substance with which the radioactive atom will combine in a highly probable reaction after primary bond rupture, giving a readily separable compound. Radical scavengers may be introduced to lower the probability of recombination of the activated atom with one of the radicals produced during its recoil. In gas phase studies it is often useful to add inert moderators which will remove kinetic energy from the recoil during collisions, without forming radioactive species which could not be separated from the target substance.

As a result of the various types of nuclear activation described earlier, the following mechanisms may lead to primary bond rupture:

(a) The activated atom may acquire sufficient kinetic energy to rupture its bonds [e.g., in (n, γ) reactions, or in fast particle reactions or in α , β , p , or n emission].

(b) Sufficient electrons may be lost from the outer shells to cause bond rupture (e.g., in vacancy cascades or shake-off processes). The possibility must be borne in mind that the charge may spread over the molecule before the activated atom can break its bonds, and a number of different modes of molecular disintegration may occur.

(c) Acquisition of electronic excitation from nuclear transformation may induce molecular dissociation (e.g., in nonadiabatic beta particle emission). Once again, spreading of the excitation over the molecule may give rise to several decomposition products.

B. BOND ACTIVATION BY RECOIL

In the case where an atom in a polyatomic molecule receives a momentum impulse from a nuclear transformation, we have to consider the way in which energy is transferred to the bond or bonds attaching the activated atom to the molecular residue, and to the molecular residue itself.

Gordus and Hsiung (102a) have treated this problem on the basis of classical mechanics, using the following assumptions:

(a) The molecule is regarded as a group of point masses, the atoms linked together with springs and thus capable of undergoing independent constrained motions in addition to the translational and rotational motions of the molecule.

(b) The recoil energy is large compared with the thermal energy of the molecule.

(c) The momentum impulse, Q , is received by the atom undergoing nuclear transformation in a time period so short that other atoms in the molecule do not increase their translational velocity. This assumption requires that the duration of the momentum impulse should be less than

the time required for dissociation, i.e., less than the period of a single vibration, $\sim 10^{-14}$ sec.

(d) The momentum impulse, Q , supplied by the recoiling atom can be resolved into a component, Q_R , perpendicular to the line joining that atom to the center of the molecule, and Q_V , in a random direction. Q_R causes rotation of the molecule, while Q_V results in a molecular vibration dependent on bond strengths and moments of inertia. In addition to the effect of recoil on vibrational states there is a rotational effect on potential energy due to stressing of the bonds by centrifugal forces. This contribution is evaluated by treating the atoms as simple harmonic oscillators about their equilibrium positions. The centrifugal force vector is resolved into a component in the direction of a given bond, causing bond stretching, and a component at right angles to the bond causing a bending vibration.

(e) When the energy laid down in a given bond, as evaluated on the basis of the above assumptions, exceeds the bond energy, E_b , then bond rupture is considered to result.

The total internal energy increase is given by:

$$E_{\text{int}} = \frac{1}{2} \sum m_i (\boldsymbol{\omega} \times \mathbf{r}_i) \cdot (\boldsymbol{\omega} \times \mathbf{r}_i) + \frac{1}{2} \sum m_i v_i^2 + V(\mathbf{r}_i) - V(\mathbf{a}_i) \quad (1)$$

where $\boldsymbol{\omega}$ is the angular motion of the molecule about its center of gravity, \mathbf{r}_i is the position vector for the i type atom with the center of gravity as origin, v_i is the vibrational velocity of the i th atom with respect to the molecule, \mathbf{a}_i is the vector defining the equilibrium position of the i th type atom, and V represents potential energy as a function of spatial position. The first term on the right hand side of Eq. (1) is the rotational energy, the second term is the vibrational energy, and the last is the potential energy of the molecule.

By evaluating the terms of Eq. (1) expressions have been derived for E_T° , the net recoil energy which must be received by the atom undergoing nuclear transformation in order that bond rupture should occur (102a). Table I shows values of E_T° necessary for C—Br rupture in organic bromides as calculated on the basis of these expressions. The original paper lists similar values for C—I and C—Cl bond rupture in chlorides and iodides.

On the basis of the calculated values of E_T° and the spectra of recoil energies from given (n, γ) reactions, calculated by the stochastic methods of Section I,A,1, it should be possible to make an estimate of the percentage of nuclear events leading to bond rupture. Some comparisons of observed and calculated frequencies of bond rupture are given in Section II,C.

The Gordus-Hsiung treatment assumes that the duration of the momentum impulse is short by comparison with the vibration period, $\sim 10^{-14}$ sec. As mentioned in Section I,A,1, hard transitions in (n, γ) cascades

TABLE I
MINIMUM NET RECOIL ENERGIES, E_T° , REQUIRED FOR
C—Br BOND RUPTURE IN ORGANIC BROMIDES (102a)

Molecule	Molecular weight	E_T° (ev)
CH ₃ Br	95	20.74
CD ₃ Br	98	18.54
C ₂ H ₅ Br	109	15.14
CF ₃ Br	149	7.38
CH ₂ Br ₂	174	6.14
CCl ₃ Br	200	4.06
CHClBr ₂	209	4.93
CF ₂ Br ₂	210	4.90
CCl ₂ Br ₂	244	3.64
CHBr ₃	253	4.76
CBr ₄	332	2.98

have half-lives in the range 10^{-14} – 10^{-16} sec., and these steps impart the bulk of the recoil energy, so that in many instances of the (n, γ) reaction the Gordus-Hsiung treatment will be valid. For beta emission, the time taken for a relativistic electron to leave a shell of electrons bound by a charge Ze is:

$$t \approx \frac{\hbar^2}{Zm_e e^2 c} \quad (2)$$

i.e., $t \lesssim 10^{-16}$ sec., so that the assumption of short duration of the momentum impulse is valid. Nevertheless, some intramolecular momentum transfer will occur, and for this reason calculated values of E_T° may be low. The error in E_T° may be expected to increase with molecular complexity.

From Table I it can be seen that E_T° declines as the molecular weight increases. Qualitatively this can be visualized as a tendency for a light recoil readily to sever its bonds with a heavy residue, whereas a heavy recoil will tend to carry a light residue with it. This effect was predicted in work by Suess (289), who had calculated that for a diatomic molecule the energy of activation of the bond is related to the energy of recoil, E_r , by:

$$E_i = E_r \frac{(M - m)}{M} \quad (3)$$

where m is the mass of the recoil and M is the mass of the molecule.

Steinwedel and Jensen (284) have also calculated the fractional distribution of internal energy between the vibrational states and rotational states, and applied a quantum mechanical approach to the problem. More recently Svoboda (290) has discussed the effect of inelastic internal collisions by the

recoiling atom on the probability of bond rupture. Wolfsberg (336) has used a quantum-mechanical treatment to evaluate the average vibrational and rotational energies supplied to a molecule as a result of nuclear recoil, and to calculate the probability of exciting to a given vibrational state from the lowest state. The same author has used this treatment to calculate the probability of dissociation of $\text{CH}_3\text{—C}^{14}\text{H}_3$ by recoil from the reaction $\text{C}^{14} \rightarrow \text{—}^{14}\beta + \text{N}^{14}$. Assuming that the parent molecule is in the ground rotational vibrational state and that the dimensions and force constants of both parent and daughter molecules are the same, the method predicts that the C—N bond energy of 2.1 ev will be exceeded whenever $E_R > 3.57$ ev. The method of Gordus *et al.*, outlined above, gives a value of $E_R > 3.53$ ev, when the assumptions are made that the CH_3 and NH_3 groups are rigid (102b).

C. BOND RUPTURE IN THE (n,γ) REACTION

The earliest experiments on bond rupture consequent on the (n,γ) reaction were done with organic halides in the gas phase where no cage of adjacent molecules restrains the activated atom. Results from various authors are shown in Table II.

Efficiencies of bond rupture are very high, usually being over 90%. This result might be expected with radiohalogen atoms recoiling with kinetic energies of hundreds of ev, and having in some cases a positive charge from conversion of the gamma quanta (314). The results show, however, that the true efficiencies for bond rupture are obtained only by working at micron pressures, where the probability of a retention-causing collision in the gas is low before the recoils strike the wall of the vessel and are trapped (314), or by adding the efficient radical scavenger NO at sufficient pressures to allow it to act as a moderator (102). Under these conditions the bond rupturing process is found to be more than 99% efficient. At higher pressures addition of elementary halogen as a trapping agent for the recoils in the case of $\text{C}_2\text{H}_5\text{I}$ reveals a similar efficiency for the rupturing mechanism (136), although the results shown for the bromine compounds irradiated at mm Hg pressures in presence of elementary bromine or HBr (35, 81) indicate that secondary reaction has occurred.

The high bond rupturing efficiency of the $\text{Br}^{79}(n,\gamma)\text{Br}^{80m}$ and the $\text{I}^{127}(n,\gamma)\text{I}^{128}$ reactions indicates either that mutual cancellation of the recoil momenta in the course of the gamma cascade cannot be an important factor in these processes, or that ionization due to internal conversion occurs in about 99% of events. Wexler and Davies (314) found that the percentage of radiohalogen atoms carrying positive charges after ejection from gaseous ethyl bromide or iodide at micron pressures was 12% for $\text{Br}^{79}(n,\gamma)\text{Br}^{80m}$, 25% for $\text{Br}^{81}(n,\gamma)\text{Br}^{82}$ and 50% for $\text{I}^{127}(n,\gamma)\text{I}^{128}$. Clearly

TABLE II
PERCENTAGES OF RADIOHALOGEN ATOMS RETAINED IN ORGANIC COMBINATION
AFTER NEUTRON IRRADIATION OF ORGANIC HALIDES IN GAS PHASE

Target irradiated ^a	Nuclear reaction	% Radiohalide in organic combination	Reference
C ₂ H ₅ Br(390) + Air(370)	Br ⁷⁹ (n,γ)Br ^{80m}	4.5	(171)
C ₂ H ₅ Br(137–217) + HBr(10.5–203)	Br ⁷⁹ (n,γ)Br ^{80m}	3–18	(325)
C ₂ H ₅ Br(1 – 3 × 10 ⁻³)	Br ⁷⁹ (n,γ)Br ^{80m}	<1%	(314)
C ₂ H ₅ Br(10–15) + NO(700)	Br ⁷⁹ (n,γ)Br ^{80m}	0.33	(102)
CH ₂ BrCH ₂ Br(40) + Air(720)	Br ⁷⁹ (n,γ)Br ^{80m}	6.9	(171)
CH ₂ Br(760) + Br ₂ (10)	Br ⁷⁹ (n,γ)Br ^{80m}	3.9–4.1	(104)
CH ₃ Br(10–15) + NO(700)	Br ⁷⁹ (n,γ)Br ^{80m}	0.25	(102)
CD ₃ Br(10–15) + NO(700)	Br ⁷⁹ (n,γ)Br ^{80m}	0.20	(102)
CH ₂ Br ₂ (10–15) + NO(700)	Br ⁷⁹ (n,γ)Br ^{80m}	0.115	(102)
CHBr ₃ (10–15) + NO(700)	Br ⁷⁹ (n,γ)Br ^{80m}	0.048	(102)
CF ₃ Br(10–15) + NO(700)	Br ⁷⁹ (n,γ)Br ^{80m}	0.105	(102)
CF ₂ Br ₂ (10–15) + NO(700)	Br ⁷⁹ (n,γ)Br ^{80m}	0.093	(102)
CHClBr ₂ (10–15) + NO(700)	Br ⁷⁹ (n,γ)Br ^{80m}	0.087	(102)
CCl ₃ Br(10–15) + NO(700)	Br ⁷⁹ (n,γ)Br ^{80m}	0.066	(102)
CBr ₄ (10–15) + NO(700)	Br ⁷⁹ (n,γ)Br ^{80m}	0.031	(102)
1,1-C ₂ H ₄ Br ₂ (10–15) + NO(700)	Br ⁷⁹ (n,γ)Br ^{80m}	0.173	(102)
C ₆ H ₅ Br(2) + Br ₂ (6 × 10 ⁻²)	Br ⁷⁹ (n,γ)Br ⁸⁰	5.56	(81)
C ₆ H ₅ Br(2) + Br ₂ (6 × 10 ⁻²)	Br ⁷⁹ (n,γ)Br ^{80m}	5.89	(81)
C ₆ H ₅ Br(2) + Br ₂ (6 × 10 ⁻²)	Br ⁸¹ (n,γ)Br ⁸²	5.40	(81)
n-C ₃ H ₇ Br(70) + Br ₂ (3.5 × 10 ⁻²)	Br ⁷⁹ (n,γ)Br ⁸⁰	5.28	(81)
n-C ₃ H ₇ Br(70) + Br ₂ (3.5 × 10 ⁻²)	Br ⁷⁹ (n,γ)Br ^{80m}	5.74	(81)
n-C ₃ H ₇ Br(70) + Br ₂ (3.5 × 10 ⁻²)	Br ⁸¹ (n,γ)Br ⁸²	5.43	(81)
C ₂ H ₅ I(80)	I ¹²⁷ (n,γ)I ¹²⁸	2.9–6.8	(136)
C ₂ H ₅ I(80) + I ₂ (0.2)	I ¹²⁷ (n,γ)I ¹²⁸	1.1–1.4	(136)
C ₂ H ₅ I(10–15) + NO(700)	I ¹²⁷ (n,γ)I ¹²⁸	0.82	(102)
CH ₃ I(10–15) + NO(700)	I ¹²⁷ (n,γ)I ¹²⁸	1.09	(102)
CD ₃ I(10–15) + NO(700)	I ¹²⁷ (n,γ)I ¹²⁸	0.68	(102)
CF ₃ I(10–15) + NO(700)	I ¹²⁷ (n,γ)I ¹²⁸	0.12	(102)
CH ₂ I ₂ (10–15) + NO(700)	I ¹²⁷ (n,γ)I ¹²⁸	0.068	(102)
n-C ₃ H ₇ I(10–15) + NO(700)	I ¹²⁷ (n,γ)I ¹²⁸	0.66	(102)
i-C ₃ H ₇ I(10–15) + NO(700)	I ¹²⁷ (n,γ)I ¹²⁸	0.30	(102)
n-C ₄ H ₉ Cl(103)	Cl ³⁷ (n,γ)Cl ³⁸	9.4–12.1	(51)
n-C ₄ H ₉ Cl(95–107) + HCl(95–102)	Cl ³⁷ (n,γ)Cl ³⁸	10.6–11.5	(51)

^a Figures in parentheses are gas pressures in mm Hg.

ionization alone cannot account for the observed efficiencies of bond rupture. Furthermore very similar bond rupturing efficiencies were obtained in experiments shown in Table II in which the Br⁷⁹(n,γ)Br^{80m} and Br⁸¹(n,γ)Br⁸² reactions were compared (81), despite the differences in ioniza-

Libby (171) has used ethanol as an "inert" diluent for CBr_4 irradiated with neutrons in the liquid state and has found that the percentage of $\text{Br}^{80\text{m}}$ retained in organic combination drops from $28 \pm 5\%$ at 1.15 mole % CBr_4 to $0 \pm 2\%$ at 0.064 mole %. This finding supports the conclusion from the gas phase experiments as to the very high efficiency of bond rupture in the $\text{Br}^{79}(n,\gamma)\text{Br}^{80\text{m}}$ reaction.

As yet relatively few attempts have been made to relate measured efficiencies of bond rupture in gas or liquid systems to the spectra of net recoil energies calculated by the stochastic methods of Section I,A,1. Gordus *et al.* (102) have calculated the net gamma ray energies, $E_{\gamma 0}$, necessary for bond rupture by the methods discussed in connection with Eq. (1), and have plotted these against the observed organic yields of Br^{80} in various organic bromides after the $\text{Br}^{79}(n,\gamma)\text{Br}^{80}$ reaction. The results are shown in Fig. 1. The data seem to support the general view that reten-

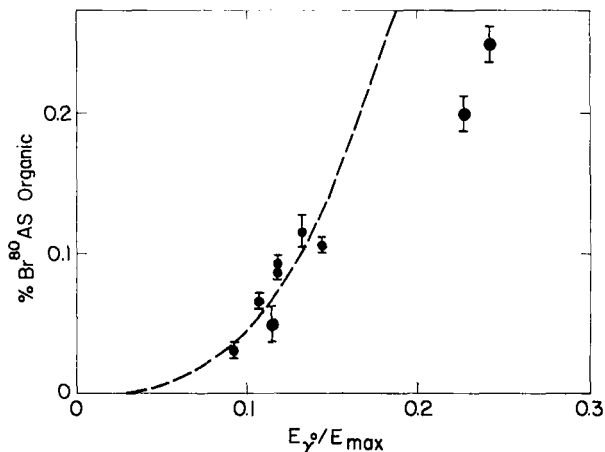


FIG. 1. Organic retention of Br^{80} as a function of net gamma recoil energy required for bond rupture (102). Dashed curve corresponds to calculated probability distribution for the $\text{Cl}^{36}(n,\gamma)\text{Cl}^{36}$ process.

tion of the Br^{80} atom in organic combination is related to the energy distribution of recoils from the (n,γ) reaction. As yet insufficient data on the $\text{Br}^{79}(n,\gamma)\text{Br}^{80}$ gamma cascade are available to allow a full recoil energy spectrum to be evaluated for this reaction, using the random walk procedure. For purposes of rough comparison, however, the dotted line in Fig. 1 corresponds to the recoil probability distribution for the $\text{Cl}^{36}(n,\gamma)\text{Cl}^{36}$ reaction.

It must be remembered that the values of E_T° used in Fig. 1 were calculated without taking into account any loss of electrons by internal conversion of the (n,γ) quanta. The value of E_T° required for bond rupture

of the positively charged molecule differs from that required for the neutral molecule. For example, $E_T^\circ = 2.77$ Mev for $\text{CH}_3\text{I}^+ \rightarrow \text{CH}_3^+ + \text{I}$ and 2.55 Mev for neutral CH_3I (102).

Assuming 25 ev as the total energy of phosphorus-oxygen bonds in tributyl phosphate (TBP), applying Eq. (3) and selecting two probable gamma cascade schemes for the reaction $\text{P}^{31}(n,\gamma)\text{P}^{32}$, it has been shown by the stochastic procedure outlined in Section I,A,1 that failure to rupture all bonds should occur in 2.2–3.5% of events (36). In such a complicated system di- and mono- P^{32} -esters are likely to be formed as well as TBP^{32} by failure to rupture bonds, as well as by "hot" and "thermal" secondary processes (see Sections III,B and III,C). Irradiation of TBP in heptane or benzene as "inert" diluents, and use of radical scavenger techniques to estimate the contribution to the organic P^{32} yield from thermal reactions has led to the value of 2–4% being obtained for the failure to rupture all bonds in TBP, in good accord with the predicted values (272).

Trimethyl phosphine gas has been irradiated in the presence of argon as a moderator to reduce the kinetic energy of P^{32} recoils from the (n,γ) reaction and thus to limit the probability of high-energy processes leading to re-entry into the parent molecule (116). Under these conditions the yields of $(\text{CH}_3)_3\text{P}^{32}$, $(\text{CH}_3)_2\text{P}^{32}\text{H}$, and $\text{CH}_3\text{P}^{32}\text{H}_2$ were 0.04–0.1%, 0.02–0.1% and 0.2–0.3% respectively. This result indicates an almost complete rupture of P-CH_3 bonds in the (n,γ) reaction.

An interesting approach to the problem of estimating the proportion of nuclear events which fail to rupture bonds has been made by Iyer and Martin in the case of the (n,γ) reaction in alkyl iodides (139). These authors have labeled iodides with the 1.27×10^7 year I^{129} isotope, and then studied the consequences of the $\text{I}^{129}(n,\gamma)\text{I}^{130}$ reaction. Mixtures of CH_3I and $n\text{-C}_3\text{H}_7\text{I}$ have been prepared in which the I^{129} isotope was present as CH_3I or $n\text{-C}_3\text{H}_7\text{I}$ or I_2 . Assuming that the probability of I^{130} being retained by secondary re-entry processes in one of the two alkyl iodides is proportional to the mole fraction of that iodide, and that a given fraction of events fails to result in bond rupture, a set of simultaneous equations can be set up to predict the specific activities in the irradiated compounds. By this means it has been found that in liquid CH_3I and $n\text{-C}_3\text{H}_7\text{I}$ failure to rupture bonds occurs in about 4% of cases. This is significantly greater than the values of 1.09 and 0.66% in the gas phase experiments of Table II, and suggests some recombination of the I^{130} atom with the radical formed by bond rupture within the initial cage of solvent molecules, or radiation-induced effects.

D. BOND RUPTURE BY CHARGING PROCESSES

After ejection of an inner electron by one of the processes described in Section I,A,2 an Auger cascade may cause bond rupture. Bonding electrons

may be lost, or Coulomb repulsion between charged regions of the molecule may cause dissociation.

The line widths observed for X-ray fluorescence and X-ray absorption edges are of the order of 2–40 eV, so that from the relationship $\Delta E \cdot \Delta t = \hbar$, the duration of the Auger cascade is 10^{-15} – 10^{-16} sec (28, 61, 241, 242, 312). Molecular vibration periods are of the order of 10^{-14} sec, so that molecules will remain intact until the charge on the activated constituent atom has been fully developed by the Auger process. When the cascade has ended, charge will tend to be distributed over the rest of the molecule. In the case of the cascade initiated by $\text{Br}^{80m} \rightarrow \text{Br}^{80} + h\nu$ in $\text{CH}_3\text{Br}^{80m}$, Wexler and Anderson (310, 312) have obtained evidence that some charge distribution occurs before the molecule disintegrates. Using the mass spectrometer developed for examining the charged fragment spectrum from nuclear events in gases (310, 312, 316) these authors have shown that fragments such as CH_3Br^+ , CH_3^+ , and C^+ are produced with a fairly high probability. Consequently in considering the mechanism of bond rupture by Auger cascades repulsion between charged regions of the molecule must be taken into account.

The Auger effect can be treated either as a radiationless transition, involving electron-electron interaction in the shells, or as a process of successive X-radiation emission and internal conversion (28). In either case the probability is highest for ejection of the electron nearest to the vacancy. At the beginning of the cascade this probability is highest for ejection of electrons from the atom in which the initial vacancy has occurred, but as the cascade reaches the periphery, electrons from molecular orbitals may be involved. In the case where the charge builds up on an atom A in a molecule A(BCD . . .), and the ionization potential of the final state A^{Z+} exceeds the ionization potentials of B, C, or D, then charge redistribution can occur by electron transfer (316).

The potential energy of the system $\text{A}^{Z+}(\text{BCD})^{Y+}$ is:

$$V = \frac{(Ze)(Ye)}{r} \quad (4)$$

where r is the effective distance between the charge center of A^{Z+} and the charge center of $(\text{BCD})^{Y+}$. The fragments A and BCD recoiling after bond rupture will have kinetic energies $V M_{\text{BCD}}/(M_{\text{A}} + M_{\text{BCD}})$ and $V M_{\text{A}}/(M_{\text{A}} + M_{\text{BCD}})$ respectively, where M_{A} and M_{BCD} are the fragment masses. After the Auger cascade in $\text{CH}_3\text{Br}^{80m}$ Wexler and Anderson have found that the most probable fragments are Br^{7+} and CH_3^+ (312). The total kinetic energy for this pair from Eq. (4) is 53 eV, considerably in excess of the C—Br bond energy of 2.3 eV. Bond rupture in this case would probably occur by simple loss of bond electrons, but in addition there is ample energy available for rupture from Coulomb repulsion.

E. BOND RUPTURE IN ISOMERIC TRANSITION

The chemical consequences of the isomeric transition $\text{Br}^{80} \rightarrow \text{Br}^{80m} + h\nu$ have been extensively studied in organic bromides. During the transition two gamma quanta are emitted in series, of energies 49 and 37 kev respectively (287). The energies of recoil from these quanta are 0.016 and 0.009 ev respectively, so that insufficient kinetic energy is available from this source for rupture of chemical bonds. The 49 kev step undergoes 100% internal conversion while the 37 kev step is converted in 55% of events (246). The conversion of the first step takes place with 84% probability in the *K* shell and 16% probability in the *L* shell. The corresponding figures for the second quantum are 87% *K* and 13% *L*. Auger cascades will be initiated by some of these conversions, while in other cases X-radiation will be emitted. Figure 2 shows the ion yields of charged bromine atoms from isomeric transition of Br^{80m} in $\text{CH}_3\text{Br}^{80m}$, as obtained by the method of charge spectrometry (312). The average charge is +6.2.

From Fig. 2 and the considerations advanced in Section II,D, it would be expected that bond rupture would be very extensive in the case of a molecule such as CH_3Br after isomeric transition. Since the daughter atom, Br^{80} , is itself beta-active its distribution can readily be followed in the reaction products. In view of the fact that the kinetic energy of the $\text{CH}_3^+ + \text{Br}^+$ couple from Coulomb repulsion would only be 7.6 ev, from Eq. (4),

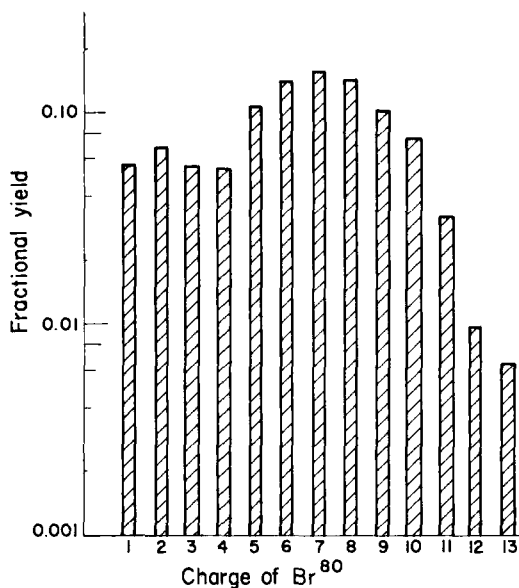


FIG. 2. Ion yields of charged bromine atoms from nuclear isomeric transition of Br^{80m} (312).

experiments to determine the absolute efficiency of bond rupture require to be done in the gas phase to avoid caging effects.

Table III shows the results of gas phase experiments on the dissociation of $\text{Br}^{80\text{m}}$ -labeled organic bromides. From the table it emerges that the bond rupturing efficiency is very high. The discrepancy between results for $\text{HBr}^{80\text{m}}$ and $\text{HBr}^{80\text{m}}$ + allyl bromide (or α,β -dibromoethylene) as a scavenger for thermalized Br atoms (104, 120) is not easily explained.

TABLE III
PROBABILITY OF BOND RUPTURE AFTER ISOMERIC TRANSITION
IN GASEOUS $\text{Br}^{80\text{m}}$ -LABELED BROMIDES

Gas phase constituents ^a	Probability of bond rupture (%)	Reference
$\text{HBr}^{80\text{m}}$	>95	(104)
$\text{HBr}^{80\text{m}}$ (90) + $\text{CHBr}=\text{CHBr}$ (2.3) + CH_3Br (5.4)	76	(120)
$\text{HBr}^{80\text{m}}$ (91) + $\text{CH}_2=\text{CHCH}_2\text{Br}$ (2.4) + CH_3Br (5.2)	76	(120)
$\text{DBr}^{80\text{m}}$ (54) + $\text{CHBr}=\text{CHBr}$ (1.4) + CH_3Br (3.1)	83	(120)
$\text{CH}_3\text{Br}^{80\text{m}}$ (120) + HBr (60)	100	(119, 120)
$\text{CH}_3\text{Br}^{80\text{m}}$ (150) + HBr (0)	94	(119, 120)
$\text{CH}_3\text{Br}^{80\text{m}}$ (45) + HBr (45)	99	(119, 120)
$\text{CH}_3\text{Br}^{80\text{m}}$ + Br_2	94.4	(50)
$\text{CH}_3\text{Br}^{80\text{m}}$ + Br_2	98.7	(104)
$\text{C}_2\text{H}_5\text{Br}^{80\text{m}}$ + Br_2	96.9	(104)
$\text{CCl}_3\text{Br}^{80\text{m}}$ + Br_2	98.0	(104)
$\text{CCl}_3\text{Br}^{80\text{m}}$ + Br_2	92.9	(50)
$\text{CF}_3\text{Br}^{80\text{m}}$ + Br_2	99.0	(50)

^a Figures in parentheses denote gas pressures in mm Hg.

Magee and Gurnee (195) have considered the implications of the experiments with allyl bromide or dibromoethylene (120), which seem to indicate that 17–24% of HBr or DBr molecules can survive isomeric transition, while in organic bromides this is not the case. For molecular survival to occur the bonds must remain intact during both the charging and discharging processes. Magee and Gurnee have selected likely charge states induced by the Auger cascade. From these states potential energy curves have been drawn up for the "homopolar" $(\text{HBr})^{Z+}$ and polar $(\text{H}+\text{Br}^{(Z-1)+})$ components of the Z^+ state. They find that for the sequence $Z(0-4+)$ there is a remarkable stability of both the homopolar bond dissociation energy and the bond distance with respect to the value of Z and the position of the missing electrons. The Coulombic repulsion curves for the polar component intersect the homopolar curves, but for $Z + 4$ the intersection occurs sufficiently far out to leave a potential minimum, i.e., a stable bond, unless direct transitions to excited states are involved. In the case of a

molecule such as CH_3Br it is found that due to the lower ionization potential of CH_3 (9.96 ev) by comparison with H (13.6 ev) the polar repulsion curves pass through the homopolar attractive minima and lead to bond rupture.

Wexler and Anderson (312) have used charge spectrometry to determine the distribution of positively charged fragments from isomeric transition in $\text{CH}_3\text{Br}^{80\text{m}}$. The accuracy of measurements in the spectrometer is limited by virtue of the fact that according to Eq. (4) the different charged fragments will attain different kinetic energies, and that mass spectrometers have differing discriminations against fragments of differing initial kinetic energies. In the fragment spectrum $(\text{CH}_3\text{Br}^{80})^+$ occurs with a probability of 9.5–10%. This suggests that ejection of only one conversion electron does not necessarily lead to bond rupture. In those isomeric transitions in which the 49 kev quantum is converted and this step is followed only by X-ray emission together with radiation of the 37 kev quantum, the $\text{CH}_3\text{Br}^{80}$ daughter will have a single positive charge. Such an ion evidently remains intact in $\sim 10\%$ of events, even though it may have been initially produced in a further fraction of events and undergone dissociation. The absence of $(\text{CH}_3\text{Br}^{80})^{2+}$ and $(\text{CH}_3\text{Br}^{80})^{3+}$ shows that multiply charged methyl bromide ions must dissociate. If the peripheral charge on the Br^{80} is greater than +1, then charge distribution over the whole molecule will occur by the charge transfer process outlined in Section II,D, since the ionization potential of CH_3 (9.96 ev) is always less than that of singly or multiply charged bromine (first ionization potential 11.84 ev). The CH_3^+ fragment is the most common in the spectrum, and this suggests that after the electron transfer process has removed one electron from CH_3 to Br^{2+} , the molecule dissociates by Coulomb repulsion. Even in the case of $\text{CH}_3^+ + \text{Br}^+$ Eq. (4) yields 7.6 ev, considerably in excess of the C—Br bond energy of 2.3 ev. The appearance of C^{2+} and C^{3+} with small probabilities in the fragment spectrum suggests that in less frequent occurrences there may be intramolecular transfers of more than one electron.

F. BOND RUPTURE IN BETA DECAY

Molecules may be disrupted after beta decay of a constituent atom as a result of acquisition of recoil energy by the emitting atom, or as a result of electronic excitation or ionization by one of the processes described in Sections I,A,2 and I,A,3.

Early studies on the chemical effects of β^- emission showed that in the $\text{La}^{143} \rightarrow \text{Ce}^{143} + \beta^-$ transition the Ce daughter in most cases was oxidized by one unit (27, 69). Wexler (308) showed that the average charge on H^3H , C^{14}O_2 , and A^{41} after β^- decay was approximately 1+.

Studies of bond rupture in the beta decay of $\text{Pb}^{210}(\text{CH}_3)_4$ using the fact

that the daughter Bi^{210} is radioactive, demonstrated that about 80% of molecules survived the transition in the gas phase at 10 mm Hg pressure (74), despite the fact that emission of the beta particle is in this case followed by gamma decay with a high conversion probability. The maximum recoil energies from beta emission (0.006 ev) and ejection of the conversion electrons (0.12 ev) could not have led to bond rupture, but electronic excitation or ionization might have been expected to do so. More recent studies (15) indicate the relatively high stability of the $\text{Bi}(\text{CH}_3)_4^+$ formed as the initial product in the beta decay.

The chemical consequences of the beta-gamma decay $\text{Te}^{131} \rightarrow \text{I}^{131}$ have been studied in solutions of dibenzyl telluride in benzene and in the solid telluride (117). In the solid phase the Te—C bond was ruptured in at least 98.2% of the nuclear events as shown by the measured I^{131} retention in benzyl iodide. Assuming isotropic beta-neutrino emission 41.4% of the I^{131} atoms should have a kinetic energy of recoil of only 1.89 ev, and the hardest gamma quantum should have imparted a recoil energy of only 1.42 ev. Charge or electronic excitation effects due to shake-off or internal conversion probably account for the high percentage of bond rupture even in the presence of a cage of surrounding molecules.

The consequences of the $\text{C}^{14} \rightarrow \text{N}^{14} + \beta^-$ decay have been studied in ethane by preparing $\text{C}^{14}\text{H}_3\text{C}^{14}\text{H}_3$, the radioactivity of one of the carbons serving to trace the species resulting from beta decay in the other (332). In 47% of nuclear transformations $\text{C}^{14}\text{H}_3\text{NH}_2$ was obtained, i.e., the C—N bonds had not been ruptured. From Eq. (3), 59% of the kinetic energy of recoil from beta emission will be available to activate the C—N bond. The bond energy is 2.1 ev, so that only recoils with an energy greater than 3.6 ev should rupture the bond. Comparison of this value with the recoil spectra calculated for C^{14} with various assumed beta-neutrino interactions showed that ~74% of recoils have energy less than this value. Some cases of the observed bond rupture must therefore have been due to electronic excitation. Wolfsberg (336) has made a quantum mechanical calculation of the contribution of excitation to bond rupture, taking the lower limit for nondissociation to be the probability of a $1s^22s2p^3$ C atom becoming a $1s^22s2p^3$ positive N atom. This probability is found to be 0.815, so that on multiplying this by the 0.74 probability of failure to rupture bonds by recoil, the rough figure of 60% is found for the chance of molecular survival, in comparison with the observed figure of 47%.

The technique of charge spectrometry, mentioned in previous sections, has allowed a better appreciation of several aspects of molecular disruption by beta decay. Use of low gas pressures allows the primary products of molecular disintegration to be studied, free from collision-induced secondary reactions, while the mass-spectrometric technique allows detection and

measurement of the charge, mass and relative abundances of the molecular fragments.

Fragmentation spectra of molecules disrupted by the beta decay of H^3 have been obtained (310, 313, 316).

Study of the decay of tritio-ethane shows that $H^3 \rightarrow He^3 + \beta^-$ invariably results in disruption of the C—He bond. The He^3 always comes off as a neutral atom, the positive charge being taken by the organic fragment. The fragment $(C_2H_5)^+$ is dominant, constituting $\sim 80\%$ of the ion beam. In the remaining 20% of cases this "initial fragment" acquires sufficient excitation energy to dissociate further. Since $(C_2H_4)^+$, $(C_2H_3)^+$, $(C_2H_2)^+$, $(C_2H)^+$ and $(C_2)^+$ are found, the initial fragment can presumably dissociate

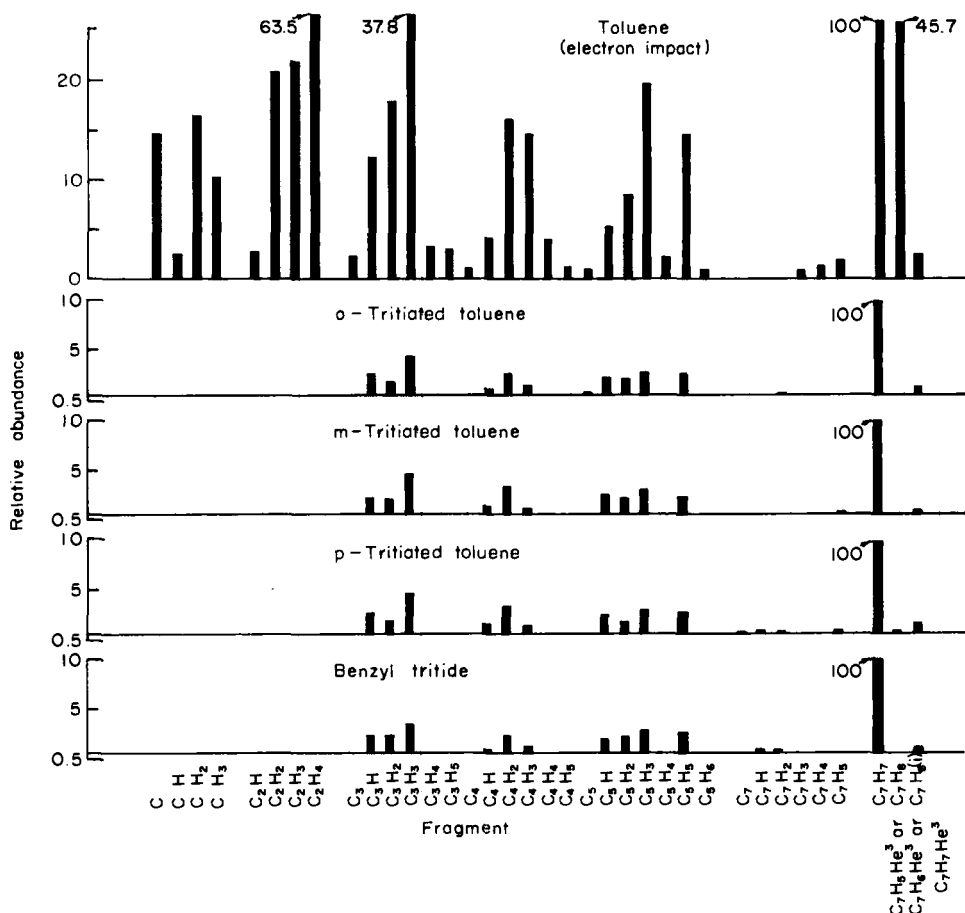


FIG. 3. Comparison of fragment ion yields from beta decay of mono-tritiated toluenes and from electron impact on nonradioactive toluene (313).

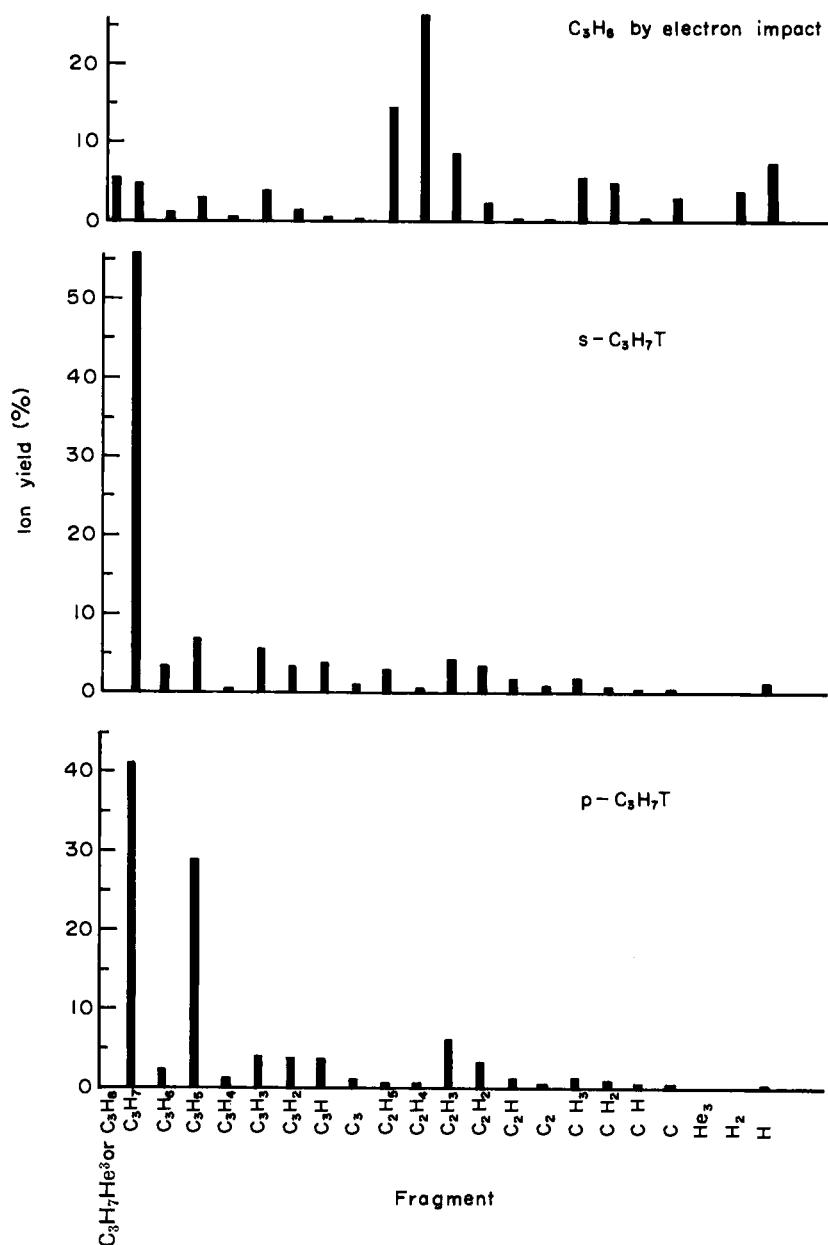


FIG. 4. Comparison of fragment ion yields from beta decay of mono-tritiated propanes and from electron impact on nonradioactive propane (313).

by loss of neutral atomic and molecular hydrogen. H^+ is not present in the spectrum to any significant degree.

Charge spectrometry has allowed some information to be obtained as to the influence of the position of the H^3 in a polyatomic molecule on the mode of disintegration (313). Fragmentation spectra have been obtained from primary and secondary mono-tritiated propane and from *ortho*-, *meta*-, *para*-, and *alpha*-monotritiated toluene, and are shown in Figs. 3 and 4. Similar general characteristics to those given for $C_2H_5H^3$ decay in the previous paragraph are found, but in addition certain specific features are present in the propane-toluene decay systems. The abundances of most of the singly charged fragments found from decay in propane are independent of the isomeric state of the compound. Exceptions to this are the fragments $(C_3H_7)^+$, $(C_3H_5)^+$, $(C_2H_5)^+$ and H^+ . The mass spectra for the four H^3 -toluenes are very similar, so that the mode of molecular disintegration in this case is largely independent of the position of the tritium in the molecule.

TABLE IV
YIELDS OF INITIAL FRAGMENT IONS FROM TRITIATED ORGANIC COMPOUNDS (310)

Molecule	Initial fragment ion	Ion yield %	Reference
CH_3H^3	CH_3^+	83	(275)
$C_2H_5H^3$	$C_2H_5^+$	80	(316)
<i>p</i> - $C_6H_4H^3$	$C_6H_7^+$	41	(313)
<i>s</i> - $C_6H_4H^3$	$C_6H_7^+$	56	(313)
$C_6H_5H^3$	$C_6H_5^+$	72	(44)
<i>o</i> - $C_6H_4H^3CH_3$	$C_7H_7^+$	78	(313)
<i>m</i> - $C_6H_4H^3CH_3$	$C_7H_7^+$	79	(313)
<i>p</i> - $C_6H_4H^3CH_3$	$C_7H_7^+$	76	(313)
$C_6H_5CH_2H^3$	$C_7H_7^+$	79	(313)

In endeavoring to interpret the results of beta fragmentation spectra it should first be pointed out that after beta emission involving no secondary electron ejection the daughter atom should bear a single positive charge. In fact $+1$ states predominate in the spectra, $+2$ ions occurring with a very low probability. The theoretical treatments of Migdal (199) and Levinger (170) show that any ionization initiated by beta emission occurs with highest probability in the outermost shells, so that bonding electrons of the excited atom are most likely to be affected. In all fragment spectra from H^3 decay in polyatomic molecules so far studied the daughter molecule ions formed directly by the transition are absent, while the yields of ions formed by splitting off neutral He^3 are high (310). The yields of such ions are shown in Table IV. In Section I,A,3 it was pointed out that on

theoretical grounds 67–70% of the $(\text{He}_3)^+$ ions should be formed in the ground state. In these cases one might expect the weak $\text{He}^3\text{—C}$ bond to rupture, but the initial fragment ions would have no energy capable of causing their further dissociation. The theoretical yield of initial ions thus predicted is in reasonable agreement with the values of Table IV. The apparent exceptions in the case of C_3H_7^+ are possibly due to the fact that the energy for H_2 removal is relatively lower for these ions than for others in the table (310, 313, 316). Transitions to low-lying energy states consequent upon beta emission may thus have been able to effect $\text{C}_3\text{H}_7^+ \rightarrow \text{C}_3\text{H}_6^+ + \text{H}_2$. The total yields of $\text{C}_3\text{H}_7^+ + \text{C}_3\text{H}_6^+$ may thus more accurately represent the percentage of events in which the initial fragment ion has zero or small energy of electronic excitation, and these total yields are 70% for *n*- $\text{C}_3\text{H}_7\text{H}^3$ and 63% for *s*- $\text{C}_3\text{H}_7\text{H}^3$, more nearly in accord with the remaining yields in the table.

It is desirable to find an explanation for the distribution of products resulting from further decomposition of the initial ion in the 20–30% of events in which sufficient electronic excitation has been imparted to it. To solve this problem Wexler and Hess (316) have applied the theory developed for the statistical treatment of mass spectra obtained from polyatomic molecules by electron impact. Rosenstock *et al.* (245) have proposed that after ionization by electron impact the molecule-ion possesses electronic and vibrational excitation energy. Decomposition does not occur until after several vibration periods, during which time a radiationless redistribution of energy amongst the various degrees of freedom can occur in random fashion with high probability. The molecule-ion then decomposes into ionized and neutral fragments when the nuclei are in the proper configuration and a sufficient amount of vibrational energy has concentrated in the necessary degrees of freedom.

In the case of H^3 decay in organic molecules it is considered that the $\text{He}^3\text{—C}$ bond is disrupted in a single vibration, since in the Franck-Condon transition the vibrational energy of the product ion exceeds the weak C—He^3 binding energy. In those cases in which the beta emission leads to higher states, the electronic excitation energy is randomly distributed over the initial ion, and step-wise dissociation of the ion occurs. The idea of randomization of energy is favored by the similarity of the dissociation spectra for the two H^3 -propanes and for the four H^3 -toluenes shown in Figs. 3 and 4. The application of statistical mass spectrum treatment is to some extent justified by the fact, shown in Fig. 3, that the types of ionic fragment are the same in both cases.

To test the applicability of the statistical treatment it is interesting to compare beta decay spectra with those obtained from molecular dissociation in charge transfer reactions (47, 48, 150, 160, 173, 174, 296). An advantage

of the charge transfer technique is that the activation energy is known and is equal to the recombination energy of the ion minus the ionization potential of the molecule, whereas in the electron impact studies the excitation energy supplied cannot be exactly determined. Table V shows considerable

TABLE V
ION YIELDS FROM H^3 DECAY, ELECTRON IMPACT AND
CHARGE TRANSFER DISSOCIATION IN PROPANE GAS

Ion	% Ion yield						
	H^3 decay in $p\text{-C}_3\text{H}_7\text{H}^3\text{a}$	H^3 decay in $s\text{-C}_3\text{H}_7\text{H}^3\text{a}$	Impact of 150-volt electrons ^a	Molecular dissociation from charge transfer with energies ^b			
				1.3 ev	3.2 ev	4.7 ev	10.4 ev
C_2H_3^+	<0.2	<0.2	6	0	0	0	0
C_2H_7^+	41	56	5	39	24	0	0
C_3H_6^+	2.2	3.4	1	7	6	0	0
C_3H_5^+	29	7	3	0	9	15	12
C_3H_3^+	4.0	5.3	4	0	0	0	38
C_2H_6^+	0.6	2.9	14	29	54	12	0
C_2H_4^+	0.5	0.7	27	22	9	8	0
C_2H_3^+	6.0	4.3	9	0	0	54	38
C_2H_2^+	3.2	3.6	2	0	0	9	8
CH_3^+	1.2	1.7	5	0	0	0	10

^a Ref. (313).

^b From figures in ref. (47).

differences in patterns of molecular dissociation from the three different modes of activation. C—C bond rupture is more frequent in both electron impact and charge transfer dissociation than in beta decay, as shown by the relatively enhanced yields of C_2 and C ions in the first two processes. Čermák and Herman (47) quote data obtained by Chupka and Kaminsky for electron impact in propane which agree well with the charge transfer dissociation spectra of Table V, after appropriate normalization of the energy axis. From this agreement they conclude that the fragmentation mechanism of excited polyatomic ions may be independent of the way in which excitation energy is supplied. The data for propane, however, seem to indicate some differences for activation by beta decay.

In the case of decomposition of toluene a somewhat different situation prevails. Impact of 50-volt electrons yields a rather different fragmentation spectrum from that obtained in beta decay, as shown in Fig. 4. The aromatic ring structure seems to be more resistant to decomposition by beta decay than by electron impact. Nevertheless, mass spectra from electron impact in mono-deuterated toluenes obtained by Meyerson and Rylander

(198, 254, 255) are rather similar to those from activation by beta decay. It has been suggested (255, 310, 313) that excited tolyl or benzyl ions from both modes of activation expand to form the 7-membered tropylium ring ion, which is the common precursor of all the observed fragments. A few differences are observed, however, in the benzyl tritide pattern, suggesting that the tropylium ion may not be the only pathway of decomposition.

Similar studies have been done using the $\text{Br}^{82} \rightarrow \text{Kr}^{82} + \beta^-$ decay in 1,2- $\text{C}_2\text{H}_4\text{BrBr}^{82}$ and $\text{CCl}_3\text{Br}^{82}$ (309, 310). The fragmentation spectra have the same general characteristics as those from H^3 decay. The C— Kr^{82} bond invariably breaks after the transition, leaving a positively charged initial ion which decomposes in some 30–35% of events.

From the ion yields after beta decay it is possible to estimate the distribution of excitation energy in the excited daughter molecular ion (310, 313). The quasi-equilibrium theory of molecular dissociation (245) is applied. The excited molecular ion is considered to dissociate by successive, competing, unimolecular reactions. Energetically plausible decomposition sequences of the type shown in Fig. 5 are constructed on the basis that energy of activation from electron impact appearance potentials (92)

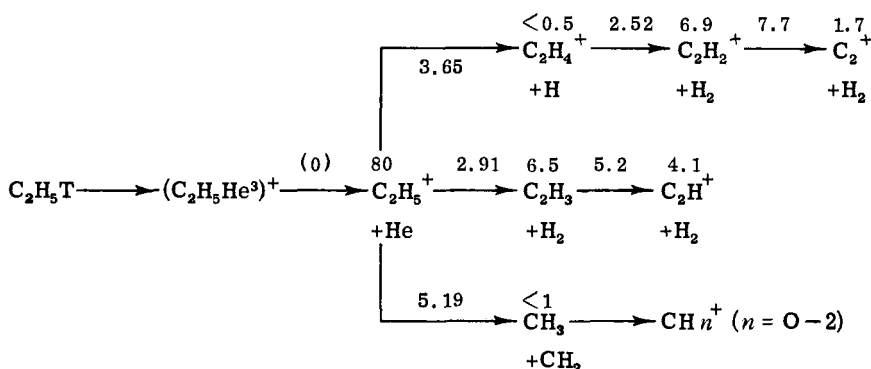


FIG. 5. A proposed mechanism for the formation of the mass spectrum from beta decay in $\text{C}_2\text{H}_5\text{H}^3$ (310). The numbers above the fragments refer to the observed relative percentage abundances. The numbers above the arrows indicate, in electron volts, the minimum energies required for the various decompositions. The reaction $(\text{C}_2\text{H}_5\text{He}^3)^+ \rightarrow \text{C}_2\text{H}_5^+ + \text{He}^3$ is assumed to require no activation energy.

must be equal to or greater than the heat of each particular unimolecular decomposition, aided by the observed presence of metastable ions in electron impact mass spectra. Supporting evidence for the validity of a scheme, such as that of Fig. 5, in which decomposition proceeds mainly by H_2 elimination, comes from electron impact studies (56). A histogram of the type shown in Fig. 6 can now be constructed in which the area under each rectangle is proportional to the experimental ion yield. The energy limits

for each ion are set by the differences between the appearance potentials of the particular ion and its daughter ion and the appearance potential of the parent ion in the sequence. The integral curve from the histogram yields the energy distribution from beta decay.

For beta decay in $s\text{-C}_3\text{H}_7\text{H}^3$ the energy distribution is found to be heavily weighted towards the lower energy values, 56% of the $(\text{C}_3\text{H}_7\text{He}^3)^+$ being formed with less than 2.1 ev (313). Above 2 ev the distribution is fairly flat tailing off to zero at about 18 ev. A similar distribution is obtained for mono-tritiated ethane (313, 316).

Comparison of the energy distributions thus found for the decay process with those quoted in Section I,A,3 from the theoretical treatments of

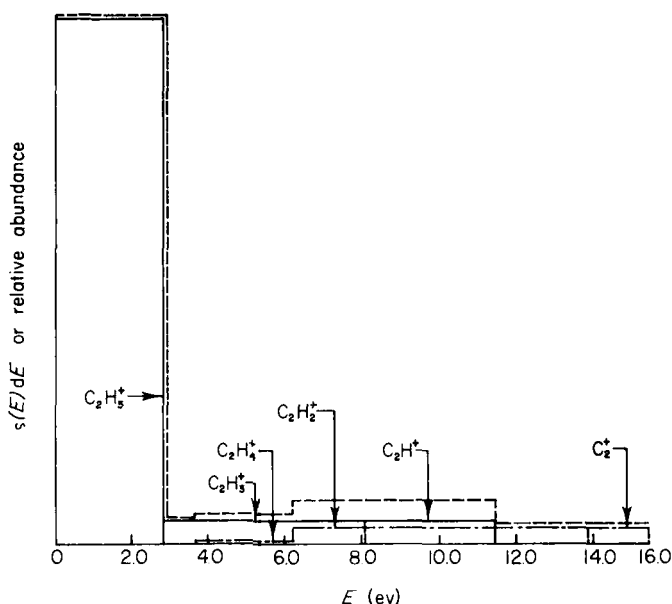


FIG. 6. Empirical breakdown histogram showing the derived distribution $p(E)dE$ of excitation energies in $(\text{C}_2\text{H}_5\text{He}^3)^+$ daughter ions following beta emission (310).

Migdal and Winther shows reasonable agreement. Theory predicts that 67–70% of the beta decays should yield zero excitation energies, while 25% of the He^3 daughters should have energies less than 20.5 ev. Experiment in the case of tritio- s -propane yields 56% of $(\text{C}_3\text{H}_7\text{He}^3)^+$ with energies less than 2.1 ev and a high energy limit of ~ 18 ev, while in the case of tritio-ethane 80% of the $(\text{C}_2\text{H}_5)^+$ have less than ~ 3.7 ev and the high energy limit is ~ 16 ev.

Beta decay effects have also been studied in tritium hydride (281, 311). The observed ion yields are $(\text{He}^3\text{H})^+$, 89.5–93.2%; $(\text{He}^3)^+$, 5.1–8.2%; H^+ ,

1.6–2.3%; $(\text{He}^3)^{2+}$, 0.14%. A marked difference from tritium decay in organic molecules is the strong tendency for $(\text{He}^3\text{H})^+$ to remain bound, at least for the $\sim 10^{-4}$ sec ion transit time in the spectrometer. Ion disruption can then occur by:



Since the $(\text{He}^3)^+$ yield is greater than H^+ there is a predominance of the reaction which involves one electron of the bond going to each fragment.

In considering the disruption of a diatomic molecule it must be remembered that the beta particle is emitted in a time which is very short by comparison with the periods of electronic and atomic motion, so that only vertical Franck-Condon transitions occur. Molecular dissociation will occur whenever the transition achieves a vibrational level higher than the dissociation limit of a bound daughter, or when a repulsive daughter state results, or when predissociative transitions can occur. The observed ion yield of 90% for $(\text{He}^3\text{H})^+$ suggests that the bulk of the transitions are to the $(\text{He}^3\text{H})^+$ ground state, and that most excited levels reached by the transfer of energy from the beta particle, or by subsequent radiation, are also attractive. Using the time-dependent sudden perturbation theory Cantwell (38) has calculated that the probability of transitions from the ground level of H^3H to the ground state of $(\text{He}^3\text{H})^+$ is 58%, and of these cases, 55% are to the three lowest vibrational levels which should be well below the dissociation limit.

Something must also be said about the role of kinetic energy of recoil in bond rupture by beta decay. The simplest case for discussion of this point is the diatomic molecule H^3H . The maximum beta energy of H^3 is 0.018 Mev so that from the formula given in Section I,A,1 the maximum recoil energy is 3.4 ev, and from Eq. (3) the bond activation energy will be 0.85 ev. The dissociation energy of $(\text{He}^4\text{H})^+$ is 1.75–2.05 ev (85), and therefore even the maximum available recoil energy will not dissociate the initial ion in its ground state (311). In addition, from the observed spectrum of H^3 beta rays it can be calculated that 92% of the recoils have $E_r < 2.0$ ev, so that $E_i > 0.5$ ev.

Although recoil energy thus plays a negligible part in decomposing $(\text{He}^3\text{H})^+$ in its ground state the possibility must be remembered that initial ions formed on sufficiently high vibrational levels may be induced by recoil to dissociate. In the case of the tritio-organic molecules referred to earlier in this section, Eq. (3) shows that almost all the recoil energy is available for bond rupture. If the C— He^3 bond were ruptured due to recoil energy alone, this would imply that the bond energy is very small since this bond is ruptured in virtually all cases and it can be calculated from the H^3 beta ray spectrum that 8% of recoils have energies less than 0.18 ev.

III. Formation of Chemical Bonds by Atoms Activated by Nuclear Transformation

A. GENERAL CONSIDERATIONS

Some of the earliest studies of the chemical effects of nuclear transformation in organic halides led to a comparison of the yields of organically bound radioactive atoms in gas, liquid and solid phases (319). These yields have commonly been called the "organic retention." Retention was usually in the range 0–10% for gases, as shown in Table II. In solids or liquids retentions were usually in the range ~20–90%. It was concluded that in the case of gas phase studies the frequency of primary bond rupture by the nuclear process was being observed, whereas in liquids or solids the initially freed radioactive atom was re-entering into organic combination (secondary retention).

Several models were advanced to account for secondary retention. These models have been well reviewed elsewhere (31, 66, 124, 319) so that here only a brief account will be given of the features particularly significant for gases and liquids. Harbottle and Sutin (124) and Yankwich (399) have discussed the implications of the models for recoil reactions in solids.

The elastic-collision "billiard-ball" model proposed by Libby (172) assumes that a recoiling atom, with kinetic energy considerably greater than bond energies, frees itself from its parent molecule and then loses its excess energy predominantly by elastic collisions with atoms of its environment. In nearly head-on collisions with atoms of similar mass most of the kinetic energy can be transferred to the struck atom, which may be dislodged from its chemical bonds. If the recoil is left with kinetic energy below a certain critical value necessary for escape from the collision site, bond formation will occur between the recoil and the molecular residue. At kinetic energies exceeding ~20 ev the energy of the incident atom is very much greater than the energies of bonds within the struck molecule, and the effective duration of the collision is very much less than the time required for intramolecular vibrational relaxation, so that energy from the collision is inefficiently transmitted along the bonds. Thus the "hot" recoil strikes a molecule which can be regarded as a loosely coupled collection of atoms.

This model has been developed further by Miller, Gryder, and Dodson (201), and by Capron and Oshima (42). The model predicts that in solids the cage of molecules surrounding the collision site would oppose escape of the suddenly cooled recoil, thus favoring high organic retention, whereas absence of such a cage in gases should give low retentions, as observed. Willard (319) has reviewed the extensive evidence bearing out these predictions in gas, liquid, and solid phase irradiations of organic halides with neutrons.

Epithermal reaction schemes were proposed as modifications to the billiard-ball model by Libby (172) and Miller and Dodson (200). It is found that nuclear activation can lead to reactions not efficiently initiated by thermal or photochemical means (see, e.g., 200 together with 243), and this suggests that some of the atoms recoiling from nuclear transformation enter into organic combination during the energy-loss process before thermalization. The reaction mechanism of Miller and Dodson focuses attention on the epithermal energy range of a few ev, in which the recoil can form an excited complex with an organic molecule, which then decomposes into various products incorporating the radioactive atom (200). Alternatively, in the "strong coupling" epithermal model, after cooling by collisions to ~ 10 ev, the recoil can undergo inelastic collisions in which it imparts energy to the struck molecule as a whole (66, 93, 172). Vibrational excitation of the molecule may then lead to dissociation into fragments which can combine with the radioactive recoil. These models account for the fact that the radioactive atom is found in molecules other than those of the parent type (see Section III,B,2), and for the fact that solutions of elementary halogens or arsenic in hydrocarbons yield organically bound radioactive atoms on neutron irradiation (37, 125, 178, 236, 273, 319). Like the billiard-ball mechanism the epithermal reaction models can predict a phase effect, since a cage of adjacent molecules may act to hold the recoil in close contact with the fragments of the molecule disintegrated by the inelastic collision.

The billiard-ball and epithermal models involve "hot" highly localized reactions which should not be influenced by low concentrations of scavengers capable of removing thermalized free radicals. The observed effect of small amounts of such scavengers on organic retention (see Section III,B,2) has suggested to Willard (319) a process in which the thermalized recoil atom encounters by diffusion some of the radicals which it has produced by collision along its track, and then combines with them. The diffusion-dependent recombination processes will be scavenger-sensitive. This mechanism has been called the "brush-heap" or "random-fragmentation" model. It predicts a phase effect on the distribution of radioactive products in two ways. In the first place the relative probability of different types of bond rupture caused by the recoil in inelastic collisions will vary with the density and crystal structure of the medium. In the second place the phase conditions will influence the relative chances of diffusion of the various fragments away from the immediate vicinity of the thermalized recoil.

The models described above have been developed almost entirely from work on neutron-irradiated organic halides. It can be seen that they predict both "hot" reactions (billiard-ball and epithermal) and "thermal"

reactions (brush-heap), a variety of products incorporating the recoil (epithermal and brush-heap) and definite phase effects (all three). Since the earlier work with organic halides the experimental basis has been considerably widened, particularly by the use of hot H^3 atoms and by work with polyvalent recoils, and the relative roles of these three mechanisms are now somewhat better understood. In addition, as will be seen, the work with H^3 recoils has suggested important revisions of the models described above.

Theoretical studies of the mechanisms involved in hot collisions have been commenced. Magee *et al.* (194, 207) have examined the probability of dissociation of diatomic molecules induced by collision with an atom having a velocity in the range $\sim 10^6$ – $\sim 10^8$ cm/sec, for which the collision is adiabatic with respect to electronic state but non-adiabatic with respect to vibrational and rotational state. In a hot collision the energy is large by comparison with the binding energy of the molecule, so that the only region of the interaction curve for which the potential energy is as large as the total energy is that for which the nucleus of the incident atom approaches very closely to one of the nuclei of the molecule. In such a region the potential energy of the system arises almost exclusively from the interaction of the atoms which are close together, so that a reasonable approximation is to treat the potential energy of the system as a sum of terms arising from individual interactions between pairs of atoms. It is found for the HBr molecule that the curve for an r^{-2} potential reasonably approximates to the curve based on the Seitz interaction potential (266). The r^{-2} potential is also to some extent justified by range-energy relationships observed for recoils (194), and has been adopted in calculations of bond rupture probability as a considerable advance on the billiard-ball potential, which is 0 for $r \geq r_0$, and ∞ for $r < r_0$. Curves of the probability of dissociation of HBr, $P_D(\Delta E)$, have been derived as a function of the energy, ΔE , transferred to the HBr molecule in a hot collision with H or Br atoms (194). It should, however, be borne in mind that the approximation of deriving the potential energy for the whole collision system from individual pair-interactions will be reasonably valid in the high energy region, but will lose validity with decrease in energy, and will be less valid for collisions in which there is a small angle between the momentum impulse of the struck atom and the direction of its bond to the rest of the molecule.

B. HOT REACTIONS RESULTING FROM NUCLEAR ACTIVATION

Hot reactions may be expected to have some of the following characteristics (322):

- (a) They may yield products not formed by thermal reactions.
- (b) They should be temperature independent.

- (c) They should not be affected by low concentrations of radical scavengers.
- (d) They may be influenced by adding inert additives that remove the kinetic, vibrational or electronic energy of the activated species before it undergoes a retention-causing collision.

1. Hot Reactions in the Gas Phase

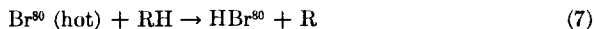
Hot reactions have been demonstrated in gas-phase studies of halogens activated by neutron capture. The reaction $I^{127}(n,\gamma)I^{128}$ in gaseous CH_4 gives 43–51% I^{128} as CH_3I^{128} (136). In this case billiard-ball collisions as originally conceived are ruled out since only I-C and I-H collisions can occur. Two possibilities have been suggested for the retention-causing mechanism. In the first case the iodine could react by imparting sufficient of its kinetic energy of recoil to the I^{128} - CH_4 complex to overcome the endothermicity of the reaction. In the second case internal conversion of the (n,γ) quanta could impart a positive charge to the I^{128} (314). During neutralization of this charge the I^{128} could acquire energy of electronic excitation, as mentioned in Section I,A,3, and the excited I^{128} could then react with CH_4 . The various displacement and abstraction reactions by which I or I^+ can react with methane are endothermic by amounts varying from 0.78 to 4.98 ev. For the kinetic energy mechanism Eq. (3) requires that the iodine atom or ion should have an energy $(128 + 16)/16 = 9$ times the endothermic energy of the reaction, i.e., in the range ~ 7 –35 ev. Clearly such an energy would be available in a considerable percentage of the nuclear events, since the maximum recoil energy from $I^{127}(n,\gamma)I^{128}$ is 182 ev, corresponding to emission of a single quantum.

An attempt has been made to discriminate between the above two mechanisms by adding inert gas moderators to remove the I^{128} kinetic energy before it collides with CH_4 , and by adding gases which have lower ionization potentials than atomic iodine to remove the I^{128} charge before collision with CH_4 (169). He, Ar, and Xe moderators reduce the CH_3I^{128} yield. The number of collisions necessary to reduce the I^{128} recoil energy from its maximum value to thermal energies can be calculated from collision theory. The probabilities that I^{128} recoil energy will be reduced below the threshold for a retention-causing reaction are found to be greater than the fractional reductions in retention, suggesting that the kinetic energy mechanism is not entirely responsible for retention. Gases such as I_2 , CH_3I , C_2H_5I , C_3H_7I , and NO, which have lower ionization potentials than I, were in general more effective than the inert gases in lowering CH_3I^{128} yield, suggesting that the mechanism based on the I^{128} charge must play some part. Further studies have shown that large excesses of inert gas moderator cannot completely suppress the retention (237).

When the curves of organic I^{128} yield versus mole fraction additive are extrapolated to unit mole fraction additive in the case of neutron irradiated $I_2 + CH_4$, it is found that the organic yield is 36% in the case of Ne, A, and Kr additives but only 11% in the case of Xe additive (237). The retention of I^{127} in organic combination in the absence of any additive is 54%. It is considered that the reduction of organic yield from 54 to 36% is the result of removal of excess kinetic energy by the inert gas moderator. The additional reduction from 36 to 11% observed in the case of xenon is not likely to be due to quenching of I^{128} excited states, since inert gases are not effective quenching agents. It is more likely that the 25% drop in organic yield is due to charge transfer from the I^{128} to the xenon. The picture emerges of 18% of organic I^{128} resulting from hot reactions involving high kinetic energy, 25% resulting from $I^{128} + CH_4$ reaction inhibited by xenon, and 11% resulting from reaction of CH_4 with I^{128} ions or highly excited atoms not quenched by xenon. When O_2 , N_2 , and CF_4 are added to $I_2 + CH_4$ mixtures before neutron irradiation, the organic yield curves extrapolate to 36%, so that these additives can only moderate the high kinetic energy reaction (237a). On the other hand C_2F_6 and CH_2F_2 reduce the organic yield to 11%, so that these gases can undergo charge transfer or perhaps competitive reaction with $I^{128} + CH_4$. NO , CH_3I , CF_3I , $n-C_3H_7I$ and C_6H_6 reduce the organic yield to zero at unit mole fraction, and are thus capable of inhibiting all reactions of I^{128} with methane. The ionization potentials of these last additives are all less than that of the iodine atom, so that the 11% $I^{128} + CH_4$ reaction may be being inhibited by charge transfer with I^{128} ions. Alternatively the I^{128} ions may be being trapped in organic form by an exoergic charge transfer reaction of the type $I^+ + CH_3I \rightarrow I_2^+ + CH_3$.

In the case of the $Br^{79}(n,\gamma)Br^{80}$ reaction in methane the efficiency of inert gas moderators in lowering the organic retention increases in the order He, Ne, A, Kr, Xe, which is the order of increased energy transfer per Br^{80} -inert gas collision (236). Furthermore a plot of organic retention versus mole fraction CH_4 extrapolates to $0 \pm 2\%$ at zero mole fraction CH_4 . In this system it seems that organically bound Br^{80} results mainly from the kinetic energy mechanism, a conclusion strengthened by the finding that Eq. (8) of the Estrup-Wolfgang theory described later is applicable.

Williams and Hamill (325) found that a certain percentage of HBr^{80} was formed as a result of the $Br^{79}(n,\gamma)Br^{80}$ reaction in gaseous $C_2H_5Br + C_2H_4 + HBr$, even at high ethylene pressures and suggested a hot gas phase reaction of the type:



Willard *et al.* (103, 136, 169) have pointed out, however, that it is

generally difficult to separate the possibility of a hot gas phase reaction of this type from the possibility of ion-molecule reactions. In the case of the $\text{Cl}^{37}(n,\gamma)\text{Cl}^{38}$ reaction in gaseous $n\text{-C}_4\text{H}_9\text{Cl}$ and $n\text{-C}_3\text{H}_7\text{Cl}$, with or without HCl , a fairly constant organic retention of 10–16% was found (51). The authors concluded that the observed constancy of retention irrespective of chain length indicated that the probability of collisions of the Cl^{38} with a chlorine atom, relative to the probability of collisions with other parts of the chain plays no part in the mechanism. They suggested that momentum-transfer properties were unimportant, and that an ion-molecule interaction probably occurred after internal conversion of the (n,γ) quanta. Ion molecule reactions of the type which could form organic halides have high velocity constants in the gas phase (88, 259, 285, 297) and large charge-exchange cross-sections may be found consequent upon facilitated transition from kinetic to excitation energy (296).

Estrup and Wolfgang (79) have developed a kinetic theory of hot-atom reactions. These reactions differ from low-energy interactions, for which $K = pZ \exp(-\Delta E/RT)$, in that $E \gg \Delta E$, so that $\exp(-\Delta E/RT) \approx 1$. It emerges that in the high energy region p is not constant but energy dependent.

The Estrup-Wolfgang theory assumes that:

- (a) the recoil loses energy in elastic collisions,
- (b) the recoil has an initial energy, E_0 , and that when the energy has been reduced by collisions into a range $E_2 - E_1$, retention-causing reactions can occur.
- (c) $E_0 - E_2$ is sufficiently large for a number of collisions to have been made before the $E_2 - E_1$ range is reached, so that a statistically well-defined distribution of energies prevails within this range.
- (d) $E_1 \gg$ thermal energies.

Applying usual theory for elastic collisions to the slowing down process (97, 306) it is found that the radioactivity of a single product of hot reaction, A_i , can be related to the activity of all products of reaction, A_s , by the expression:

$$\frac{A_i}{A_s} \frac{\alpha}{f} \approx I_i - \frac{f}{\alpha} K_i. \quad (8)$$

In this equation α is the logarithmic energy decrement given for elastic collisions by:

$$\alpha = 1 - \frac{(M - m)^2}{2Mm} \ln \left[\frac{M + m}{M - m} \right] \quad (9)$$

where m is the mass of the hot atom, and M the mass of the struck molecule (97).

In Fig. (8), f is the relative probability of collisions between the hot atom and molecules capable of giving the product for which A_i is measured. I_i is an integral of the form:

$$I_i = \int_{E_1}^{E_2} \frac{p_i(E)}{E} dE \quad (10)$$

in which $p_i(E)$ is the energy-dependent collision efficiency with a type i compound. K_i is given by:

$$K_i = \int_{E_1}^{E_2} \frac{p_i(E)}{E} \int_E^{E_2} \frac{p(E)}{E} dE dE \quad (11)$$

Equation (8) can be used to test the validity of the theory. If the radioactivity of a single product can be determined, then a plot of $\alpha/f \times A_i/A$, against f/α should approximate to a straight line, at least for small values of f . If a straight line is obtained this yields some evidence that the reaction considered is a hot one.

Tests of this kind have been applied by Estrup and Wolfgang to products from the $\text{He}^3(n,p)\text{H}^3$ reaction in CH_4 with inert gas moderator (79, 80). In previous work (77, 78, 103) it had been shown that HH^3 , CH_3H^3 , and CH_2H^3 are probably formed by hot reactions. Small amounts of radical and ion scavengers such as I_2 gas did not affect the yield of these products, whereas there was a marked depression of the HH^3 yield due to thermal abstraction of H from CH_4 or of the combination of thermalized H^3 with radiation-formed species to form higher tritiated hydrocarbons. The presence of excess helium reduced the yield of the hot products by acting as moderator (77). Altering the temperature during the irradiation did not affect the yield of hot products (77). Nitric oxide and oxygen could also be used as scavengers to test which of the products were formed by hot reaction (161, 247).

Figure 7 shows that Eq. (8) does in fact apply to the activities of CH_3H^3 in the presence of inert gas moderators. Rack and Gordus (236) have applied the Estrup-Wolfgang theory to the total yield of organically retained Br^{80} after activation by neutron capture in CH_4 with inert gas moderators and have found evidence of a linear relationship between α/f [% Br^{80} as organic] and f/α within fairly large margins of error. Similar results were obtained with the $\text{I}^{127}(n,\gamma)\text{I}^{128}$ reaction in CH_4 (237).

It has been pointed out (189) that the Wolfgang-Estrup theory assumes energy loss by elastic collisions, an assumption valid for monatomic inert gas moderators in methane, but not necessarily applicable in other cases. It has been maintained (331) that the theory is not sensitive to the assumption of elastic collisions. In the regions of low moderator concentration and thus largely inelastic collisions the expressions are not sensitive to the col-

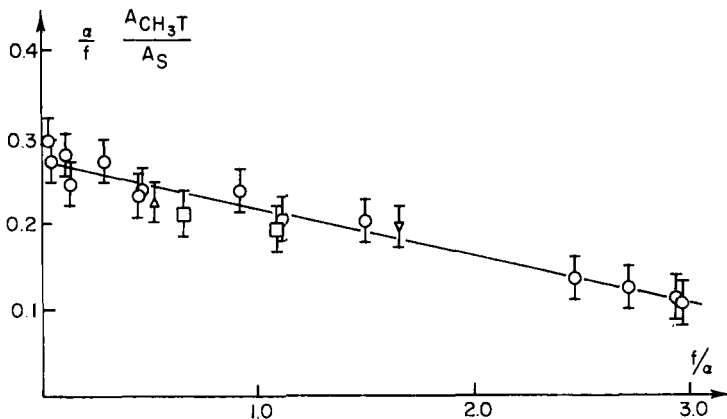


FIG. 7. Relationship between $(\alpha/f)(A_i/A_s)$ and f/α of Eq. (8) for H^3 recoils in methane with inert gas moderators (79).

lision parameter, α , while in the α -sensitive region of high moderator concentration the bulk of collisions will be elastic.

Gordus *et al.* (102c) have given a preliminary announcement of a hot atom reaction model based on the treatment developed by Miller *et al.* (201) to deal with high-energy reactions in binary liquid systems. The treatment of Gordus *et al.* allows direct calculation of the average reaction probability per energy increment, I of Eq. (10), from thermodynamic and transport property data, and can be adapted to include the effects of moderation by inert gases. The model apparently accounts successfully for the HH^3/DH^3 yield ratio for H^3 recoils in H_2 - D_2 mixtures (164), the $A_{CD,H^3}/A_s$ values for H^3 recoils in CD_4 with inert gas moderators (66), and the observed yields of various products of reaction of hot H^3 , Br^{80} and I^{128} atoms with gaseous CH_4 , C_2H_6 , and C_3H_8 .

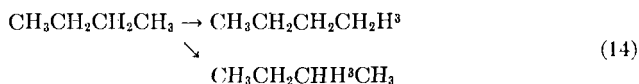
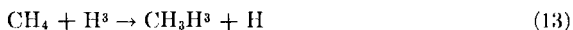
Semiquantitative agreement has been obtained between the observed probability of formation of H^3 - n -pentane from H^3 recoils in n -pentane gas as a function of He^4 moderator concentration and the probability of collision of an H^3 atom with n -pentane before thermalization, calculated from simple collision theory (67).

With the establishment of the validity of the concept of hot atom reactions at relatively high kinetic energies it becomes of importance to study their systematic chemistry, to gain information as to their energy dependence and collision efficiencies, and to investigate the way in which energy is transferred and reaction is induced in the hot collision. After information of this type has been gained it should be possible to test the validity of the reaction models discussed in Section III,A.

In recent years the systematic chemistry of reaction of hot hydrogen

atoms with organic molecules has begun to be investigated, using the $\text{He}^3(n,p)\text{H}^3$ or $\text{Li}^6(n,\alpha)\text{H}^3$ reactions with recoil energies of 2.730 and 0.192 Mev respectively (128, 129, 247, 251, 302).

A prominent scavenger-insensitive reaction in alkanes is substitution or displacement of a carbon-bonded hydrogen (161–164, 301, 303):



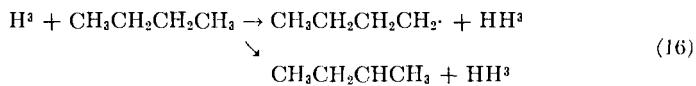
The high yield of the recoil tritium substitution reactions with molecules such as methane or cyclopropane (77, 161, 163), with which thermal hydrogen atoms react with low efficiency, confirms the hot or epithermal nature of the substitution reaction.

The moderator-sensitive part of the high organic yield of radio-iodine (136, 169), radiobromine (104) and radiochlorine (51, 83), observed when the halogens undergo radiative neutron capture in gaseous hydrocarbons as discussed earlier, shows that hot halogen atoms can initiate a direct displacement reaction of the type of Eq. (12).

Hot hydrogen abstraction is also commonly observed (77, 129, 247, 303):

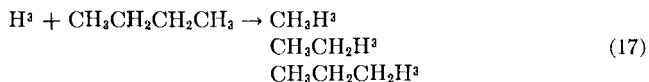


e.g.,

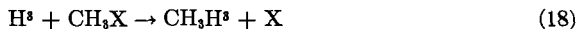


The abstraction reaction is also observed at thermal energies, although with a much lower collision yield (16, 17). It should be pointed out that observation of the HH^3 product is not in itself proof of abstraction, since this product might be eliminated from an excited molecule. On the other hand hydrogen loss would be random, so that the low yield of tritiated alkenes found in practice shows that H^3 elimination from an excited molecule is relatively unimportant.

A hot reaction with tritium may less frequently lead to replacement of an alkyl group to form a degraded alkane (77, 78, 162, 303):



Fluorine, chlorine, bromine, and iodine in alkyl halides can be displaced by a hot hydrogen atom (225):



Halogens and nitro-groups can also be displaced by hot hydrogen reactions in aromatic systems (247, 318).

Relatively infrequently a hot tritium atom may displace two hydrogen atoms or one hydrogen atom and an alkyl group to form a radical (129, 162, 303), e.g.:

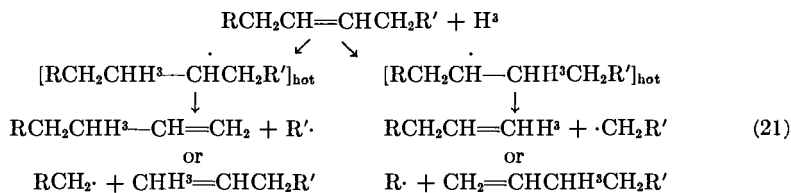


The resulting radical may combine with iodine scavenger to yield an alkyl iodide, or it may break a C—C bond without rearrangement to give a smaller radical and an alkene:



Only methyl and ethyl iodides have been found so direct combination with scavenger is only possible for methyl and ethyl radicals. Larger radicals always decompose by reaction (20) until methyl or ethyl radicals are formed.

In the case of recoil tritium reactions with alkenes it is found that most of the hot reactions are similar to those described for alkanes (301, 302). Oxygen can be used as a scavenger for thermal atoms and radicals. Some H^3 -labeled alkenes of smaller molecular weight than the parent are formed in relatively large yields. It is proposed that in these instances a hot H^3 atom is added to a double bond, forming an excited radical, which will probably decompose to a smaller radical and an olefine by breaking a weak bond (156, 186):



Since the addition of a hydrogen atom to a double bond is exothermic one might expect the reaction to proceed with thermalized H^3 atoms. The yield of the product is not appreciably affected by small amounts of oxygen as radical scavenger, which suggests that the mechanism is not a thermal one. On the other hand, when helium is introduced as a moderator the yield of reaction products is greatly reduced (301).

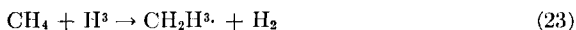
It has also been shown that there is an increase in the yield of the major alkene fragments at low pressures (166), which indicates that one of the intermediates in the sequence of Eq. (21) is sensitive to collisional deactivation.

It should be borne in mind that yields of alkenes of lower molecular weight could in some cases be explained by direct displacement of alkyl groups. However, such a mechanism does not readily explain the large yields of $\text{CH}_2=\text{CH}_2$ and $\text{CH}_2=\text{CHCH}_3$ but small yield of $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ from $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$, or the formation of $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ from $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_3$.

There are considerable difficulties in extracting information from hot atom studies as to the energy dependence of collision efficiencies for high-energy interactions, or as to the modes of transfer of energy to the struck molecule. The Estrup-Wolfgang theory contains $p(E)$ in the definite integral, I , of Eq. (8). Nevertheless some information on collision efficiency energy dependence can be obtained by studying the relative energies at which various products can appear in a given system.

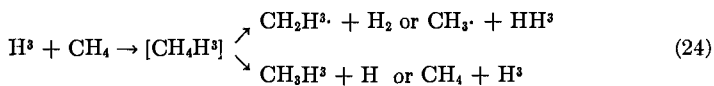
Tritium has been allowed to recoil in systems in which reactions with saturated or unsaturated positions are competitive. The specific activities of propane and transbutene, for example, are very similar after irradiation of a system containing a mixture of the two gases, indicating that a hot H^3 atom reacts with comparable efficiency at saturated and unsaturated positions (162), despite the fact that the relative rates of exchange with thermal deuterium atoms differ by a factor of more than 1000 (298). Varying the pressure of an inert gas moderator, such as helium, alters the energy distribution of the recoils in the range of their reaction-causing collisions with competing organic constituents. As the moderator concentration rises in the propane-acetylene system there is a linear rise in the specific activity ratio acetylene/propane (247). The reaction efficiency will start from zero at H^3 kinetic energies lower than the activation energy, then rise to a maximum, and again fall to zero at energies too high to allow stable bond formation during collision. The propane-acetylene results can be explained by assuming that the curve of reaction efficiency as a function of kinetic energy passes through its region of high efficiency at a lower energy value in the case of acetylene than in the case of propane.

When H^3 recoils through methane in the presence of I_2 , CH_3H^3 , and $\text{CH}_2\text{H}^3\text{I}$ are formed as a result of the direct displacement and abstraction reactions:



When these reactions are allowed to occur in the presence of varying concentrations of helium or neon moderators and iodine scavenger, the curves of relative yields of CH_3H^3 and $\text{CH}_2\text{H}^3\text{I}$ against mole fraction CH_4 are very similar, suggesting that the reactions of Eqs. (22) and (23) proceed with a very similar energy dependence of the reaction efficiency.

In general it is observed that displacement or abstraction reactions of the type of Eqs. (12) and (15) together account for about 90% of the hot H^3 reactions, while less than 10% involve displacement of an alkyl group as in Eq. (24) (129, 303). The probability of C—H bond rupture is thus about four times greater than that of the C—C rupture. This finding perhaps indicates that hot displacement reactions do not go via a common collision complex of sufficient lifetime to permit internal equilibration of energy. Magee and Hamill (196) have developed a theoretical treatment to account for photochemically hot reactions, i.e., 1–2 ev, which is based on the applicability of absolute reaction rate theory and the involved assumption of equilibration of energy between all degrees of freedom. Wolfgang *et al.* (129) consider that while this theory may be valid for the energy range for which it is intended, extension to the range which is of interest here is not valid since such an equilibrated complex should break a weak bond at least as often as a strong one. These authors point out that if HH^3 and CH_2H^3 were produced from methane by decomposition of a common activated complex with indistinguishable H^3 and CH_4 hydrogen atoms as follows:



then the ratio HH^3/CH_2H^3 would be expected on a statistical basis to be 2:3. In fact the highest value of the observed ratio is 9:1 (77).

Experiments on stereochemical effects in hot hydrogen displacement reactions throw further light on energy transfer in hot gas phase reactions. Recoil H^3 reacts with gaseous optically active *sec*-butyl alcohol to give 91% retention of configuration about the asymmetric carbon atom during displacement of the hydrogen bonded to it, or during displacement of the hydrogen in the methyl and ethyl groups (128, 130). Similar retention of configuration has been found in solid phase irradiations of optically active glucose (146, 249), alanine (145, 250) and maleic and fumaric acids (247), although the possibility of constraint to retain configuration by the surrounding lattice somewhat limits the usefulness of conclusions drawn from solid phase experiments.

The greater probability of C—H than C—C bond rupture, the retention of optical configuration, and the absence so far of evidence for equilibration of energy in the collision complex, have together suggested a rather simple mechanism for hot reactions with H atoms. It has been proposed (128), that the hot H^3 atom can approach the H atom, which will be removed, over a relatively wide range of directions. Approach along the C—H bond axis will not give displacement, since H^3H juxtaposition is hindered, although abstraction could occur in this situation. The picture is

thus developed of approach of the hot H^3 atom within a cone of small angle leading to abstraction, while approach within a cone of wider angle leads to displacement.

A consequence suggested by this simple theory is that steric factors arising from molecular structure should influence the ratio of efficiencies for displacement and abstraction reactions. The abstraction/displacement ratio is found experimentally to be unity in the case of methane, having perhaps no obstruction for wide angle approach to any of the four hydrogens. As hydrogen atoms are replaced by the bulkier methyl or ethylene groups, the efficiency for the wide-angle displacement reaction should be reduced relative to that for the small angle abstraction, say by a factor $(1 - \Omega)$. Thus for an alkane containing n hydrogens, of which n_1 are primary, n_2 are secondary, and n_3 are tertiary, on the rather simple assumption that any attached group offers the same obstruction, we would expect:

$$\frac{\text{Abstraction yield}}{\text{Displacement yield}} = \frac{n}{n_1(1 - \Omega) + n_2(1 - \Omega)^2 + n_3(1 - \Omega)^3} \quad (25)$$

Using a value 0.45 for the obstruction parameter Ω , it has been found that a good correlation is obtained between the values of abstraction yield/displacement yield calculated from Eq. (25) and those obtained experimentally for a series of non-cyclic alkanes and cyclopentanes (128).

The dependence of abstraction/displacement ratios on steric obstruction of the displacement reactions has been disputed by Root and Rowland (128), who consider that abstraction is dependent on C—H bond strength and will be facilitated at a more weakly bonded secondary carbon. More work will be needed to resolve this point.

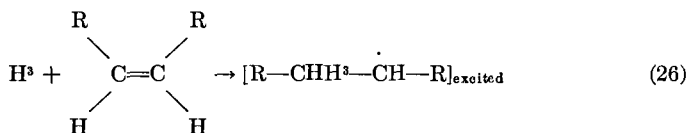
Considerations of steric hindrance would also suggest that displacement of an alkyl group as in Eq. (17) should be less frequent than displacement of an atom as in Eq. (12), and this is found to be the case (128). The probability of forming an alkane product RH^3 is found to increase with increase in the number of R groups in the molecule as expected, so that, for example, the relative yield of CH_3H^3 increases in the series cyclopentane < *n*-pentane < isopentane < neopentane (128). The reaction of recoil H^3 with neopentane yields eight times as much methane- H^3 as isobutane- H^3 (128), and this can be interpreted as showing that the H^3 preferentially reacts with the group which has the larger overall angle of approach, i.e., with the smaller of the two groups joined by the C—C bond.

Recoil H^3 reactions with toluene gas have been studied (1). The distribution of H^3 in the labeled toluene is CH_3 , 22%; *ortho*-, 17%; *meta*-, 14%, and *para*-, 16%. There is thus a distinct preference for H^3 reaction with the methyl hydrogen, but a relatively minor orienting effect with regard to the ring positions.

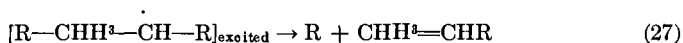
Comparison of the activities in various products formed by H^3 recoils in gaseous alkenes with those obtained with alkanes lends further support to the "cone-of-approach" interpretation of hot hydrogen reactions outlined above. Abstraction and displacement reactions will occur at C—H sites in alkenes in the same way as in alkanes, but in addition reaction at the double bond will yield decomposition products by the mechanism of Eq. (21), thus reducing the yields of HH^3 and H^3 -parent type molecules. One would thus expect a rise in the relative yield of HH^3 with increase in number of carbon atoms in a mono-alkene, and that this yield should always be smaller than for the corresponding alkane. This is found to be the case (302).

In considering the transfer of energy to a struck molecule in a hot reaction it must be remembered that unless the departing group takes off all excess energy the radioactive daughter molecule will not be in thermal equilibrium with its environment. Excess energy may be removed by collision, or may lead to decomposition or intramolecular rearrangement of the hot reaction product. In cases in which collision deactivation competes with decomposition or rearrangement, the distribution of reaction products will be sensitive to gas pressure or presence of an inert moderator. When H^3 recoils in cyclopropane with NO scavenger, for example, a displacement reaction leads to formation of a vibrationally excited H^3 -cyclopropane molecule. This molecule can isomerize to propylene. The propylene yield decreases with increase in the pressure of cyclopropane (163, 247). Similar reactions have been observed with *cis*- and *trans*-1,2-dimethyl-cyclopropane (247).

The pressure-sensitivity of the yield of the major fragments from the reaction of hot H^3 with alkenes (166) has already been mentioned in this section. It has also been shown (162, 247) that recoil H^3 reacts with olefins to yield a radical:



A pressure-dependent competition is found to exist between decomposition of the radical:



and collisional de-excitation to a thermal radical which reacts to give a saturated molecule. Thus the yield of labeled propylene from *trans*-butene-2 and *cis*-butene-2 via the reaction of Eq. (34) is higher at lower pressures.

The amount of excess energy transferred to the hot reaction product must often be small, since the yield of radioactive products requiring multiple bond rupture is frequently low. Only traces of acetylene, for example, are formed from hot H^3 reactions with alkanes, while the yield of methyl acetylene and allene by reaction with alkenes is less than 1% (128, 165). The small amount of excess energy in the hot reaction product can sometimes effect an intramolecular rearrangement without decomposition. Thus it is found (128) that in 30% of hydrogen displacements at the sp^2 carbon atom in *cis*- and *trans*-dichloroethylenes the initial configuration is lost by an intramolecular process which has an energy of activation of about 2 eV. The fact that such a low energy intramolecular process occurs in a minority of events, together with the infrequency of multiple bond rupture, suggests that the amount of excess energy deposited in the hot reaction product is often very small, and it may require a relatively low energy process of isomerization e.g., rotation about a double bond to reveal it. This suggestion is supported by the finding that in the stable alkanes, where the only collisional process which could dissipate the excess energy is decomposition into radicals, the yield of such radicals is found to be only $\sim 5\%$. In addition part of the observed radical yield could have been given directly by a process of the type shown in Eq. (19). In the case of the isomerization of cyclopropane to yield propylene, discussed in the previous paragraph, the energy of excitation of the H^3 -cyclopropane daughter must have been about 4 eV, by comparison with the known energy of 3 eV for this isomerization when accomplished thermally.

The picture of hot hydrogen reactions in the gas phase outlined in previous paragraphs is thus one of a predominance of hydrogen displacement and abstraction reactions, the relative frequency of these depending on the angle of approach of the incoming H^3 to the struck hydrogen atom. In the case of the direct displacement reaction it is interesting to enquire if this occurs as a result of a single billiard-ball collision of the type outlined in Section III,A. The evidence of alkyl group replacement and intramolecular rearrangement given above already shows that some energy is transferred to the rest of the struck molecule. Direct evidence has been obtained of the inadequacy of the simple billiard-ball model from experiments with H^3 recoils in CH_4 and CD_4 (66). On the basis of classical mechanical collision theory of the type underlying the Wolfgang-Estrup kinetics, the billiard-ball model predicts an isotope effect of 3.06 for the ratio I_{CD_4}/I_{CH_4} , where I is defined by Eq. (10). This can be seen intuitively from the fact that H^3 will be more effectively stopped in a head-on collision with D than with H. In fact no isotope effect greater than 20% is found. Thus the simple billiard-ball mechanism is not probable for gas phase H^3 reactions. Energy must be coupled into the struck molecule, and this in turn necessitates that

the bulk of the displacement reactions must occur in the "strong-coupling" epithermal region with H^3 energies $< \sim 10$ –20 ev.

Recent experiments throw light on the mechanism of displacement of heavy atoms and groups by H^3 recoils (225). In the series CH_3F , CH_2F_2 , CHF_3 , and CF_4 , with scavenger added to suppress thermal reactions, there is a decrease of probability of displacement of F by H^3 from a value of 5.3% per C—F bond in CH_3F to 0.1% per bond in CF_4 . On the other hand there is a much smaller decline of H replacement by H^3 . A parallel result is obtained for the chloro- and bromo-methanes. The small decline in H replacement can be explained as an effect of steric hindrance on the wide-angle approach of H^3 to the struck atom, as outlined in previous paragraphs. In the case of an F atom struck by H^3 the greater mass of the fluorine may cause it to move away from its bond more slowly than a struck H atom, so that the incident H^3 may take more time to occupy its position. Thus the H^3 tends to be further from the position required for sp^3 binding and may more readily escape or be scavenged by the displaced fluorine. On the other hand rotation of the struck molecule may bring the H^3 atom into the correct alignment for tetrahedral binding. The authors of the work consider that the heavier the substituents on the struck molecule, the less likely is sufficiently rapid rotation to be accomplished and the lower will be the H^3 retention. No such restriction applies in the case of H^3 -H replacement. This model for the first time suggests a rotational component of importance in hot reactions. The writer feels, however, that the mechanism may need to be found in terms of competitive reactions of the dislodged F atom and the carbon-containing radical with the H^3 atom, without evoking a rotational mechanism. Available thermochemical data indicate a lower energy of activation for H^3 reaction with $CH_3\cdot$ than with $CF_3\cdot$.

Further light on high-energy gas phase reactions has come in recent years using radioactive carbon recoils. Recoil C^{14} atoms from the reaction $N^{14}(n,p)C^{14}$ have an initial kinetic energy of 45,000 ev. The cross-section for activation of N^{14} with pile neutrons is small and the C^{14} half-life is long, so that gas phase studies require high-sensitivity C^{14} assay procedures, and analytical techniques for separation of trace amounts of labeled products (32, 334, 335, 338), as well as irradiation times of a few days at thermal neutron fluxes of $\sim 10^{13}$ n/cm²/sec. The relatively high gamma doses which accompany such irradiations introduce the undesirable complication of radiation-promoted reactions (see Section III,C). To overcome this limitation use has recently been made of the 20.5 minute C^{11} produced by a neutron transfer reaction between a beam of 120 Mev C^{12} ions and a platinum foil (184a,b).

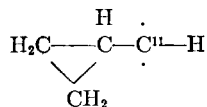
When hot C^{11} atoms are allowed to pass into gaseous O_2 , NO, NO_2 , N_2O , Co, CO_2 , and SO_2 , the main product in all cases is $C^{11}O$ (184a,b). CO_2

formation is low in all systems except the oxides of nitrogen, where it can rise to as much as 43% of the total volatile activity. The reaction of C with O_2 is strongly exoergic so that in absence of a third body $C^{11}O_2$ will decompose. This limitation does not apply in the case of reactions with NO_2 and CO_2 to form $C^{11}O$, and it is suggested (184a,b) that the high yield of the radioactive monoxide in these cases is due to the greater ease with which the incident C^{11} atom can displace a terminal atom in the complex with molecules such as $O=C=O$, $O=N=O$, or $O=S=O$. The high yield of $C^{11}O_2$ in the case of N_2O must result from $C^{11} + N_2O \rightarrow C^{11}O + N_2$ as the highly exoergic primary reaction. By analogy with other systems, such as H reaction with O_3 , in which a nonequilibrated energy distribution in the products yields a high proportion of energy in the product containing the new bond (182), it is suggested that the highly excited $C^{11}O$ reacts further by $C^{11}O + N_2O \rightarrow C^{11}O_2 + N_2$.

When C^{11} recoil atoms react with H_2 , $C^{11}O$, and $C^{11}H_4$ are formed in roughly equal yields (184a,b). The monoxide arises from oxygen impurity in the gas or on the vessel walls. Such a high sensitivity to oxygen suggests a low reactivity of C atoms with H_2 . C^{14} recoils give a high yield of CH_4 in gaseous ammonia after a pile irradiation involving $\sim 2.4 \times 10^8$ rads gamma dose (329, 338). C^{11} atoms in an X-ray field of low intensity do not form methane in gaseous ammonia, but when some radiolysis is allowed to occur $C^{11}H_4$ is found as the major product (184a,b), so that we are presumably not observing a high-energy methane synthesis.

Recoil C^{11} has been allowed to react with gaseous hydrocarbons (184a,b). The chief results can be summarized as follows.

The main product in all systems is $C^{11}H\equiv CH$. Since this product occurs after recoil in methane it can result from C^{11} reaction with C—H bonds ("C—H bond insertion"). In the case of cyclopropane the yield of $C^{11}H\equiv CH$ is about twice as high as in other systems. C—H bond insertion here would yield:



which can decompose into ethylene and acetylene simply by electronic rearrangement without group migration. This may favor the observed high acetylene yield by comparison with other systems in which acetylene formation cannot occur at all carbon atoms by simple electronic rearrangement. In the addition of C^{11} to propane sufficient energy is released to allow rearrangement to $CH\equiv CH$ in 25–30% yield, $CH_2=CH_2$ in 12–20% yield, and unsaturated C_3 fragments. Less drastic rearrangement can yield

$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_3$ in 1.5–2.4% yield and $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ in 2.5–3.0% yield (185).

C^{11} recoils can also react with $\text{C}=\text{C}$ bonds. Yields of stable carbon addition products are higher in the case of $\text{CH}_3\text{CH}=\text{CH}_2$ irradiations than in the case of $\text{CH}_3\text{CH}_2\text{CH}_3$. It is suggested that the first step is direct C^{11} addition to the double bond, followed by electronic rearrangement, breaking of a $\text{C}-\text{C}$ bond and H atom migration in the excited intermediate (184a,b).

Significant amounts of C^{11} -*n*-butane and isobutane are formed when C^{11} recoils in propane, suggesting that the methylene radical may be involved, but the yields show this to be less frequent than the direct insertion reaction.

No evidence has as yet been obtained in gas phase studies of a $\text{C}-\text{C}$ bond insertion reaction. If this occurs at all it is much less probable than the reactions outlined above.

The chemistry of N^{13} recoils from the $\text{C}^{12}(d,n)\text{N}^{13}$ reaction in various gases has been studied in recent work (155, 260). Cyanides are mainly formed in the alkyl halides. HCN is the chief product, although halocyanides appear in greater yield as the amount of halogen in the target gas increases. No ammonia is found, suggesting that an abstraction reaction may not be occurring. In work with highly energetic deuterons it is difficult to avoid radiation effects since a fairly dense column of ions and radicals will be formed along the deuteron track. In the case of the reaction of N^{13} recoils with methanol vapor, the distribution of reaction products was not significantly influenced by addition of Br_2 scavenger so that some truly hot reactions may be involved.

2. Hot Reactions in the Liquid Phase

Although many aspects of high-energy reactions consequent on nuclear activation have been clarified by gas phase studies of the type described in the previous section, the bulk of the earlier work from which the concept of hot reactions emerged was done in liquid and solid organic halides, utilizing the (n,γ) reaction. The organic halides were convenient because the relatively high neutron capture cross-sections and the short half-lives of the activated halogen atoms allowed work with low intensity neutron sources. The relatively well explored photochemistry of these compounds permitted comparison with reaction mechanisms activated by light absorption. Thermally activated halogen-halide exchange reactions were found to proceed to a negligible extent in systems selected for study, although this possibility has to be borne in mind (190).

Three complications presented themselves in the course of this work. In the first place minute amounts of impurities capable of reacting with thermalized halogen atoms could obscure the effects of reactions specifically

activated by energy derived from the nuclear process, and rigorous procedures had to be adopted for purifying target materials (e.g., 202, 319, 323). Preparative gas chromatography on a scale capable of handling the required amounts of targets should make an important contribution here (126). A second difficulty was that of calculating the exact spectrum of recoil energies from the (n,γ) reactions, although as discussed in Section I,A,1 the spectrum from the $\text{Cl}^{35}(n,\gamma)\text{Cl}^{36}$ reaction has recently been evaluated with reasonable accuracy, and procedures are available for dealing with the other reactions when gamma cascade schemes become better known. This difficulty has not seriously impeded work in the field, one reason being that many product distributions seem to be independent of the initial energy of the recoil, as described later. The third difficulty of work with organic halides has been the large number of reactions involved and the large variety of products formed (e.g., 54, 286, 323). This has undoubtedly greatly complicated the initial chemical interpretation of the reaction mechanisms, and has necessitated development of techniques for the separation of trace amounts of radioactive products for which often no carrier could be added. The rapid advances recently made in this field have been greatly facilitated by the application of gas chromatography, coupled with high sensitivity radiometric assay of the separated products (82, 84, 126, 131, 144, 274, 334, 335, 338).

Evidence was obtained in earlier work which supported the view that the billiard-ball mechanism of Libby, outlined in Section III,A, could account for at least some of the organic retention in the liquid phase. As predicted by this model, in organic halides the greater part of the organic retention frequently occurred in compounds of the parent type (34, 91, 93, 171, 172, 323), although this was not found to be the case with the polyvalent atoms of phosphorus (36, 37, 272), arsenic (37, 191, 273), and antimony (115). The prediction that solid compounds should show a greater retention than the same compounds in liquid state, due to a more pronounced caging effect round the collision site was fulfilled in the case of several organic halides (51, 91, 93, 99, 167, 240), although this was not found to be the case in $\text{C}_2\text{H}_5\text{I}$, $i\text{-C}_4\text{H}_9\text{I}$, or $s\text{-C}_4\text{H}_9\text{I}$ (167). The retention during irradiation of a solid phase was found to be dependent on the crystalline structure of the phase in the case of $n\text{-C}_4\text{H}_9\text{Br}$ (248).

The effect of dilution with an "inert" solvent in lowering the retention in organic halides (171, 172, 200, 305), or in organic arsenic compounds when radical scavengers are used to suppress thermal reactions (37, 272, 273), can readily be interpreted as a result of moderation of the recoil to energies below those effective for the billiard-ball mechanism (172). It should be pointed out, however, that retention of P^{32} in butyl esters of phosphoric acid in the presence of oxygen as radical scavenger is increased

on dilution with *n*-heptane or benzene (272), although in this case the solvent may not be inert. The noninert nature of the diluent can lead to increase in organic retention in the case of organic halides diluted with hydrocarbons (100, 200).

Evidence soon accumulated to show that the elastic-collision model could not account for all high-energy organic retention in the liquid phase. It was found that solutions of elementary halogens in hydrocarbons could yield organically retained radioactivity on neutron irradiation (19, 51, 93, 99, 100, 136, 178, 200, 239, 262, 321). Similarly, phenyl arsenic compounds were found to be formed by neutron irradiation of arsenic trichloride in benzene (37, 58, 273). Under these conditions retention-causing collisions of the billiard-ball kind envisaged by Libby are excluded. In addition many compounds other than the parent type were often found in the organic radioactive fraction after neutron irradiation of the organic halides (34, 93, 98, 127, 132, 203, 286, 323), contrary to the expectations of the original billiard-ball mechanism.

By adding traces of elementary halogen as inorganic and organic radical scavengers to organic halides before neutron irradiation, it was found that at least two kinds of retention-causing mechanism were operative in the liquid phase. The first mechanism presumably involves diffusion of radicals over a sufficient distance to give a high probability of their interception by traces of elementary halogen, and was revealed by a sharp drop in the curve of organic retention versus mole fraction of scavenger at low concentrations of the latter. The second mechanism presumably involves hot localized reactions, and is operative in the region of the curve which was insensitive to scavenger concentration (100, 137, 167, 203, 205, 319). A typical curve of organic retention versus scavenger concentration is shown in Fig. 8. It is possible that the effect of aniline in depressing the organic retention, discovered by Lu and Sugden (175), may be due to a similar radical scavenging action of amines, since the curves of retention as a function of scavenger concentration, and the distribution of radioactive products are similar for aniline, butylamine and bromine additives (34), although other explanations can be advanced for this effect (132, 172, 286). Willard and Goldhaber (100) have discussed nine possible elementary reactions involving radiobromine from the point of view of their classification as hot or thermal on the basis of the scavenger method.

The finding that a multiplicity of products can be obtained both in gas and liquid phase irradiations in the presence of halogen scavengers (323) shows that a number of reactions must be of the bimolecular displacement type, rather than reactions of the radioactive atom with radicals after diffusion. In the liquid phase conditions are complicated by comparison with gas irradiations. The finding that in the liquid phase radical scavengers

depress the yield of radioactive organic products, together with the formation of radioactive organic species by halogen recoils in pure hydrocarbons, indicates that many inelastic collisions occur during recoils in liquids, leading to fragmentation of molecules, and that the radioactive atom is combining with these fragments. Such findings constituted the earlier experimental basis of the random fragmentation theory of Willard, outlined in Section III,A.

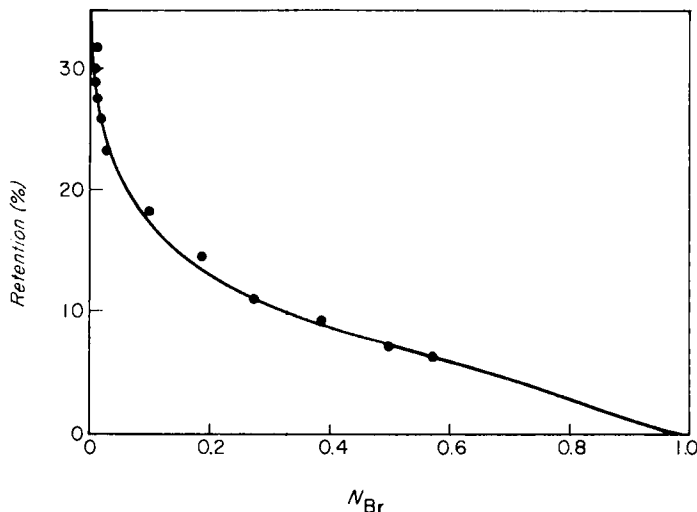


FIG. 8. Organic retention of Br^{80m} in neutron irradiated ethyl bromide as a function of the molar fraction, N_{Br} , of bromine (202).

It has been of considerable interest to use the scavenger technique to obtain data on the systematic chemistry of the scavenger-insensitive hot reactions, the effects of environmental conditions on their yields, and their dependence on the kinetic energy of the recoiling species.

The effect of Br_2 scavenger on the yield of eleven organic- Br^{82} products formed by the $Br^{81}(n,\gamma)Br^{82}$ reaction in *n*-propyl bromide and isopropyl bromide has been determined (54). Three classes of products were observed. Products such as 1,1,2-tribromoethane and higher boiling point fractions had their yield increased threefold by the bromine scavenger at 5 mole % concentration. It is suggested that this type of product is formed when a bromine molecule is present at the site where the Br^{82} enters into combination by a hot process, so that the scavenger molecule is involved in synthesis of the new compound. An alternative explanation might be the formation of a Br^{82} -olefin during a hot collision, and subsequent addition of Br_2 to this molecule. A second class of products is that for which a relatively small depression of yield is caused by the addition of scavenger. This group

includes 1,3-dibromopropane, 1,2-dibromopropane, *n*-hexyl bromide, ethylene bromide (from *n*-propyl bromide) and methylene bromide (from isopropyl bromide). The third group includes those compounds for which the yield is depressed by 35% or more by addition of the scavenger, and in which hot and thermal reactions are thus involved to roughly the same extent, viz., *n*-propyl bromide, isopropyl bromide, ethyl bromide, methyl bromide, and ethylene bromide (from isopropyl bromide). It seems that in this system compounds which may result from reaction of a thermalized Br^{82} atom with a radical formed by the breaking of a C—Br or a C—C bond are more susceptible to scavenger action than those which involve the breaking of C—H bonds. Reactions involving C—H bond rupture thus tend to be either a one-step displacement reaction of the type of Eq. (12), in which a bromine replaces a hydrogen atom, or a combination with a radical formed in a collision by H removal before that radical has had a chance to move more than a very few molecular diameters.

In the case of neutron irradiation of CH_2Br_2 and CHBr_3 (34) yields of $\text{CH}_2\text{BrBr}^{80}$ and $\text{CHBr}_2\text{Br}^{80}$ from Br—Br displacement or from radical formation by C—Br bond rupture were found to be depressed by scavenger by 21% and 26%, respectively. On the other hand yields of higher bromo-derivatives were depressed by scavenger as follows: in CH_2Br_2 target, $\text{CHBr}_2\text{Br}^{80}$ depressed by 59%, and $\text{CBr}_3\text{Br}^{80}$ + higher boiling point fractions depressed by 55%; in CHBr_3 target, $\text{CBr}_3\text{Br}^{80}$ + higher b.p. fractions depressed by 51%. Thus only about half the processes involving radical formation by C—H bond rupture or hydrogen substitution are hot in this system. Later work on the system (126) has yielded similar values for the scavenger-sensitive fraction of the yields of parent-type molecules, and has shown the extensive participation of hot processes in reactions yielding products more highly brominated than the parent molecule. Work on this same system and other halo-methanes has revealed some discrepancies, however, the following values being obtained for the participation of scavenger-sensitive processes in reactions leading to formation of the parent molecule (220): $\text{Br}^{80\text{m}}$ and Br^{82} in CH_2Br_2 , 59%; $\text{Br}^{80\text{m}}$ and Br^{82} in CHBr_3 , 51%; $\text{Br}^{80\text{m}}$ in CCl_3Br , 63%; Br^{82} in CCl_3Br , 65%; $\text{Br}^{80\text{m}}$ in CCl_2Br_2 , 41%; Br^{82} in CCl_2Br_2 , 50%. The basis of the disagreement on the relative role of hot processes in forming parent CH_2Br_2 and CHBr_3 is not clear, but may be due to differences in purification procedures.

The yield of $\text{CCl}_3\text{Br}^{80}$ from neutron capture by elementary bromine in CCl_4 decreases at first rapidly and then more slowly with increase in bromine concentration (137). The yield of $\text{CCl}_2\text{BrBr}^{80}$ goes through a maximum and then declines, while the yield of higher b.p. material goes through a minimum followed by a maximum. It is found that the mono-bromo parent is being formed by processes which are ~50% hot and ~50%

involving thermalized Br^{80} atoms. The formation of the dibromo-derivative probably proceeds via production of a $\text{CCl}_2\text{Br}^{80}\cdot$ radical in a high-energy collision. At high Br_2 concentrations $\text{CCl}_2\text{Br}^{80}$ formation will ensue, but at low Br_2 concentrations $\text{C}_2\text{Cl}_5\text{Br}^{80}$ will be formed, accounting for the peak in the higher b.p. yield.

In the case of a liquid CH_3I target the addition of iodine scavenger depressed the yield of $\text{CH}_3\text{I}^{128}$ from the (n, γ) reaction by $\sim 43\%$, whereas the yield of CH_2I_2 was not significantly influenced and a small increase appeared in the yield of higher b.p. fractions (167).

Analysis of curves of organic retention versus scavenger concentration for the organic halides suggests that in addition to scavenger-sensitive thermal reactions and scavenger-insensitive hot reactions there is a group of reactions which is slowly suppressed by high bromine concentrations (126). This group has been called "hot-spot diffusive" to illustrate the concept that a hot atom may yield the last portions of its energy in a "hot spot" in a liquid, similar to terminal hot spots in recoil tracks in solids (124, 339), and then may combine in this region with local decomposition products. High bromine concentrations are necessary before a reasonable probability exists of a scavenger molecule being found in such a hot spot. An example of such a reaction is that leading to the formation of bromoethane by combination of two one-carbon fragments formed in the hot spot, requiring $\sim 50\%$ mole fraction Br_2 to depress its yield by a significant amount (126). A second example is the formation of parent type molecules from neutron-irradiated CH_2Br_2 or CHBr_3 , quoted earlier. Analysis of the curves of organic retention versus scavenger concentration suggests that $\text{CH}_2\text{Br}^{80}\text{Br}^{80}$ molecules are formed in neutron-irradiated CH_2Br_2 by processes which are 21% hot, 47% hot-spot diffusive, and 32% thermal. The analogous figures for CHBr_3 are 32%, 45%, and 23% respectively (126). On the other hand preliminary experiments on other bromo-alkanes suggest that classification into hot, hot spot-diffusive, and thermal processes may not always be so clear cut (126).

The probability of formation of radioactive organic products by high-energy processes should be proportional to the probability of a hot atom encountering a molecule capable of undergoing a retention-causing reaction during the high-energy part of its recoil, i.e., the high-energy retention, R_E , should be proportional to $1 - N_s$, where N_s is the mole fraction of scavenger. Such linear relationships have been found for bromine (202) and iodine (167) at scavenger concentrations above those necessary to suppress hot reactions. Fig. 8 shows a typical example. Extrapolation of the high energy region of the curve to zero scavenger concentration yields the fraction of retention-causing collisions occurring by means of a hot process (100, 252). For a given reaction product the ratio of R_E at

$N_s = 0$ to R_E at $N_s = 0.27$ is $[1/(1 - 0.27)] = 1.37$. Products which show a greater ratio than this are presumably being formed in part by thermal, diffusive processes. Milman and Shaw (202) have used this analysis to examine the division of the products found in neutron-irradiated C_2H_5Br into those formed by hot and by diffusive processes. The percentage participations of hot processes in the reactions leading to formation of a given product were: $C_2H_5Br^{80}$ (parent), 26%; CH_2BrBr^{80} , 79%; $CH_3CHBrBr^{80}$, 66%; $CH_2BrCH_2Br^{80}$, 92%; CBr_2CBrBr^{80} (residue), 100%. When it is remembered that $\sim 78\%$ of the organic retention is in the parent molecule it is clear that the majority of diffusive reactions yield the parent molecule.

If billiard-ball collisions were predominant in the high-energy processes, then one might expect an increased participation of R_E in the over-all retention with increase in the number of bromine atoms per molecule. Milman and Shaw (203) have used the extrapolation method of the previous paragraph to obtain the following values of R_E/R_{total} in the stated target molecules: C_2H_5Br , 14%; CH_2BrCH_2Br , 17%; CH_3CHBr_2 , 19%; $CH_2BrCHBr_2$, 17%; $CHBr_2CHBr_2$, 18%. These findings suggest that the high-energy interactions in this series are not a simple elastic-collision replacement process of the billiard-ball type. In a bromine-rich medium the recoil will be much more rapidly thermalized because Br—Br collisions are more effective for energy transfer than Br—C or Br—H collisions (172). Since the energy transfer process is thus more localized in the case of bromine-rich molecules, a thermalized recoil will find itself in a region of higher local radical concentration than in the case of mono-bromo-derivatives. One might therefore conclude that the chance of recoil-radical combination prior to the scavenger-sensitive diffusive process should be greater, i.e., R_E/R_{total} should be higher in the bromine-rich molecules. However, in the case of the bromine-rich molecule there is more chance of the radical which combines with the recoil being a Br atom, leading to inorganic retention. This local generation of atomic scavenger may account for the saturation effect observed for R_E as the number of bromine atoms per molecule is increased.

In contrast to the saturation effect of the previous paragraph, Nesmeyanov and co-workers (220) have found an increase of 6–8% in the hot process yield of the radioactive parent molecule per added Br atom in the series CCl_3Br , CCl_2Br_2 , CH_2Br_2 , and $CHBr_3$. These authors have concluded that the elastic collision model gives an adequate account of at least part of the hot processes leading to formation of the parent-type molecule. In the case of CH_3Br , CH_2Br_2 , and $CHBr_3$ the amount of parent molecule formed by hot reactions was approximately in the ratio 1:2:3, which suggests that the chance of forming radioactive parent molecules by a hot process is directly proportional to the number of Br atoms available for

replacement by collision with an energetic Br atom (127). Evidence for an increase in retention due to increased efficiency of moderation in a small volume has come from experiments in which the yields of bromoethanes from CH_3Br , CH_2Br_2 , and CHBr_3 were 3.1, 6.2, and 10.3%, respectively (125). The higher concentration of reactive fragments thus induced would be expected to cause a higher proportion of bromoethanes, since the formation of a bromoethane requires a collision between two one-carbon fragments.

It would be of considerable interest to extract from the data any information as to whether the high-energy retention in organic halides is produced by a process which can be treated as essentially an atom-atom collision, or whether the process involves the struck molecule as a whole. Evidence for involvement of the whole molecule in gas phase experiments with H^3 has already been discussed in Section III,B,1. The difficulty of theoretical treatment of polyatomic molecules has been indicated in Section III,A.

Nesmeyanov and co-workers have proposed that the probability of molecular dissociation and thus of high-energy retention might be related simply to the maximum fraction of energy which can be transferred as internal energy to a struck molecule of mass M by a recoil of mass m . This fraction is $M/(m + M)$ of the energy transferred in the collision. When the retention in monosubstituted products is plotted against $M/(m + M)$ a straight line is obtained for a number of aliphatic bromides and chlorobromides (218, 220, 222). This suggests that the probability of a hydrogen displacement by a bromine atom may be proportional to the excitation energy of the struck molecule. The lack of isotope effect in H^3 displacement reactions in CH_4 or CD_4 gas, indicating coupling of energy into the whole molecule as mentioned in Section III,B,1 seems to bear on this same point. In addition it has been found that increased Br^{80} retention accompanies increased molecular weight in the series from ethyl to n -amyl bromide (286).

Some evidence has been obtained that hot reactions, revealed by the scavenger technique, can be subject to specific chemical influences within the molecule. The ratio of *ortho*- to *meta*- to *para*-isomers of bromofluorobenzene formed as a result of the (n,γ) process in 3 mole % solutions of Br_2 in $\text{C}_6\text{H}_5\text{F}$ is about 3:2:3, instead of the 2:2:1 ratio expected if hydrogen displacement occurred on a purely statistical basis (323). It is interesting to compare this finding with the relatively simple picture advanced in Section III,B,1 to account for hot reaction mechanisms in H^3 recoil studies, in which steric availability of carbon-bound hydrogen atoms mainly seems to govern the probability of their displacement. Irradiation of $\text{C}_6\text{H}_5\text{I}$ seems to yield only the $\text{C}_6\text{H}_5\text{I}^{128}$ product; $\text{C}_6\text{H}_5\text{Br}$ yields $\text{C}_6\text{H}_5\text{Br}^{82}$ and

$C_6H_4BrBr^{82}$ isomers; while C_6H_5Cl yields $C_6H_5Cl^{38}$, $C_6H_4ClCl^{38}$ isomers and $\sim 10\%$ aliphatic chlorides, so that the number of detectable species increases from iodo- to bromo- to chloro-benzene (323). More importantly, perhaps, the aromatic ring seems relatively resistant to rupture in hot collisions, and this recalls the finding in H^3 recoil studies in gaseous alkanes, mentioned in Section III,B,1, that the energy coupled into the molecule is generally insufficient to cause extensive C—C bond rupture. When the $Br^{81}(n,\gamma)Br^{82}$ reaction takes place in 3 mole % Br_2 in C_6H_5Br , C_6H_5Cl , and C_6H_5F the yields of $C_6H_5Br^{82}$ are 22, 16, and 3%, respectively, indicating that displacement of the carbon-bound halogen atom from the aromatic ring is progressively more difficult in going from bromine to fluorine. This is perhaps one more piece of evidence to be added to that given earlier in this section for the idea that increased efficiency of energy transfer in elastic collisions may be related to the probability of displacement reactions, since the energy transfer efficiency declines in the series Br—Br, Br—Cl, Br—F collisions.

Willard (319) has pointed out that in addition to chemical properties the physical features of the medium may play an important part in deciding the course of high-energy interactions in the liquid phase. In a liquid the molecule struck by a recoil is backed by a close-packed and sometimes intertwined wall of other molecules, so that energy may be dissipated by breaking bonds in a rather indiscriminate fashion. Little work has been done so far to investigate this aspect of high-energy reactions, although it would seem that a useful approach might be a systematic study of the relative role of hot processes in the formation of separated products as a function of inert diluent concentration, or as a function of the viscosity and molecular complexity of the irradiated target.

It has been suggested (99) that an increased caging effect might result from a decrease in free space between the molecules (i.e., an increase in density), or from a change in molecular aggregation, or from a combination of these. In the case of neutron-irradiated CCl_3Br the progressive drop in retention, broken sharply at the melting point, as temperature is increased, has been explained as due to the decrease in density and diminished caging effect (99). The increase in organic retention due to hot processes in (n,γ) activation of iodine or bromine in hydrocarbons increases with increase in chain length from *n*-pentane to *n*-octane or *n*-decane (2, 100). This may be due to increased molecular intertwining in the cage walls. A similar explanation might account for the finding that the organic retention after neutron irradiation increases with chain length in the homologous series of alkyl bromides from methyl to amyl and possibly hexyl bromide (143, 286). It should be pointed out, however, that there is no increase in retention in the series CH_3I , C_2H_5I , $n-C_3H_7I$, and $n-C_4H_9I$ when irradiated

in the liquid or solid phase (167). In addition there is no clear evidence that the increased retention in the homologous series from ethyl to *n*-amyl bromide is due to increase in the proportion of smaller molecular size products (286), which might have been expected to be the case if increased intertwining of molecules had resulted in more extensive molecular fragmentation in a high-energy collision. The increased retention seems to be mainly in molecules of the parent type.

An important approach to the study of hot reactions in the liquid phase is the examination of their dependence on the kinetic energy of the recoiling fragment. For work with halogen-containing compounds the effects of the isomeric transition $\text{Br}^{80\text{m}} \rightarrow \text{Br}^{80} + h\nu$ in molecules labeled with $\text{Br}^{80\text{m}}$ can be compared with the effects of the $\text{Br}^{79}(n,\gamma)\text{Br}^{80}$, $\text{Br}^{79}(n,\gamma)\text{Br}^{80\text{m}}$ and $\text{Br}^{81}(n,\gamma)\text{Br}^{82}$ reactions. As discussed in Section II,E, the isomeric transition yields a recoil energy which is much less than that needed to break chemical bonds, but a highly charged species may result from internal conversion. In the case of the (n,γ) reaction there is a considerable kinetic energy of recoil, and charge may also be acquired as a result of internal conversion of some of the weaker quanta in the gamma cascade (314). Comparison of the chemical consequences of the two types of nuclear process may thus throw light on the relative effects of kinetic energy and charge neutralization in the observed hot reactions. This type of comparison has been used to study the role of kinetic energy versus Auger charging in the decomposition of bromate ions in solution and in the solid state (32, 33, 35, 293). Comparison of the consequences of the three (n,γ) reactions for bromine given above might also be expected to illuminate the role of initial recoil energy in hot reactions. In addition, by varying the energy of the neutrons captured in the (n,γ) process it is possible to vary the recoil energy.

In the case of iodine-containing compounds comparison has been made of the effects of the $\text{I}^{127}(n,\gamma)\text{I}^{128}$, $\text{I}^{127}(\gamma,n)\text{I}^{126}$, $\text{I}^{127}(d,p)\text{I}^{128}$ and $\text{I}^{127}(n,2n)\text{I}^{126}$ processes. The (γ,n) reaction yields recoils with a maximum kinetic energy for single quantum emission of 182 ev, although mutual momentum cancellation will reduce the effective recoil energy in most of the events, as discussed in Section I,A,1. The recoil energies from the $(n,2n)$, (d,p) , and (γ,n) processes are of the order of 100,000 ev.

With elementary iodine present as scavenger the organic retentions in CH_3I and $\text{C}_2\text{H}_5\text{I}$ subjected to (d,p) , $(n,2n)$, (γ,n) and (n,γ) reactions were found to be the same (261). It is also interesting that the yields were similar from the hot plus diffusive reactions in the nonscavenged targets. Comparison of the retentions for the $(n,2n)$ and (n,γ) reactions in air-saturated $\text{C}_2\text{H}_5\text{I}$, *n*- $\text{C}_3\text{H}_7\text{I}$, *iso*- $\text{C}_3\text{H}_7\text{I}$, *n*- $\text{C}_4\text{H}_9\text{I}$ and *sec*- $\text{C}_4\text{H}_9\text{I}$ showed very similar values in both solid and liquid targets (177). Furthermore, the distributions

of activity in the various products formed from the (n,γ) and $(n,2n)$ reactions in solid or liquid C_2H_5I were similar. The implication from these studies is that the retention-causing reactions are very little influenced by the magnitude of the kinetic energy supplied to the recoil by the nuclear event. This would be consistent with the view that the radio-atom does not have a significant probability of combining with species formed by molecular fragmentation at the commencement of its track, but that the retention-causing hot reactions (and of course the diffusive reactions) occur predominantly towards the end of the track, when the recoil has significantly cooled. The situation in this case would resemble that discussed for chemical reactions undergone by recoils in solids, in which the initial recoil energy may not be important, and the decisive region for chemical reaction may be a terminal "hot zone" in which ~ 300 ev of energy are dissipated in a small volume, causing melting, chemical decomposition and vacancy production in the lattice around the recoiling species (123, 124, 339).

In contrast to the above findings it has been observed that when equimolar mixtures of CH_3I and $n-C_3H_7I$ are subjected to the (n,γ) reaction the ratio of specific activities CH_3I/C_3H_7I is 1.8, whereas for the $(n,2n)$ reaction with 14.1 Mev neutrons the ratio is 2.3 (139). Although the solutions were not de-aerated no scavenger was added, however, and this energy-dependent effect may not result from hot processes.

It has been found that some dependence of the organic retention on the recoil energy may exist in the solid phase, the $Br^{81}(n,\gamma)Br^{82}$ reaction in n -propyl bromide showing 93% retention as against 80% for the $Br^{79}(n,\gamma)-Br^{80}$ and $Br^{79}(n,\gamma)Br^{80m}$ reactions (91). In the liquid state no significant differences in retentions were found between the three nuclear reactions. Later work confirmed that in the liquid n -propyl bromides there was no difference in retentions for these three (n,γ) reactions (52, 263), but indicated that differences were also absent for the solid phase (263).

When retentions from the $Br^{79}(n,2n)Br^{78}$ process in liquid and solid n -propyl bromide and isopropyl bromide, with and without Br_2 scavengers were compared with those from the $Br^{81}(n,\gamma)Br^{82}$ reaction, the retention of the 100,000 ev recoil Br^{78} was in all cases significantly greater than the ~ 100 ev Br^{82} (263). It has been found in later work that the $(n,2n)$ reaction gives a greater organic retention for solutions of iodine in cyclohexane by comparison with the (n,γ) reaction, but no difference in retentions is observed for liquid n -propyl iodide (262). Neutron energy has been shown to have no effect on retentions in liquid n -propyl bromide, by using Sb-Be photoneutrons, Po-Be neutrons, cyclotron neutrons, and pile neutrons of differing degrees of moderation (52, 263).

Comparison of the $Br^{80m}:Br^{80}$ isomeric transition with the $Br(n,\gamma)$

reactions rather strikingly demonstrates the fact that the products of hot reactions in liquid organic bromides do not depend upon the initial recoil energy supplied by the nuclear process. For example, the distribution of some 20 products in $n\text{-C}_3\text{H}_7\text{Br}$ was found to be nearly identical for the I.T. and (n,γ) transformations (84). A similar situation is found for the two nuclear processes in solutions of bromine in CCl_4 , $\text{C}_6\text{H}_5\text{F}$, $\text{C}_6\text{H}_5\text{Cl}$, and $\text{C}_6\text{H}_5\text{Br}$, the same relative yields of labeled products being produced by both transformations at all bromine concentrations (137, 323). Plots of the organic retention versus free bromine concentration in both $n\text{-C}_3\text{H}_7\text{Br}$ and $i\text{-C}_3\text{H}_7\text{Br}$ are superimposable for activation by $\text{Br}^{80\text{m}} \rightarrow \text{Br}^{80}$, $\text{Br}^{79}\text{-(}n,\gamma\text{)Br}^{80\text{m}}$ and $\text{Br}^{79}\text{(}n,\gamma\text{)Br}^{80}$ (54). In the case of the $\text{Br}^{79}\text{(}n,\gamma\text{)Br}^{80}$ and $\text{Br}^{80\text{m}} \rightarrow \text{Br}^{80}$ processes, reactions carried out with elementary bromine in pure hydrocarbons show the same increase of organic retention with chain length for both nuclear activations.

The general similarity between the effects of the bromine I.T. and (n,γ) reactions in organic liquids suggests that perhaps ion-molecule reactions are involved in the scavenger-insensitive retention-causing processes. We have seen that some contribution from ion-molecule reactions cannot be ruled out in the studies of the hot gas phase reactions of halogen and hydrogen atoms outlined in Section III,B,1. It is possible that charge neutralization processes may lead to fragmentation of organic molecules in a way similar to that caused by inelastic collisions. On the other hand it has been pointed out in Section I,A,1 that charge neutralization may result in $\sim 10\text{--}20$ ev of kinetic energy being imparted to the pair resulting from the charge transfer reaction, and this may be sufficient to allow the Br atom to behave like a hot recoil towards the end of its track (319, 323).

The retention of I^{131} in benzyl iodide after beta decay of Te^{131} in benzene solutions of dibenzyl telluride is depressed by addition of elementary iodine in a way resembling the effect of scavengers on the products of (n,γ) reactions in organic halides (117). The I^{131} atoms are here recoiling with energies of only $\sim 2\text{--}4$ ev and retention-causing reactions are presumably due to the charge and electronic excitation of the recoil. Interpretation is complicated in this system, however, because of the possibility of addition of iodine to the telluride.

Differences in organic retentions have been reported for the $\text{Br}^{79}\text{(}n,\gamma\text{)-Br}^{80\text{m}}$ and $\text{Br}^{79}\text{(}n,\gamma\text{)Br}^{80}$ reactions in brominated alkyls (39, 40, 41, 43). No differences have been found for the yields of $\text{Br}^{80\text{m}}$ and Br^{80} in n -propyl bromides at low gamma doses (52, 248), although the ratio of $\text{Br}^{80\text{m}}$ and Br^{80} retentions can be caused to vary by allowing some radiolysis to occur with gamma doses in the range $\sim 10^3\text{--}10^5$ rads (52, 53). The existence of an isomer effect in the presence of radiolysis products together with the use of relatively impure reagents in the earlier experiments in which an

effect was found has suggested that the observed differences in retentions could have been due to the relatively higher probability of reaction with impurities by the isotopes or isomers of longer mean lives. In later work with irradiation times arranged so as to reduce differences in mean lives it has been found that in *n*-propyl bromide the $\text{Br}^{80}/\text{Br}^{80m}$ ratio is changed by treatment with alumina using nonthermalized Ra/Be neutrons, whereas the ratio is unchanged for irradiations with thermalized neutrons (6). A similar finding has been made with the $\text{Br}^{80m}/\text{Br}^{82}$ ratio (7). Attempts to verify these observations have not been successful (323).

Greater retentions of Br^{82} than Br^{80m} have been found in neutron-irradiated ethylene dibromide (205), but it was found to be difficult to obtain reproducible organic yields in this target (205, 269), which suggests that impurities were not easy to eliminate, or that decomposition of this compound readily occurs to yield impurities with which the longer-lived Br^{82} has a greater chance of reacting (205).

On the whole the evidence of the previous paragraphs does not suggest that differences in retention of bromine isotopes or isomers occur as a result of differences in high-energy processes, but rather that the differences observed are due to reactions of thermalized Br atoms with impurities or decomposition products. This viewpoint is supported by the finding that the isotope effect in neutron-irradiated alkyl bromides can be suppressed by addition of allyl bromide (22), a known trap for thermalized Br atoms (118, 120, 326). No isotope effect has been found in the compounds CH_2Br_2 and $\text{C}_2\text{H}_5\text{Br}$ (202, 218) which do not readily decompose or form unsaturated compounds.

In the compounds CCl_3Br , CCl_2Br_2 , CH_2ClBr , CHCl_2Br , and CHClBr_2 it has been found that the isotope effect for Br^{82} and Br^{80m} is independent of irradiation time and thus is not related to the mean lives of radioactive atoms in the target. The effect is independent of scavenger concentration but does not exist in the solid phase (219, 220, 222). This finding indicates a true high-energy isotope effect. In the series of chlorobromomethanes it has been found that the difference in retention, ΔR , between Br^{82} and Br^{80m} declines linearly with increase in the ratio of diffusive retention, R_0 , to total retention (219, 222), again indicating a nondiffusive isotope effect. In CH_2BrI , ΔR is in the opposite direction to that observed for the other bromo-compounds (219). In CHBr_2F the usual ΔR effect is observed in liquid but not in solid phase (222).

It can be seen from the above paragraphs that there is rather conflicting evidence as to the role of initial recoil energy on the nondiffusive hot processes. In liquids nondiffusive isotope effects exist in the substituted methanes, but not in the propyl bromides, and in the halo-methanes the direction of the effect seems to depend on the composition of the target rather

than on the initial recoil energy. With the present data it is difficult to draw firm conclusions, but rather convincing evidence for a relatively unimportant role of the magnitude of recoil energy imparted by the nuclear event comes from the closely similar effects of the (n,γ) and I.T. processes.

Relatively little work has been done so far to distinguish between hot and diffusive reactions of polyvalent recoils, although such work might be expected to throw light on the relative probabilities of forming one, two or three bonds in a localized hot process (36, 273). It has been shown that P^{32} formed by the $S^{35}(n,\alpha)P^{32}$ reaction in neutron-irradiated solutions of CS_2 in benzene or chloro-benzene can replace hydrogen to form derivatives of mono-, di-, and tri-phenylphosphine (221). The curve of retention of As^{76} as monophenyl-arsenic versus $AsCl_3$ concentration in benzene after (n,γ) reaction shows a strongly $AsCl_3$ sensitive region, and an $AsCl_3$ insensitive region which declines linearly with increasing $AsCl_3$ concentration, in a very similar way to that for halogen scavengers in organic halides (58). $AsCl_3$ may be able to scavenge phenyl radicals either by direct chemical combination or as a result of Cl_2 -yielding radiolysis in the pile, and this may be one of the reasons why the yield of phenyl- As^{76} compounds is considerably lower for irradiations of $AsCl_3$ in benzene than for irradiations of triphenylarsine in benzene (37, 273). Furthermore addition of $AsCl_3$ to a solution of triphenylarsine in benzene depresses the phenyl- As^{76} yield (272). These findings suggest that As^{76} atoms recoiling in benzene are able to form bonds with phenyl radicals in a hot process, involving hydrogen replacement, or combination with a phenyl radical formed in an inelastic collision by diffusive or nondiffusive processes.

Using iodine and oxygen scavengers and dilution with "inert" solvents an attempt has been made to estimate the relative participation of hot and thermal processes in retention-causing reactions for the $As^{76}(n,\gamma)As^{76}$ process in triphenylarsine and the $P^{31}(n,\gamma)P^{32}$ reaction in tributylphosphate (272). The hot reactions have a dominant role in formation of organic mono-derivatives of both As^{76} and P^{32} , whereas thermal reactions are most important in the formation of tri-derivatives. The formation of di-derivatives is of an intermediate character. The findings suggest that a mono-derivative is first formed in a hot process, and that a diffusive process then leads to combination of the mono-derivative radical with a second or third organic radical to give the di- and tri-derivatives. Presence of oxygen or other radical scavengers tends to fix the recoil as the mono-derivative. There is evidence that in the case of P^{32} recoils the formation of the di-derivative can take place in the hot zone.

Studies with H^3 atoms activated by the $Li^6(n,\alpha)H^3$ process in liquids have considerably widened our views on the nature of hot reactions in the liquid phase (129, 247, 251). For liquid phase studies diphenyl picryl

hydrazyl (DPPH) can be used as a radical scavenger (234), in addition to elementary halogens or oxygen.

In liquid methane or ethane the primary labeled compounds from H^3 recoil are HH^3 and the parent compound in roughly equal proportions, accounting for 88 and 79% of the H^3 activity respectively (333). The remainder of the H^3 is distributed among nonparent hydrocarbons, both saturated and unsaturated, with molecular size up to C_4 and greater. The similarity of the product distribution for the gaseous and liquid alkanes suggests that the retention-causing mechanisms outlined in Section III,B,1 for gases may also be operative in the liquid phase (251). We may thus expect to find that direct displacement or abstraction reactions of the type of Eqs. (12) and (15) may be operative for H^3 recoils in liquids, and that cage effects and the physical condition of the medium may not influence the pattern of organic retention to the same extent as with recoiling halogen atoms.

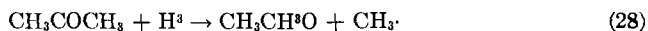
Studies of the products of H^3 recoil in liquid ethyl and methyl alcohols and acetone (251) show that the greater part of the activity is present in the parent compound as shown in Table VI. The similarity in distributions

TABLE VI
CHEMICAL STATE OF H^3 ATOMS REACTING WITH
ALCOHOLS AND ACETONE (251)

Target Product	Liquid CH_3COCH_3					
	Liquid C_2H_5OH	Liquid CH_3OH	No additive	DPPH added	Water added	Solid acetone
HH^3	51%	—	—	—	—	—
CH_3H^3	4%	—	—	—	—	—
CH_2H^3OH	1%	23%	—	—	—	—
$C_2H_4H^3OH$	22%	—	—	—	—	—
CH_3CH^3O	2%	—	9%	10%	8%	5%
$CH_3COCH_2H^3$	—	—	25%	22%	25%	24%
$-OH^3$	20%	29%	12%	22%	48%	17%

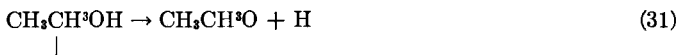
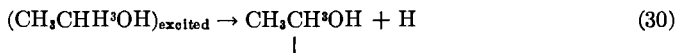
of H^3 in acetone products, with or without DPPH, with the exception of $-OH^3$, again supports the conclusion that retention of H^3 in organic liquids is occurring mainly by a nondiffusive process.

Degradation of the labeled acetaldehyde product from acetone showed that ~95% of the H^3 is present in the $-CH^3O$ group, this compound being formed by the hot reaction:



analogous to the alkyl group displacement reaction of Eq. (17). A similar mechanism probably accounts for the production of $\text{CH}_2\text{H}^3\text{OH}$ from $\text{C}_2\text{H}_5\text{OH}$ and CH_3H^3 from $\text{CH}_3\cdot\text{CH}_3$ (333).

The 2% yield of $\text{CH}_3\cdot\text{CH}^3\text{O}$ from $\text{C}_2\text{H}_5\text{OH}$ in Table VI has been postulated to proceed via the usual H replacement reaction of Eq. (12), which in this case leaves an excited molecule:



In support of this reaction sequence are the finding of aldehydes as frequent products of radiolysis or photolysis of alcohols (179, 180, 229) and the greater tendency for loss of H from the $-\text{CH}_2-$ rather than the CH_3- group in gamma ray induced radiolysis or electron impact fragmentation of ethyl alcohol (29).

Studies have been made of the distribution of activity from H^3 recoils in a series of liquid carboxylic acids (76). The yields of activity in the parent-type molecules were independent of I_2 or O_2 scavengers, indicating hot processes. Diffusive reactions were those giving the small yields of molecules such as $\text{C}_2\text{H}_5\text{H}^3$ or $\text{C}_3\text{H}_7\text{H}^3$ from CH_3COOH , i.e., molecules having more atoms than the parent and thus not formed by direct hot reaction. This is a similarity with gas phase H^3 recoil systems (77, 78) in which "synthesis" products with more atoms than the parent were formed entirely by scavenger-sensitive reactions.

In the liquid carboxylic acids 99% of hot reaction products can be formed by breaking a single bond, which indicates a predominance of displacement reactions involving an atom or a group as in Eqs. (12) or (17). As in gases insufficient energy is coupled into the molecule to permit extensive fragmentation in most cases, and this applies despite the stiff wall of molecules backing the struck molecule in the liquid phase. There is a low yield of rearrangement or isomerization products, e.g., $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$ and $(\text{CH}_3)_2\text{CHCH}_3$ from $\text{CH}_3(\text{CH}_2)_4\text{COOH}$ or $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ and $\text{CH}_3(\text{CH}_2)_2\text{CH}_3$ from $(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{COOH}$. This indicates that an activated complex with equilibrium distribution of energy is not being formed. Nevertheless, the yield of H^3 -hydrocarbons resulting from decarboxylation is relatively high, suggesting that some residual energy after displacement may be transmitted along the molecule. A relatively high vulnerability of the $-\text{COOH}$ group to direct displacement could, however, also explain this result (see, e.g., 142).

In the liquid carboxylic acids there is an approximately linear relationship between the ratio $\text{HH}^3/\text{CH}_3\text{H}^3$ in the products and the ratio $\text{C—H bonds}/\text{C—CH}_3\text{ bonds}$ in the target (76). This suggests that the amount of a given product in a hot displacement reaction depends largely on the fraction of total bonds which can be broken to give that product. Assuming that other steric or intramolecular factors do not complicate the issue it is possible to use such a simple "bond rupture probability" model to calculate the expected distribution of activity in the products from a given target molecule. There is found to be a reasonably good agreement between an activity distribution calculated on this basis for the liquid carboxylic acids and the distributions actually obtained. The deviations actually observed between the two distributions throw light on the relative importance of steric and intramolecular factors. For example, the observed yield of HH^3 is higher than theoretical, and there is a low yield of H^3 in labile form and in liquid products other than the parent acid. This suggests that C—H bond attack is relatively more probable than any other attack, a conclusion similar to that from the gas phase studies described in Section III,B,1. The higher yield of HH^3 than H^3 -parent acid indicates that C—H bond attack favors abstraction rather than displacement. Furthermore HH^3 formation is found to be relatively more probable with secondary than with primary C—H bonds, a finding that can be related to the results of gas phase experiments discussed in connection with Eq. (25).

These studies have been extended to phenyl-acetic acid which was in liquid state during the irradiation (75). The amount of H^3 taken into the ring in this compound is greater than that incorporated into the side-chain (except for the carboxylic hydrogen), the specific activity of ring hydrogen being about 40 times greater than that of the methylene hydrogen. The more efficient labeling of aromatic than aliphatic groups also emerges from experiments with H^3 in solid *o*-toluic acid, in which the specific activity of a ring hydrogen is twice that of a methyl hydrogen, and from the observation that the hydrolysis of recoil H^3 -labeled isopropyl benzoate yields benzoic acid with an H^3/H ratio more than three times greater than that of the isopropyl alcohol (24).

The behavior of C^{14} recoils in liquid systems has been studied in a number of recent works using the $\text{N}^{14}(n,p)\text{C}^{14}$ reaction with pile neutrons (328, 329).

When C^{14} atoms recoil in pentane radioactive hexanes are obtained. In one study the yields of *n*-hexane and 2-methyl-pentane were found to be in the ratio of 1.52/1 (329). This is very close to the ratio of 1.5/1 which would be found if hydrogen replacement by C^{14} is occurring on a statistical basis with equal probability for all H atoms. Similarly the ratio *n*-hexane/3-methyl pentane yield is 3.2/1, again close to the value of 3/1 for statistical

replacement. Other experiments (176, 260) have not yielded the expected ratios, the yields of *n*-hexane and 3-methyl-pentane being relatively higher than expected. It has been suggested that the presence of radiochemical impurities in the separated products may have accounted for the discrepancies. Statistical replacement of H by C¹⁴ in toluene to produce the xylenes and ethyl benzene has also been observed (329).

The data on the whole suggest that C¹⁴ recoils are able to replace H atoms in aliphatic chains or aromatic rings with a fairly equal probability for each hydrogen position. The reaction could be a direct displacement reaction of the type of Eq. (12). Alternatively a bare C¹⁴ atom may be stopped in a head-on collision with a C atom bound in a molecule in the high energy region of the recoil process, and may then abstract H atoms from molecules in the solvent cage walls forming a C¹⁴H₃· radical and creating organic radicals with which the labeled species would then combine (176).

It has been shown that C¹⁴-toluene is formed when C¹⁴ atoms recoil in liquid benzene in the presence of DPPH or 1,3,5-trinitrobenzene as radical scavengers (294), so that in this case a nondiffusive hot process is involved. Experiments have been done using various mole fractions of different amines as nitrogen sources for the (*n,p*) reaction in benzene. It has been found that the C¹⁴-toluene yield depends on the availability of hydrogen from the nitrogenous compound (329). This result supports the picture of hydrogen abstraction to form a C¹⁴H₃· radical prior to the retention-causing reaction, although this radical might conceivably be formed and interact with a benzene ring in a second high-energy collision rather than after thermalization of the recoil.

C¹⁴ can also replace C or N atoms in molecules of the medium in which recoil occurs. Both statistical and nonstatistical behavior have been observed.

In aromatic systems the percentage of C¹⁴ retentions per C or H position in the molecule are very similar (329), showing that the replacement reaction yields depend primarily on the relative probability of striking a C or H atom in the molecule and not on the mass of the replaced atom. This is a difference from the case of Br recoils in mono-halogenated benzenes, described earlier, in which more efficient energy transfer in atom-atom collisions seems to lead to higher organic retentions. The simple statistical picture with C¹⁴ recoils does not apply in all cases, however, since C replacement from the CH₃-group in toluene to yield C¹⁴-toluene occurs with considerably greater probability than the formation of the same product by NH₂- replacement in aniline, despite the similar masses of the N and C atoms (329).

Although calculations of specific activities expected per C or H atom or

the relative yields of various products can yield some information on the relative frequencies of location of the initial point of attack at different molecular sites, degradation of the products to ascertain C^{14} distribution is required to illuminate intramolecular rearrangements. The distribution of radioactivity between methyl carbon and ring carbons in the case of C^{14} -toluene, formed by NH_2 - replacement in aniline, resembles quite closely the distributions for C^{14} -toluene formed by H replacement in benzene, for C^{14} -*o*-xylene from toluene by H replacement or for C^{14} -toluene prepared from toluidines formed by aniline ring H replacement. This perhaps indicates a common intermediate. On the whole C replacement by C^{14} in simple aromatic compounds seems to result in only moderate deviations from statistical behavior in both liquid and solid phase.

In the case of aliphatic compounds less work has been done in the liquid phase. The replacement of H by C^{14} recoils in pentane and methanol has been found to be twice as probable as C replacement in the chain (329).

The experiments with C^{14} recoils have already served to show that the mass of the replaced atom or group in the molecule does not have much influence on the probability of C^{14} retention. They also show that completely random and uniform labeling does not occur, nor does completely specific labeling. In all cases isotope distributions in the products show that some intramolecular process results in redistribution of the C^{14} after its incorporation into the molecule. Chemical effects are thus of considerable importance in the pathways leading to the final products and lead to marked deviations from strictly statistical behavior. Considerable differences from statistical distribution have been observed with C^{14} recoils in solid systems in work not reviewed here (25, 30, 96), although in some solids the predictions of statistical replacement have been fairly closely fulfilled (216, 330, 342).

C. THERMAL OR DIFFUSION-DEPENDENT REACTIONS AFTER NUCLEAR ACTIVATION AND RADIATION EFFECTS

In this review attention has been concentrated on the high-energy interactions resulting from nuclear activation, since this field represents the strongly specific contribution of the nuclear technique to the subject of chemical reactions. Nevertheless, a considerable volume of work has been done to elucidate the chemical behavior of the radioactive atoms when they have reached thermal energies, which can only be partially indicated here.

In liquids the study of diffusive reactions may throw light on the way in which radical nests are generated along the recoil track, and possibly on the distribution of the various types of radicals produced in inelastic collisions as a function of track length traversed and thus of recoil energy at the moment of collision.

Diffusive reactions yield mainly parent-type molecules in neutron-irradiated liquid ethyl bromide and ethylene bromide (202, 205). Extensive analysis of diffusive reaction products in liquid *n*-propyl and isopropyl bromides has been done (54), and indicates once again the predominance of parent-forming reactions and the relative absence of reactions involving radicals produced by extensive molecular fragmentation. A similar picture is found for CH_3Br and CH_2Br_2 (127).

No correlation has been found between bromine content of target molecules and relative participation of diffusive processes in reactions leading to organic retention, but the diffusive retention seems to rise with number of H atoms (220). This may be related to the suggestion made in Section III,B,2 in connection with the saturation effect for the ratio R_E/R_{total} , namely that increase in the number of halogen atoms per target molecule may increase the probability of local generation of elementary halogen scavenger.

Diffusive retention depends on the way in which radicals will diffuse away from the recoil track. Various theoretical approximations have been made to solve the appropriate diffusion equation (68, 157, 193, 204, 256) and have been successfully applied to diffusive reactions in neutron-irradiated aliphatic bromides (204), bromo-methanes and chloro-bromomethanes (220).

Radiation effects may have a considerable influence on the course of diffusive reactions as various radiolysis products become available for reaction with the thermalized radioactive atoms. This effect can be calculated (167) and demonstrated (248) to be sometimes of little importance with low gamma intensity neutron sources. Even here, however, thermalized radioatoms may react with organic radicals produced by radiolysis in the course of the irradiation (53, 167).

When nuclear reactors are used as neutron sources the intense gamma fields may sometimes induce a considerable fraction of the target to undergo radiolysis. When as much as several percent of the target has suffered decomposition hot processes may be affected as well as diffusive reactions. For example, when C^{14} recoils react with a sample of NH_3 gas receiving $\sim 10^8$ rads of gamma radiation, a high yield of C^{14}H_4 is observed even in the presence of inert gas moderators (338). When C^{11} recoils are used in a low radiation field, however, no C^{11}H_4 production is observed (184a,b).

Different compounds may have markedly different radiation sensitivities. For example, Cl^{38} retention in the radiolysis-resistant *n*-propyl chloride remains fairly constant up to a total pile gamma dose of $\sim 10^7$ r, while in *n*-propyl bromide a marked increase in retention occurs after 10^4 r, probably due to HBr^{80} reaction with propyl radicals and propene molecules produced by radiolysis (286). Gamma radiation may also induce molecular

isomerization, the formation of isopropyl chloride from *n*-propyl chloride being a linear function of the gamma dose received in the reactor (286).

The reactions undergone by H^3 recoils in gas phase and liquid systems may be highly sensitive to radiation effects. Heavy particle bombardment by the recoil tritons, alphas or protons from neutron reactions with He^3 or Li^6 may induce radiation damage in both target molecules and already formed radioactive species. Many radiation effects are reported in the papers referred to in discussing H^3 recoil reactions in Sections III,B,1 and III,B,2 (e.g., 67, 161-163, 247, 258, 317, 318).

ACKNOWLEDGMENT

The author would like to thank D. L. Baulch and M. Henchman for helpful comments on the material of this review.

List of Symbols

α	Logarithmic energy decrement for elastic collisions
A_i	Radioactivity of product <i>i</i> of hot reaction
A_s	Radioactivity of all reaction products
e	Charge of electron
E_b	Bond energy
E_β	Energy of emitted beta particle
E_i	Bond activation energy
E_{int}	Internal energy of a polyatomic molecule
E_{γ_0}	Net gamma energy required for bond rupture
E_r	Rotational energy
E_R	Recoil energy
E_T°	Net recoil energy necessary for bond rupture
f	Probability of collision between hot atom and molecule
I_{exc}	Lowest electronic excitation level
I_i	Definite integral involving $p(E)$, Eq. (10)
I_n	Nuclear angular momentum
K_i	Definite integral involving $p(E)$, Eq. (11)
m	Mass of recoil atom
M	Molecular weight
m_c	Mass of atom C in polyatomic molecule
m_e	Mass of electron
m_i	Mass of <i>i</i> th atom in polyatomic molecule
N_{Br}	Mole fraction bromine
N_s	Mole fraction scavenger
$p(E)$	Energy-dependent reaction collision efficiency or distribution of excitation energies
$P_D(E)$	Probability of molecular dissociation
R_E	High energy retention
Π	Nuclear parity
Q	Momentum impulse
r	Distance between nuclei or charge centers
\mathbf{r}_i, r_i	Position vector for <i>i</i> th atom in a polyatomic molecule
V	Potential energy

v_i	Vibrational velocity of i th atom in a polyatomic molecule
Z	Nuclear charge
ω, ω	Angular velocity
Ω	Obstruction parameter for H^3 collisions with molecular H atoms

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GASEOUS HYDROXIDES

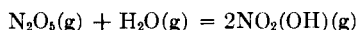
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I. Introduction

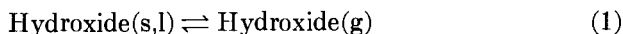
The hydroxides¹ are one of the four main groups of compounds in oxide-water systems, one of the oldest and most studied areas of inorganic chemistry. We classify as hydroxides solid, liquid, or gaseous compounds derived, either experimentally or formally, from an oxide and water, e.g.,



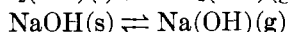
Gaseous hydroxides of both nonmetals and metals are known. The first group contains species, such as nitrogen dioxide hydroxide, $\text{NO}_2(\text{OH})$, and boron trihydroxide, $\text{B}(\text{OH})_3$, which have been known for a long time. Gaseous metallic hydroxides, on the other hand, have only recently been described, though they are now known to exist over the whole range between room temperature and 2000°C.

Gaseous hydroxides may be divided into two types with different equilibria underlying their formation.

(a) Vaporization or Sublimation Equilibrium



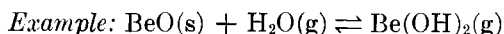
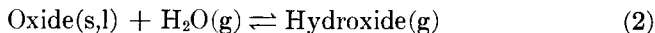
Examples: $\text{NO}_2(\text{OH})(\text{l}) \rightleftharpoons \text{NO}_2(\text{OH})(\text{g})$



¹ Compounds in oxide-water systems, which are also known as aquoxides, have been divided, according to the mode of bonding of the water, into four main groups: hydroxides, oxide hydrates, hydronium compounds, and oxide aquates; cf. O. Glemser, *Ergebnisse und Probleme von Verbindungen der Systeme Oxid-Wasser. Angew. Chem.* **73**, 785 (1961).

0	I	II	III	IV	V	VI	VII	VIII
He	LiOH Li ₂ (OH) ₂ Li ₃ (OH) ₃	Be(OH) ₂	B(OH) ₃ BOOH (BOOH) ₃	CO(OH) ₂ ?	NO ₂ OH NOOH	O	F	Ne
Ne	NaOH Na ₂ (OH) ₂	Mg	Al(OH) ₃ ?	Si(OH) ₄	PO(OH) ₃	SO ₂ (OH) ₂	ClOH ClO ₃ (OH)	Ar

FIG. 1. Gaseous hydroxides of elements of the second and third periods.

(b) *Reaction Equilibrium*

This division is to some extent arbitrary, for some of the gaseous hydroxides now known may be considered as formed according to either Eq. (1) or Eq. (2). There is, however, a series of compounds which can be produced only according to Eq. (2). These have not yet been isolated, and their existence is inferred indirectly from equilibrium studies based on the transfer method or the effusion method, the latter being coupled with mass spectrometric studies. Such measurements enable us to postulate reactions leading to the formation of hydroxides and lead to conclusions, based on thermodynamic data, about the conditions for their existence. Furthermore, under the conditions existing in the oxyhydrogen flame, gaseous alkali metal hydroxides and hydroxylic radicals may be observed, as is described later.

The molecular structures of gaseous hydroxides has been completely elucidated only in a few instances with the aid of infrared and Raman spectroscopy, microwave spectroscopy, or electron diffraction. Often only the molecular weight can be deduced, in which case the mass spectrometer is the chief tool. It is not yet possible to say if the occurrence of gaseous hydroxides is restricted to particular groups of elements of the periodic system. Figure 1 shows the gaseous hydroxides formed by elements in the second and third periods.

II. Systems of the Type $\text{Hydroxide(s,l)} \rightleftharpoons \text{Hydroxide(g)}$

A. NONMETALLIC HYDROXIDES

Nitrogen dioxide hydroxide, $\text{NO}_2(\text{OH})$, is a gaseous hydroxide which has been thoroughly investigated. Forsythe and Giauque (25) determined the thermodynamic data shown in Table I. Interpretation of the infrared spectrum confirmed the entropy value in Table I, and also showed the

TABLE I
PHYSICAL DATA FOR $\text{NO}_2(\text{OH})(\text{g})$ AND $\text{NO}(\text{OH})(\text{g})$

	Heat of vaporization (cal/mole)	Enthalpy of formation $\Delta H_{298.2}^\circ$ (kcal/mole)	Standard entropy $S_{298.2}^\circ$ in (cal/mole $^\circ\text{C}$)	Free energy of formation $\Delta G_{298.2}^\circ$ (kcal/mole)	Dipole moment D
$\text{NO}_2(\text{OH})$	9355 (20 $^\circ\text{C}$)	-31.99	63.62	-10.46	2.16
$\text{NO}(\text{OH})$	—	-18.58	61.46	-10.81	—

existence of an energy barrier of about 10 kcal/mole to the rotation of the hydroxyl group.

After Badger and Bauer (4) had detected the hydroxyl group in the absorption spectrum of $\text{NO}_2(\text{OH})(\text{g})$, the structure was determined by Maxwell and Mosley (47) and by Akishin *et al.* (2) from electron diffraction, by Cohn *et al.* (22) from the infrared spectrum and by Millen and Morton (50, 50a) from the microwave spectrum. We consider the results of the last authors, which are given in Fig. 2, to be the most reliable. Only the O—H distance is uncertain; it is assumed to be 0.96 Å, as in water.

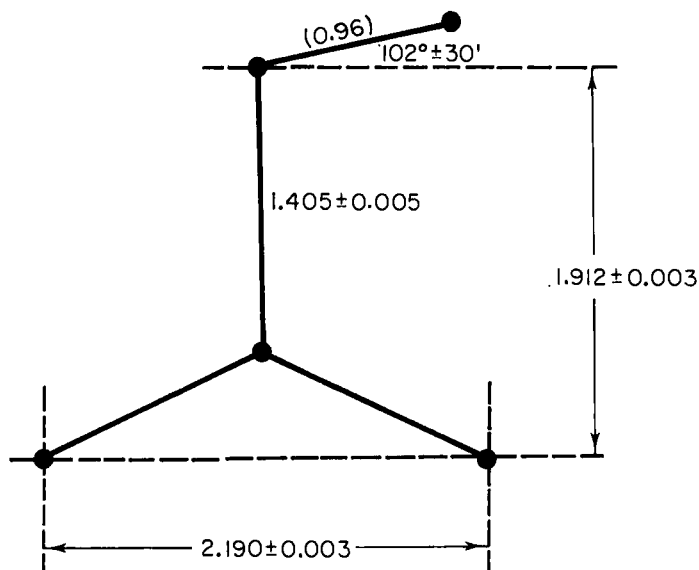


FIG. 2. Structure of the gaseous $\text{NO}_2(\text{OH})$ molecule according to Millen and Morton.

Nitrogen oxide hydroxide, $\text{NO}(\text{OH})$. Some time ago Melvin and Wulff (48) found a number of bands between 3100 and 3900 Å in the absorption spectrum of gaseous mixtures of $\text{NO}(\text{g})$, $\text{NO}_2(\text{g})$, and $\text{H}_2\text{O}(\text{g})$ which they attributed to $\text{NO}(\text{OH})(\text{g})$. This conclusion was questioned, but Porter (57) was able to substantiate it. In the infrared spectrum of $\text{NO}(\text{OH})(\text{g})$ a doubling of most of the bands occurs owing to *cis-trans* tautomerism. [For further references, see Palm (56).] For this equilibrium

$$K_{25^\circ} = \frac{p_{\text{trans}}}{p_{\text{cis}}} = 2.5$$

The *cis* form is believed to be about 500 cal/mole richer in energy than the *trans* form. (The statement that the interconversion of the two forms is hindered by an energy barrier of about 12 kcal/mole is, however, open to

doubt.) The structures shown in Fig. 3 have been proposed for the two forms. A third isomer in which the hydrogen atom is bonded to nitrogen can be excluded on the basis of the infrared spectrum.

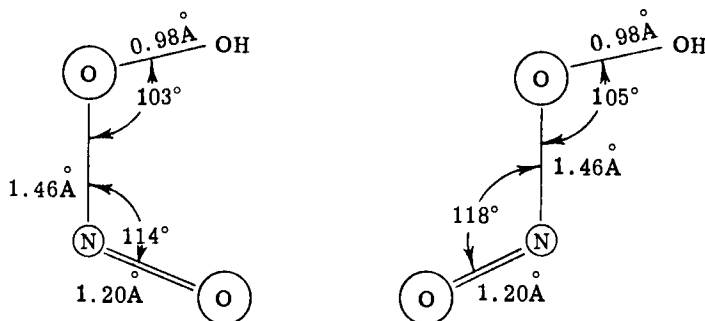


FIG. 3. Structures of *cis*- and *trans*-NO(OH)(g), according to Palm.

Jones *et al.* (43) obtained the structural data for *cis*- and *trans*-NO(OH)(g) shown in Table II from their infrared spectra. The observed N—O distance of 1.20 Å is almost that expected for a N=O bond. While these authors used the equilibrium $\text{NO(g)} + \text{NO}_2\text{(g)} + \text{H}_2\text{O(g)} \rightleftharpoons$

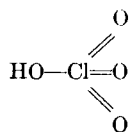
TABLE II
DISTANCES AND ANGLES IN *cis* and *trans*-NO(OH)(g)

	O—H (Å)	O—N (Å)	N—O (Å)	HON (angle)	ONO (angle)
<i>cis</i> -NO(OH)	0.98	1.46	1.20	(103°)	114°
<i>trans</i> -NO(OH)	0.98	1.46	1.20	(105°)	118°

2NO(OH)(g) as a basis for their infrared investigation at 25°, Ashmore and Tyler (3) carried out vapor pressure measurements at 20–80°C. Their thermodynamic data are given in Table I.

Other gaseous nonmetallic hydroxides. Hedberg and Badger (37) used infrared spectroscopy to detect gaseous chlorine hydroxide or ClOD in mixtures of $\text{Cl}_2\text{O(g)}$ with $\text{H}_2\text{O(g)}$ or $\text{D}_2\text{O(g)}$. Assuming the O—H distance to be 0.96 Å, as in water, and the O—Cl distance to be 1.70 Å, as in Cl_2O , the angle H—O—Cl is 113°.

The structure of gaseous chlorine trioxide hydroxide, ClO_3OH , was determined by Akishin *et al.* (1) by electron diffraction. Their results agree with a molecule



having C_{3v} symmetry. The molecular parameters are: $r(\text{Cl} = \text{O})$, 1.42 ± 0.01 Å; $r(\text{Cl} - \text{O})$, 1.64 ± 0.02 Å; HOClO ; $100^\circ \pm 2^\circ$. The position of the hydrogen atom was not determined.

Vapor pressures of condensed phosphoric acids have also been investigated over a wide range of temperatures and compositions. From measurements of molecular weight at 1020°C of the vapor obtained by vaporizing phosphoric acid with varying ratios of H_2O to P_2O_5 , it was concluded that a mixture of water and P_4O_{10} vapor and/or a low molecular weight ultra-phosphoric acid approximating to $\text{P}_3\text{O}_7(\text{OH})$ was present. Presumably the vapor contains water in addition to several low-molecular-weight ultra-phosphoric acids, including P_4O_{10} , the end member of this series of acids (13, 74, 76, 80).

Gaseous phosphorus oxide trihydroxide, $\text{PO}(\text{OH})_3$, (17), sulfur dioxide dihydroxide, $\text{SO}_2(\text{OH})_2$, (84) and selenium dioxide dihydroxide, $\text{SeO}_2(\text{OH})_2$ (72) are also known. Gaseous boron hydroxide will be dealt with in Section III.

B. METALLIC HYDROXIDES

1. The Mass Spectrometric Method of Investigation

The first vapor pressure measurements on alkali hydroxides were made by von Wartenberg and Albrecht (82, 83) and Jackson and Morgan (40) more than forty years ago. At that time it was impossible to make any deductions as to the nature of the species formed on vaporization, but we are now well informed on this subject as a result of recent work. In this work, the mass spectrometer has played a predominant role, since it permits the separation and identification of the separate gaseous species produced and hence enables us to determine their thermodynamic properties.

In the method of Chupka and Inghram (19, 20) a Knudsen cell, used for measuring vapor pressures, is combined with a mass spectrometer. The gas leaving the Knudsen cell, which is in equilibrium with the solid phase, is transferred to the ionization chamber of a mass spectrometer. The ions resulting from electron bombardment are observed in the mass spectrometer. The temperature dependence of the logarithm of the concentration of the volatile product (deduced from the observed ion intensity and the temperature) permits the calculation of the enthalpy of vaporization from the Clausius-Clapeyron equation. Absolute values of the vapor pressure may be determined by calibrating the measuring apparatus, using substances with known vapor pressure relationships. The following relationship is generally valid:

$$P_x = kTJ_{x^+} \quad (3)$$

P_x = vapor pressure of the component x ; k = proportionality constant to allow for the calibration; T = temperature of the effusion cell when J_{x^+} is measured; J_{x^+} = observed ion intensity of the component.

It is, of course, a prerequisite for valid observations that thermodynamic equilibrium is attained and that the ions observed are correctly assigned to the primary neutral species. The investigation therefore also involves a series of further measurements and observations, the nature of which is determined by the complexity of the problem and the presence of disturbing effects; these will not be dealt with more fully here.

The use of this method is not restricted to the determination of vapor pressures. It has been possible to apply it, after some modification, to the study of reactions between oxides and water, which is of special interest here. According to Chupka *et al.* (21), the effusion cell and ionization chamber may be evacuated separately. In this way, the mass spectrometer may be used with relatively high pressures of water vapor introduced by means of a needle valve in the effusion cell.

2. Results

From infrared spectroscopic studies of the gas phase over solid NaOH, KOH, and RbOH, Spinar and Margrave (71) believed gaseous hydroxides of the composition $M^+(OH)^-$ to be present. Porter and Schoonmaker (58, 59, 61, 65, 67) and also Perkowitz *et al.* (8), used the combined method, (involving the effusion cell and mass spectrometer) which has already been described to study the vaporization and sublimation equilibria of some alkali metal hydroxides. They also studied mixed solid phases of the type $Me_aMe_b(OH)_2$, where Me_a and Me_b are two metals of the series sodium, potassium, rubidium, and cesium. It was not possible, for reasons which will be mentioned shortly, to include LiOH in this investigation, but application of a modified technique to the system $Li_2O + H_2O$ was successful.

The essential conclusion from the study of these equilibria is that gaseous hydroxides are in fact formed. Tables III and IV summarize the results for the reactions studied and data derived from them. The authors discuss a number of interesting observations and conclusions arising from the work. Thus, Berkowitz, Meschi, and Chupka deduce a nonlinear structure for lithium hydroxide from a comparison with the lithium halides. In agreement with the structure proposed for Li_2F_2 and in keeping with the structures of other dimeric lithium halides and of Li_2O , they assume the planar diamond-shaped structure for $Li_2(OH)_2$, shown in Fig. 4. The thermodynamic functions determined with this model have been used to evaluate the observed results by applying the third law (cf. Section III.A.2.b). The ΔH_T° values so obtained are compared in Table IV with ΔH_T° values determined by the slope method [Section III, Eq. (17)].

Agreement is very satisfactory, except for the dimerization reaction $2\text{LiOH(g)} = \text{Li}_2(\text{OH})_2(\text{g})$, for which the authors consider the third-law value of 64 kcal to be more reliable.

TABLE III
ENTHALPY VALUES FOR THE SUBLIMATION-VAPORIZATION OF SODIUM
AND POTASSIUM HYDROXIDES

	ΔH_T (kcal/mole) ^a		T (°K)	
	Na	K	Na	K
I $\text{MeOH(s)} \rightleftharpoons \text{MeOH(g)}$	46.4 ± 3	43.9 ^b	298	298
II $\text{MeOH(l)} \rightleftharpoons \text{MeOH(g)}$	43 ± 3	44.6 ± 3	660	298
III $2\text{MeOH(s)} \rightleftharpoons \text{Me}_2(\text{OH})_2(\text{g})$	—	36 ± 2	—	626
IV $2\text{MeOH(l)} \rightleftharpoons \text{Me}_2(\text{OH})_2(\text{g})$	28 ± 3	—	660	—

^a In reactions III and IV the percentage of dimer is given.

^b Kelley, from the data of von Wartenberg.

When the solid phase consists of a mixture of various hydroxides, as in the investigations of Porter and Schoonmaker, gaseous species of the type $\text{Me}_a\text{Me}_b(\text{OH})_2(\text{g})$ are found. Equilibrium constants for the reaction

TABLE IV
ENTHALPY VALUES FOR REACTION IN THE FORMATION
OF GASEOUS LITHIUM HYDROXIDE

	ΔH_T (kcal/mole)		$T^\circ\text{K}$	
	A ^a	B ^b	A	B
$\text{Li}_2\text{O(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{LiOH(g)}$	78 ± 3	80 ± 2	1300	1300
$\text{Li}_2\text{O(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{Li}_2(\text{OH})_2(\text{g})$	14 ± 2	16 ± 4	1250	1500
$2\text{LiOH(s)} \rightleftharpoons \text{Li}_2(\text{OH})_2(\text{g})$	44 ± 3	45 ± 3	500	600
$\text{Li}_2(\text{OH})_2(\text{g}) \rightleftharpoons 2\text{LiOH(g)}$	58 ± 3	64 ± 4	1300	1300

^a Estimated from the slope of the graph of $\ln K$ vs $1/T$.

^b Estimated by the "third-law" method.

$(\text{Me}_a)_2(\text{OH})_2 + (\text{Me}_b)_2(\text{OH})_2 \rightleftharpoons 2\text{Me}_a\text{Me}_b(\text{OH})_2$ are given in Table V. The experimental values correspond approximately with the value $K = 4$, which is to be expected from entropy considerations $\Delta_R H \approx 0$ for the above reactions. Since polymeric gaseous alkali halides exist, the formation of gaseous alkali hydroxide halides [e.g., $\text{Na}_2(\text{OH})\text{F}$] is also very likely (68).

The occurrence of polymeric gaseous species as products of the vaporization process is not restricted to alkali hydroxides but is a phenomenon which is observed with many oxides. Aggregation numbers lie between 2 and 4 or higher. Brewer (10) has shown that there is a simple relationship between

the dimerization energy, ΔH_D , and ΔH_1 , the enthalpy of vaporization of the monomer, according to which the ratio between monomer and dimer or polymer is established as a function of temperature. Thus if $\Delta H_D > \Delta H_1$,

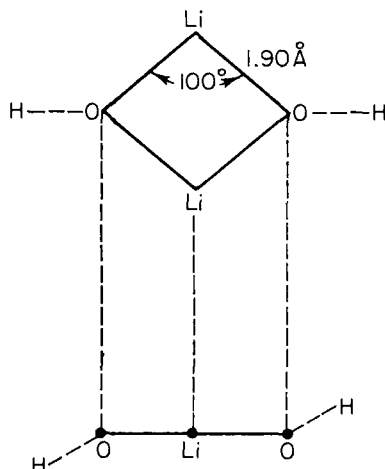


FIG. 4. Proposed structure for $\text{Li}_2(\text{OH})_2$.

the dimeric species will be the main product of vaporization at lower temperatures; with rising temperatures the monomeric species will predominate. This relationship is found for sodium and potassium hydroxides.

TABLE V
EQUILIBRIUM CONSTANTS FOR THE REACTION
 $(\text{Me}_a)_2(\text{OH})_2(\text{g}) + (\text{Me}_b)_2(\text{OH})_2(\text{g}) \rightleftharpoons 2\text{Me}_a\text{Me}_b(\text{OH})_2(\text{g})$

$\text{Me}_a\text{OH}-\text{Me}_b\text{OH}$	K	$T(^{\circ}\text{K})$
RbOH—CsOH	4.2 ± 0.1	673
KOH—RbOH	5.2 ± 1.0	693–718
NaOH—KOH	4.9 ± 0.3	883
NaOH—RbOH	2.8 ± 0.3	823
KOH—CsOH	3.5 ± 1.0	629

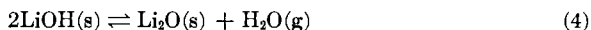
Energies of dimerization for the various alkali hydroxides are set out in Table VI. Apart from the value for LiOH, results for the dimerization energies are obtained with mixed solid phases. The value for LiOH was obtained directly and is thus independent of the values for the other alkali hydroxides, which are relative. It agrees with the observed trend of decrease in dimerization energy with increase in atomic number of the alkali metal.

The sublimation equilibrium of lithium hydroxide could not be studied

TABLE VI
ENTHALPIES OF DIMERIZATION OF VARIOUS ALKALI HYDROXIDES
 $2\text{MeOH(g)} \rightleftharpoons \text{Me}_2(\text{OH})_2(\text{g})$

MeOH	ΔH_T (kcal/mole of Dimer)	T°K
LiOH	-64	1300
NaOH	-54	660
KOH	-48	883
RbOH	-45	823
CsOH	-40	692

in the way used for the other alkali metal hydroxides; the decomposition equilibrium



lies so far to the right at the operating temperature that the resulting partial pressure of H_2O interferes with the use of the mass spectrometer.² It is necessary, therefore, to study the reverse reaction in the presence of a much smaller partial pressure of water vapor than corresponds to the decomposition of LiOH .

Schoonmaker and Porter (68) worked in the temperature range 780–900°C, but with a maximum water vapor partial pressure of 10^{-2} mm of mercury. They discussed the possible influence of the water vapor partial pressure on the ratio of monomer to dimer, and concluded that the low pressure used was unfavorable for the formation of dimer or excluded the production of this species. They also worked with mixtures of Li_2O and Na_2O as the solid phase under the same reaction conditions. From this investigation it was found that the energy of dimerization to $\text{Li}_2(\text{OH})_2$ was about 4 to 6 kcal/mole of dimer different from that to $\text{Na}_2(\text{OH})_2$; this leads to a value of 58–60 kcal for LiOH , in agreement with that obtained by the slope method.

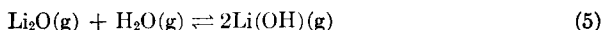
Berkowitz *et al.* were able with their technique to control the water vapor partial pressure at about 0.1 mm Hg. They worked in the temperature range 830–1130°C and found that the main product was LiOH(g) , with smaller amounts of $\text{Li}_2(\text{OH})_2(\text{g})$ and traces of $\text{Li}_3(\text{OH})_3(\text{g})$.

These investigations, in which the gaseous hydroxide is prepared by reaction of the metal oxide with water vapor, are of interest not only as a

² Direct observation of sublimation (vaporization) was practically impossible because of the strongly corrosive nature of LiOH . Even in work with KOH and NaOH the activity of the fused alkali hydroxide was observed to be influenced by the crucible material (MgO). This results in a slight uncertainty in the data in Table III, which was pointed out in ref. 60, without numerical corrections being made.

contribution to our knowledge of the gaseous alkali hydroxides, but also because they deal with a type of reaction in which the (apparent) increase in the vapor pressure of an oxide is brought about by a foreign gas (H_2O). This is further discussed in Section III. Mass spectroscopic studies of these reactions (so far as metal oxides are involved) are not yet available.

The relationship is made clearer by the work of van Arkel *et al.* (77). It was shown that Li_2O has an increased vapor pressure in the presence of water vapor, and this leads to greater vaporization of the oxide in the oxygen stream than when water vapor is absent. The product vaporized in these experiments was trapped by means of a cool finger and identified by X-ray methods as LiOH . (As the authors pointed out, the nature of the gaseous product was not necessarily proved by this method.) In view of the work of Smith and Sugden (70), who showed that LiOH is stable at 2000° , van Arkel, Spitzbergen, and Heyding assumed the reaction



C. INVESTIGATIONS IN THE OXYHYDROGEN FLAME

Sugden and his co-workers (73) assume the formation of gaseous alkali hydroxides in an oxyhydrogen flame into which aqueous alkali metal salt solutions (mostly nitrates or acetates) are sprayed. Both vaporization and ionization of the metal atoms take place. Assuming equilibrium is obtained (though this has not been proved directly for the part of the flame studied), the electron concentration may be calculated by Saha's method (64). It may also be determined experimentally by measuring the absorption of microwave radiation. Only for sodium do the values agree; the discrepancies for the other alkali metals may be understood if the formation of gaseous alkali hydroxide and OH^- ions is assumed.

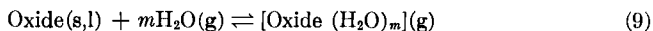


A further possible way of studying such flames is by the photometric examination of the flame spectra in the visible and ultraviolet region. The spectra of the alkali and alkaline earth metals have been known for a hundred years and are used in determining them by flame photometry. Formerly molecules such as Ca_2 or the oxides were assumed to be carriers for the spectra of the alkaline earth metals. From a comparison with the halide spectra, and from spectrophotometric measurements, James and Sugden (41), Lagerquist and Huldt (45) and Gaydon (29) came to the conclusion that the band spectra in these flames arose mainly from the radicals CaOH , SrOH , and BaOH .

Magnesium salts in the oxyhydrogen flame show a characteristic band spectrum in the near ultraviolet which is due to MgOH (16). Under similar conditions GaOH, InOH, and TlOH (15), MnOH (55), and CuOH (14) occur; the last of these is said to be responsible for the well known green coloration of flames by copper salts.

III. Systems of the Type $\text{Oxide}(s,l) + \text{H}_2\text{O}(g) \rightleftharpoons \text{Hydroxide}(g)$

Experiments have shown that various oxides react with water vapor to form gaseous products. The observations may be described in terms of the hypothesis of an increase in the vapor pressure of the oxide in presence of water vapor. For high pressures and with strong attractive forces such effects as solubility of solid bodies in gases are known. For the systems considered here, however, the increase in vapor pressure at atmospheric pressure is appreciably greater than would be expected from a simple physical model. It is apparent from this that there must be considerable interaction between the oxide and water vapor, which may be formulated by the reaction scheme in Eq. (1), in which



the expression on the right denotes only over-all composition, no indication of the mode of bonding being given. A study of this heterogeneous equilibrium yields information about the association number, m , and the interaction energy between oxide and water vapor, and hence about the nature of the gaseous compound formed. In our case it provides information on the possibility of forming a gaseous hydroxide. Reactions which can be described by the equilibrium of Eq. (9) may be divided into two groups: A. Reactions at atmospheric pressure; B. Reactions at higher pressures.

A. REACTIONS AT ATMOSPHERIC PRESSURE

Heterogeneous reactions at high temperatures may be represented as approximately obeying the ideal gas laws. From (9) it follows that

$$k_m = \frac{p_{[\text{oxide}(\text{H}_2\text{O})_m]}}{p_{\text{H}_2\text{O}}^m}$$

or, in shortened form

$$k_m = \frac{p_{\text{hyd}}}{p_{\text{H}_2\text{O}}^m} \quad (10)$$

The equilibria in question may be examined by vapor pressure measurements, preferably made by the transfer method or, at pressures $<10^{-5}$ to 10^{-6} atm, by the Knudsen effusion technique. Measurements with the Knudsen cell in association with the mass spectrometer have been made

for the equilibria under consideration here in the cases of lithium hydroxide and the boron hydroxides. Infrared emission spectroscopic studies have also been made for the system $B_2O_3(l)-H_2O(g)$, and the results agree well with those obtained by mass spectrometric and transfer methods. The transfer method has various advantages arising from the ease of manipulation, the reliability of the measurements, and the possibility of varying the conditions of the experiment widely. It is understandable, therefore, that this method has been used frequently for the study of the reactions under consideration. However, in spite of the simple technique involved in the transfer method, some precautions must be taken to obtain dependable measurements. Because of their general interest, we will now consider briefly the method and the limitations attending the interpretation of the results obtained.

1. *The Transfer Method of Investigation*

In this method water vapor or mixtures of it with other gases (N_2 , O_2) are passed over the oxide at the temperature of the experiment, and the gas stream becomes saturated to the equilibrium pressure. In this way, material is drawn from the reaction zone without disturbing the equilibrium, provided the experiment is conducted properly. The material is condensed outside of the reaction zone, so that its quantity may be determined. In the simplest case this is done by weighing (the loss in weight of the specimen in the reaction tube may also be measured). The amount of material transferred per unit volume of carrier gas is then determined as a function of the partial pressure of water vapor and the temperature. In essence it is a question of making sure, by choice of the conditions of the experiment, that the amount of substance transferred by the carrier gas in unit time (\dot{n}) under otherwise identical conditions varies linearly with its flow rate (\dot{v}). This function, $\dot{n} = f(\dot{v})$ in a general case is shown in Fig. 5. The extent of the regions A, B, and C depends on the conditions of the experiment. In A a transfer due to diffusion is added to that due to the equilibrium pressure of the substance. Region B represents the ideal case of proportionality, while in C the transfer gas is not saturated. The supersaturation in region A may be overcome experimentally by increasing \dot{v} . The risk of unsaturation in C may be reduced by reducing the gas space over the sample and by increasing the length of the cell. It is possible to make region B sufficiently large by suitable construction of the transfer cell. Further details of the theory and technique may be obtained from recent publications (38).

Data are collected in Table VII in order to give an impression of the results of transfer experiments with WO_3 , MoO_3 , TeO_2 , and BeO . They also illustrate the apparent increase in vapor pressure, resulting from the interaction of the solid oxide with gaseous water, which was mentioned earlier.

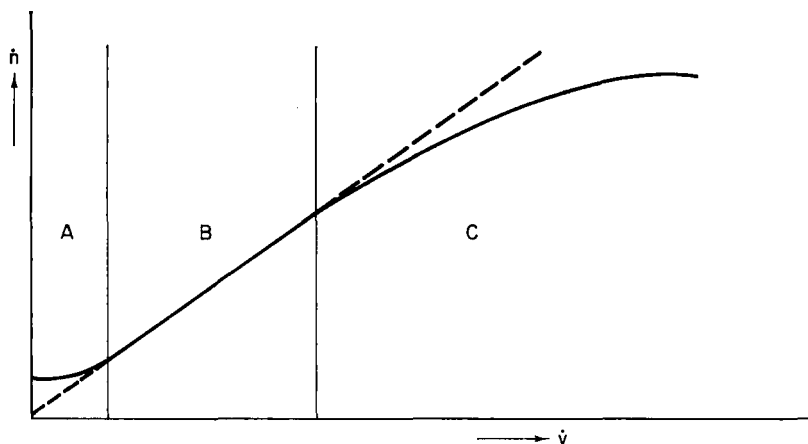


FIG. 5. Amount of substance, \dot{n} , transferred per unit time as a function of the flow rate, \dot{v} .

TABLE VII
RESULTS OF MEASUREMENTS BY THE TRANSFER METHOD

	T	Carrier gas			Apparent vapor pressure of oxide	Oxide transported as gaseous compound	Approximate duration of experiment
		O ₂	H ₂ O	$p_{\text{H}_2\text{O}}$			
	(°K)	l(STP)	l(STP)	(mm Hg)	(mm Hg)	(mg)	(hr)
WO ₃	1323	9.13	0.57	44	0.151	21.0	1.6
	1323	—	9.10	751	2.43	305.0	1.5
MoO ₃	933	13.69	0.36	19	0.140	17.1	2.3
	933	1.84	13.2	650	1.021	132.6	2.5
TeO ₂	923	30.78	3.28	71	0.020	6.7	5.6
	923	—	32.00	748	0.141	42.8	5.3
BeO	1586	—	62.30	736	0.089	8.4	15.2
	1822	—	6.46	738	0.533	5.2	7.8

2. Evaluation of Results

The mixture of water vapor with a gas (the dilution component) which is inert with respect to the system will be referred to as the carrier gas. The volume V of the dilution component is determined, for example, with the aid of a flow meter or a small gas holder.

The water vapor component, $m_{\text{H}_2\text{O}}$, is obtained by weighing the water frozen out after separating the substance transferred. The reaction temperature T , the total pressure P (which is almost the same as the barometric pressure) and the mass of the substance transferred, m_{oxide}^+ , are also known.

Applying the usual corrections, and knowing, or assuming, the molecular weight of the gaseous compound produced (cf. Section III,A,13), partial pressures may be calculated from Dalton's law as:

$$p_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{\Sigma n_i} \cdot P \quad p_{\text{oxide}}^+ = \frac{n_{\text{oxide}}^+}{\Sigma n_i} \cdot P \quad (11)$$

The term n_i denotes the number of moles of the components i.e., $\Sigma n_i = n_v + n_{\text{H}_2\text{O}} + n_{\text{oxide}}^+ = n_{\text{carrier gas}} + n_{\text{oxide}}^+$; $n_{\text{oxide}}^+ = (m_{\text{oxide}}^+/M_{\text{oxide}}^+)$; n_v = number of moles of dilution component; M_{oxide}^+ = molecular weight of the gaseous product. It frequently happens that $n_{\text{oxide}}^+ \ll n_{\text{carrier gas}}$, so $\Sigma n_i \approx n_{\text{carrier gas}}$. The term p_{oxide}^+ may be defined as the apparent vapor pressure of the oxide under the conditions used. This is the sum of the saturation pressure of the oxide, p_{oxide}^* ,³ and the vapor pressure of the reaction product, p_{hyd} ; from this it is possible to determine the association number m and the equilibrium constant k_m .

a. *Association Number m and the Equilibrium Constant k_m .* If p_{oxide}^+ is plotted against $p_{\text{H}_2\text{O}}$ as an isotherm, a straight line is obtained for the association number $m = 1$; the slope of this gives the equilibrium constant k_m .

$$p_{\text{oxide}}^+ = p_{\text{hyd}} + p_{\text{oxide}}^* \quad (12)$$

From this expression, by combination with Eq. (10), we obtain

$$p_{\text{oxide}}^+ = k_m p_{\text{H}_2\text{O}}^m + p_{\text{oxide}}^* \quad (13)$$

If there were not interaction between the oxide and water vapor this straight line would be parallel to the abscissa: $p_{\text{oxide}}^+ = p_{\text{oxide}}^*$. In Fig. 6, results for the system $\text{WO}_3 + \text{H}_2\text{O}$ are shown; they are typical also of the other systems studied. The linear relationship between p_{oxide}^+ and $p_{\text{H}_2\text{O}}$ shows that the association number m is unity in this case. As will be seen later, the association number for the boron hydroxides can have values other than unity. In the general case when $m \neq 1$, its value is derived from the equation

$$\log p_{\text{hyd}} = m \log p_{\text{H}_2\text{O}} + \log k_m = \log (p_{\text{oxide}}^+ - p_{\text{oxide}}^*) \quad (14)$$

b. *Thermodynamic Data.* The experimental relationship between the increase in the saturation pressure of the oxide, p_{oxide}^* , by p_{hyd} and the partial pressure of H_2O in the reaction equilibrium at different tempera-

³ This is true in the case when the degree of polymerization, x , of the gaseous oxide [e.g., $(\text{MeO})_x$] is equal to y , that for the gaseous hydroxide [e.g., $\text{Me}_y\text{O}_{y-1}(\text{OH})_2$]. If $x \neq y$ we obtain $p_{\text{oxide}}^+ = p_{\text{hydroxide}} + p_{\text{oxide}}^*$. (x/y), assuming that other possible vaporization or reaction products have a negligible effect. If $p_{\text{oxide}}^+ \gg p_{\text{oxide}}^*$, which is often observed at lower temperatures, this relationship is simplified. It then follows that $n^+ = n_{\text{hydroxide}}$; $p_{\text{oxide}}^+ \approx p_{\text{hydroxide}}$.

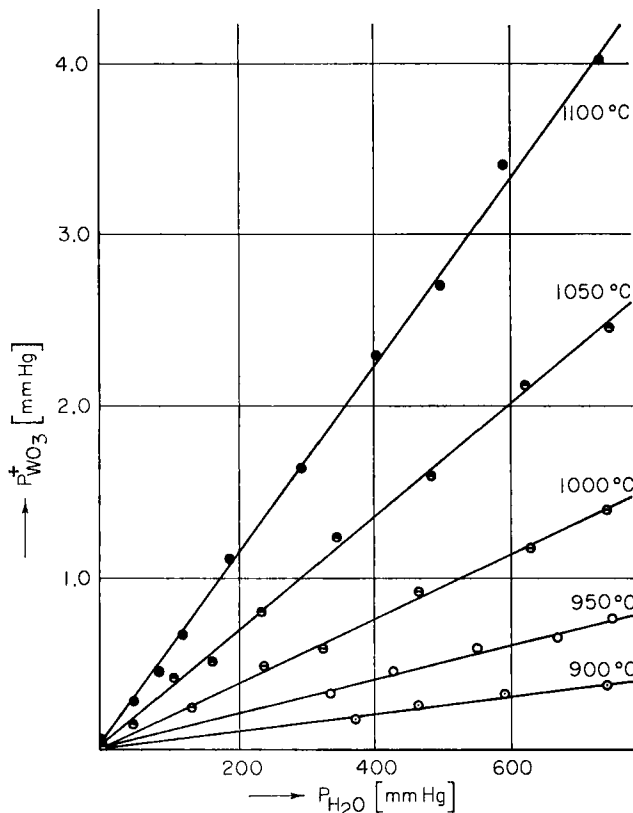


Fig. 6. Apparent vapor pressure of WO_3 as a function of the partial pressure of water vapor.

tures may be interpreted in terms of an association (without compound formation) involving dipole-dipole forces or hydrogen bonds. Since, however, the association number is definite and small it is possible to make more far-reaching conclusions. It is necessary to differentiate between the stoichiometrically equivalent alternatives of the formation of a gaseous oxide hydrate and a gaseous hydroxide; hydroxide formation is very likely if the interaction energy is relatively large.

The enthalpy of the homogeneous reaction $Oxide(g) + H_2O(g) \rightleftharpoons Hydroxide(g)$ provides a measure of the interaction energy, which is obtained from the enthalpy of sublimation (or vaporization) of the pure oxide and the enthalpy of the heterogeneous reaction. The latter may be determined from the temperature dependence of the equilibrium constants.

$$\frac{d \ln k_m}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (15)$$

Using a power series for C_p , integration of this equation leads to an expression of the form

$$R \ln k_m - \sum \nu_i \left(a_i \ln T + \frac{b_i T}{2} + \frac{c_i T^2}{6} \right) = C - \frac{\Delta H^\circ}{T} \quad (16)$$

where ΔH° and C are integration constants.

As a rule it is not necessary to evaluate the observations in terms of this relationship since further simplifications may be introduced. For a limited temperature range $\Delta C_p \approx 0$, and one then obtains the expression

$$R \ln k_m = \frac{-\Delta H^\circ}{T} + C \left(\text{or, generally, } \log k_m = \frac{-A}{T} + B \right) \quad (17)$$

which is used by nearly all authors in the first evaluation of their experimental results, together with the following relationship:

$$\Delta G_\theta^\circ = \Delta H_{T'}^\circ - \theta \Delta S_{T'}^\circ = -R\theta \ln k_m \quad (18)$$

In this expression $\Delta H_{T'}^\circ$ and $\Delta S_{T'}^\circ$ are taken as constant for a limited temperature range T'

$$\Delta H_{T'}^\circ = \Delta G_{T'} + T \Delta S_{T'}^\circ \quad (19)$$

Alternatively, $\Delta H_{T'}$ may be evaluated by the "third-law" method; $\Delta G_{T'}$ is calculated from values for k_m and T , and if $\Delta S_{T'}$ is known $\Delta H_{T'}$ may be obtained. $\Delta S_{T'}$ may be calculated from tabulated values. Entropy values for compounds which have not yet been investigated may be estimated or determined by the methods of statistical mechanics on the basis of assumptions about the molecule.

The "free energy function" (referred to 0°K)

$$\frac{G_T^\circ - H_0^\circ}{T} = \frac{H_T - H_0^\circ}{T} - S_T^\circ \quad (20)$$

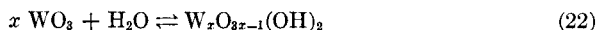
or, for a chemical reaction

$$\Delta \left(\frac{G_T^\circ - H_0^\circ}{T} \right) = \frac{\Delta G_{T'}^\circ}{T} - \frac{\Delta H_0^\circ}{T}, \quad (21)$$

is frequently used in these calculations. The ΔH_0° values may be calculated for various values of $\Delta G_{T'}$ and T . From this a mean value may be determined, from which statements about the scatter of the separate measurements can be made. ΔH_0° may be recalculated for any required temperature. Comparison of the values of $\Delta H_{T'}^\circ$ obtained by applying the third law with those determined from Eq. (17) is revealing, for from their good agreement far-reaching conclusions about the consistency of the calculation and the model assumed can be drawn.

3. Limitations of the Method of Evaluation of Results

From the experimental point of view both the determination of the increase in vapor pressure of the oxide in presence of water vapor and the association number m are quite definite. On the other hand information obtained from the enthalpy of the reaction can be interpreted, even with caution, only if some hypothesis is used to provide a value for the molecular size of the stoichiometrically equivalent reaction product. The measurements give no information on the molecular size of the compound produced. For example, in formulating the heterogeneous equilibrium such as



a value of x must be assumed. The significance of the determined enthalpy value is then doubtful. Reactions involving more than one unit of oxide, e.g., with $x = 3$, cannot be excluded, since Berkowitz *et al.* (6) observed trimeric gaseous molecules of W_3O_9 in studying the sublimation equilibrium of WO_3 , and corresponding results have been reported for MoO_3 (7) and BeO (21). In order to limit this uncertainty when evaluating equilibrium data, it is sometimes possible to postulate several models for the gaseous reaction product formed, corresponding to the several gaseous products of sublimation observed with the mass spectrometer. Enthalpy values determined in this way demonstrate the tendency for a strong interaction between the oxide and water.

More concrete deductions can be made if additional considerations, such as the estimates of entropy and notions of structures, are taken into account. For example, as will be seen later, it may be shown that in the reaction of WO_3 , $x = 1$.

In order to make sound deductions it is necessary to determine the molecular magnitude. This can be done in several ways. The use of the mass spectrometer is especially important, since it makes possible the individual observation of each reaction product; this consideration is also important when other complications, such as the combination of the reaction products and the existence of competing equilibria, occur.

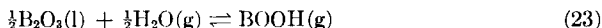
4. Results

The interaction with water vapor described at the beginning of this section is observed for seven oxides, namely, B_2O_3 , Li_2O , BeO , ZnO , MoO_3 , WO_3 , TeO_2 . In all cases the reaction products are described as gaseous hydroxides. Too few systems have been investigated for it to be worth attempting a systematic interpretation, but further studies in this field should broaden our knowledge and make it possible to establish more general relationships. The impulse for such further work will come, as

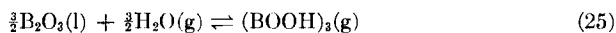
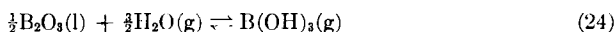
hitherto, from problems connected with the properties of materials and corrosion, from preparative and geochemical work, and, not least, from general studies. It seems safe to predict that further oxides will be found to form volatile hydroxides in presence of water.

A review of the results of work up to the present time is given in Table VIII, in which thermodynamic data on the reactions studied are collected. Apart from the reactions with Li_2O and B_2O_3 for which the third law method was used, the data were determined on the basis of Eq. (17). Table VIII also includes values for the constants A and B in the expression $\log k_m = (-A/T) + B$ [cf. Eq. (17)] and references.

a. Gaseous Boron Hydroxides. It may be shown by the transfer method (46, 46a) that the reaction between $\text{B}_2\text{O}_3(\text{l})$ and $\text{H}_2\text{O}(\text{g})$ at higher temperatures can be described essentially by the equation



It was concluded from the investigation that $\text{BOOH}(\text{g})$ was not the only reaction product, though it was the most important. Other possible reactions may be formulated, such as



As was explained in the introduction it is not possible to elucidate fully several simultaneous reactions by the transfer method without introducing hypotheses.

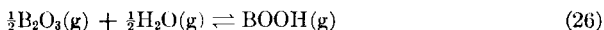
The position is clearer when the mass spectrometer is used, and the work of Meschi *et al.* (49) will therefore be discussed first. These authors studied the reaction in the system $\text{B}_2\text{O}_3(\text{l})$ and $\text{H}_2\text{O}(\text{g})$ at $1060^\circ\text{--}1450^\circ\text{K}$ with the combined use of the effusion method and the mass spectrometer, as described in Section II. The partial pressure of water in these experiments could be varied from 0.05 to 0.14 mm of mercury. The ions H_2O^+ , BOOH^+ , $(\text{BOOH})_3^+$, and $\text{B}(\text{OH})_3^+$ were found. The most interesting result was that the main product detected was $\text{BOOH}(\text{g})$: both the trimeric species and $\text{B}(\text{OH})_3(\text{g})$ were present to the extent of $<1\%$ of the amount of monomer. White *et al.* (86) confirmed this result.

The occurrence of BOOH^+ as a secondary product, formed perhaps from $(\text{BOOH})_3(\text{g})$, was shown to be very unlikely on the basis of intensity measurements. The observed dependence of the BOOH^+ peak intensity on the partial pressure of water made this quite certain. The authors found a relationship corresponding to an association number $m = 0.5$ [cf. Eq. (13)] rather than $m = 1.5$, which would have been expected if the main product had been the trimer. The enthalpy of the reaction was found from Eq. (17) to be 42.3 kcal/mole ($T = 1060^\circ\text{--}1450^\circ\text{K}$). This value agreed

TABLE VIII
THERMODYNAMIC DATA ON REACTIONS OF SOME OXIDES WITH $\text{H}_2\text{O}(\text{g})$

	T' °K	$-A$	B	$\Delta H_{T'}$ (kcal/mole)	$\Delta S_{T'}$ e.u.	ΔG^θ (kcal/mole)	θ (°K)	Reference
$\frac{1}{2}\text{B}_2\text{O}_3(\text{s}) + \frac{1}{2}\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{BOOH}(\text{g})$	1060–1450	—	—	42.3	—	—	—	(49)
$\text{Li}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons (2\text{LiOH})(\text{g})$	1100–1400	—	—	7.90	43.6	21.8	1310	(8)
$\text{BeO}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Be}(\text{OH})_2(\text{g})$	1462–1823	9060	1.63	41.5	7.4	29.0	1673	(35)
$\text{ZnO}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Zn}(\text{OH})_2(\text{g})$	1573–1623	—	—	102.2	48.8	25.3	1573	(30)
$\text{MoO}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{MoO}_2(\text{OH})_2(\text{g})$	873– 963	7731	5.45	35.3	24.9	16.20	963	(32)
$\text{WO}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{WO}_2(\text{OH})_2(\text{g})$	1173–1373	8725	4.10	39.9	18.8	14.11	1373	(32)
$\text{TeO}_2(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{TeO}(\text{OH})_2(\text{g})$	923– 973	7290	4.11	33.4	18.8	18.70	973	(32)

within the limits of error with the value of ΔH_T° determined by the third law method. Values for the homogeneous reaction

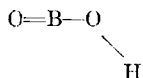


were calculated from a direct determination of the equilibrium constants by the third-law method; the mean value was $\Delta H_T^\circ = -1.4$ kcal.

The enthalpy of sublimation of B_2O_3 may be determined from the ΔH_T° values for the homogeneous reaction (26) and the heterogeneous reaction (24).⁴ This then serves as a check. Values of ΔH_{298}° and hence ΔH_0° values were determined for both reactions from the free energy function. Twice the difference [ΔH_0° for reaction 15 — ΔH_0° for reaction (26)] gives the enthalpy of sublimation, ΔH_0° , for B_2O_3 ; Meschi *et al.* found the value 99 ± 6 kcal/mole, while White [private communication; cf. (8)] finds 94.5 kcal/mole.

Although the agreement of the above value is apparent, it is very interesting to compare them with the results of other investigations. The system $\text{B}_2\text{O}_3\text{--H}_2\text{O}$ affords a beautiful example of how the most varied methods give results which are in agreement and which therefore enable us to draw firm conclusions. It is very desirable that several methods should be applied to other systems, and indeed the first experiments in this direction are in hand.

White *et al.* (86) have studied the infrared emission spectrum of the gas phase of the system $\text{B}_2\text{O}_3(\text{l})\text{--H}_2\text{O}(\text{g})$ in the temperature range 1250 to 1450°K with water vapor pressures from 1 to 15 mm Hg. Their results show the production of $\text{BOOH}(\text{g})$ as the main product of the interaction. The spectroscopic data are consistent with the structure



containing a linear $\text{O}=\text{B}-\text{O}$ group. The authors found an enthalpy change ΔH_T° of 39 ± 2.5 kcal/mole ($T = 1350^\circ\text{K}$) for reaction (23), a value which agrees with the mass spectrographic result. The value was obtained from the variation in intensity of the 2030 cm^{-1} band with temperature. In this connection, Fig. 7 shows the results of observations of the equilibrium $\frac{1}{2}\text{B}_2\text{O}_3(\text{l}) + \frac{1}{2}\text{D}_2\text{O} \rightleftharpoons \text{BOOD}(\text{g})$ in the form of a plot of the logarithm of partial pressure of $\text{BOOD}(\text{g})$ against $1/T$.

The band at 2030 cm^{-1} was the strongest of those observed under the conditions used. It lies very close to 2040 cm^{-1} , at which frequency a strong band is observed in the investigation of the B_2O_3 vaporization equilibrium.

⁴ Otherwise values for the homogeneous reaction are calculated from the enthalpy values for the pure oxide and those for the heterogeneous reaction.

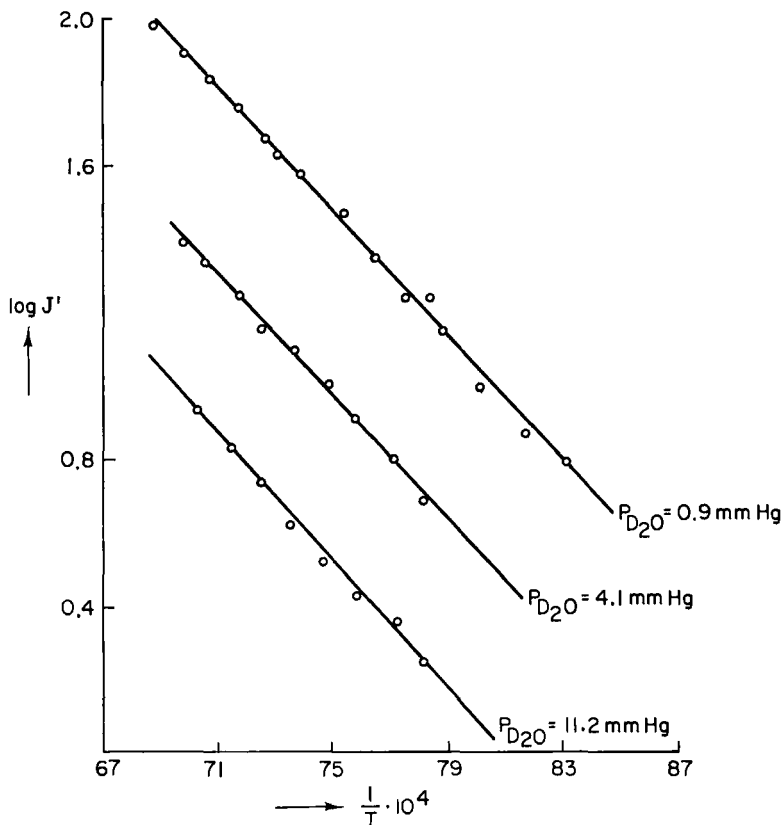


FIG. 7. Variation of the intensity of the 2030 cm^{-1} band of BOOD with temperature for different partial pressures of water vapor. J' is put equal to $JT \exp(h\nu)/(kT)$ in order to relate the observed intensity (J) to the partial pressure of the species observed. D_2O is used instead of H_2O for technical reasons.

The authors were able to show beyond question that at 2030 cm^{-1} a gaseous species other than $\text{B}_2\text{O}_3(\text{g})$ is present: for example, the intensity of the band at 2030 cm^{-1} was already appreciably developed at temperatures at which bands of the $\text{B}_2\text{O}_3(\text{g})$ spectrum were scarcely observable. Variation of the intensity with temperature gave a different picture from that observed in the vaporization of $\text{B}_2\text{O}_3(\text{l})$. More convincing is the fact that the intensity depended on the D_2O partial pressure, being almost zero when the D_2O partial pressure was zero.

This relationship between intensity and D_2O partial pressure may also be used to make deductions about the stoichiometry of the reaction. Corresponding measurements, evaluated according to Eq. (13), gave association numbers of 0.5 to 0.7. The theoretical value for the formation of $\text{BOOH}(\text{g})$

according to Eq. (23) is 0.5; for the formation of $\text{B}(\text{OH})_3(\text{g})$ or $(\text{BOOH})_3(\text{g})$ it would be 1.5. The experimental results therefore indicate clearly that the course of the reaction follows Eq. (23).

It has been pointed out already that the mass spectrographic results agree well with those obtained by infrared spectroscopy and by the transfer method. Table IX, in which the values found for the enthalpy of formation of $\text{BOOH}(\text{g})$ by various methods are collected, demonstrates this correlation.

TABLE IX
ENTHALPY OF FORMATION IN KCAL/MOLE BORON HYDROXIDE
DETERMINED BY VARIOUS METHODS

Method	Mass spectroscopic (49)	Infrared spectroscopic (86)	Transfer method (62)
HBO_2	-137.5^a	-135 ± 3	-134.9 ± 1
$(\text{HBO}_2)_3$	-540 ± 10	537 ± 10	-537.5 ± 3

^a All units are kcal/mole.

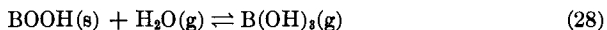
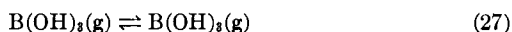
It must not be overlooked that the good agreement would be still more convincing if the measurements by the transfer method related to a wider range of materials. One of the advantages of this method is that the partial pressure of water vapor can be varied widely. Randall and Margrave (62) have done this, though they limited themselves to a few measurements. Interpretation of their results gives an association number $m \approx 1.5$ at 1073°K : only at higher temperatures (1273°K) is a value of $m \approx 0.5$ observed. This was found only at low H_2O partial pressures (10^{-1} to 10^{-2} atm), while at H_2O partial pressures $> 10^{-1}$ atm a value of $m \approx 1.5$ resulted. They thus showed that, as already mentioned, there are probably several gaseous species in the system $\text{B}_2\text{O}_3(\text{l})\text{-H}_2\text{O}(\text{g})$ as the temperature and H_2O partial pressure are varied. This is in agreement with theoretical considerations (24) and also with the results of other investigations.

For all the methods the determination of the enthalpy of formation of $(\text{BOOH})_3(\text{g})$ is less certain (cf. Table IX), though it is clear that the detection of this species is not in question. Meschi *et al.* obtained a positive ΔH_T° value for the reaction $\frac{3}{2}\text{H}_2\text{O}(\text{g}) + \frac{3}{2}\text{B}_2\text{O}_3(\text{l}) \rightleftharpoons (\text{BOOH})_3(\text{g})$ using Eq. (16) as a method of evaluation, while a negative value was given by the third law method. They concluded from this that equilibrium was incompletely established at lower temperatures; under these conditions the partial pressure of the trimer is too small for reliable evaluation. Conditions are more favorable at higher temperatures. Using the reaction $\text{B}(\text{OH})_3(\text{g}) + \text{B}_2\text{O}_3(\text{l}) \rightleftharpoons (\text{BOOH})_3(\text{g})$ the authors used the equilibrium constant at 1451°K to deduce a value of ΔH_{1451}° of -3 kcal/mole by the third law

method. From this they found the enthalpy of formation of the trimer to be -540 kcal/mole.

With the other methods of investigation it is necessary to make assumptions about the partial pressures of the species $\text{B(OH)}_3(\text{g})$, $\text{BOOH}(\text{g})$ and $(\text{BOOH})_3(\text{g})$ which are postulated. These may be supported by data on the known behavior of $\text{B(OH)}_3(\text{g})$ and by conclusions based on changes in the reaction conditions (24).

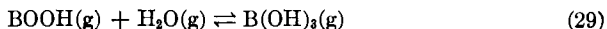
Any report on gaseous boron hydroxides would be incomplete without consideration of the volatility of B(OH)_3 at lower temperatures, which has been known for a long time (34, 75, 75a). According to von Stackelberg *et al.* (81) the system $\text{B(OH)}_3\text{-H}_2\text{O}$ at 110° to 180°C may be described by the following equations:



The vapor pressure of B(OH)_3 is independent of the water vapor partial pressure at 140°C .⁵ At this temperature the solid phase $\text{B(OH)}_3(\text{s})$ is transformed into $\text{BOOH}(\text{s})$. Above 140° one observes a proportionality between $p_{\text{H}_2\text{O}}$ and $p_{\text{B(OH)}_3}$ and relationships which are the same as for other oxide-water systems. The authors used the transfer method; their results are summarized in Fig. 8.

Let us consider the isotherms for 149, 160, and 180°C , for which the relationship $p^+ = p_{\text{B(OH)}_3} + p_{\text{oxide}}^s = k_m \cdot p_{\text{H}_2\text{O}} + p_{\text{BOOH}}^s$ holds. The term p_{BOOH}^s is the saturation pressure of the solid phase $\text{BOOH}(\text{s})$. The linear relationship between p^+ and $p_{\text{H}_2\text{O}}$ indicates the association number $m = 1$, which supports the formulation shown in Eq. (28).

In contrast to these the 109° isotherm takes the form $p^s = p_{\text{B(OH)}_3}^s$ because of the change in the solid phase; in this case p^+ is equal to $p_{\text{B(OH)}_3}^s$, since it is independent of $p_{\text{H}_2\text{O}}$. Thermodynamic data derived from the measurements are to some extent uncertain, though this fact does not alter the main conclusions on the reactions under discussion. The enthalpy of sublimation of $\text{B(OH)}_3(\text{g})$ was determined as 23.4 kcal/mole and that of $\text{BOOH}(\text{s})$ as 27 kcal/mole (uncertain). An enthalpy of reaction of -19 kcal/mole (uncertain) was found for the homogeneous reaction



These investigations on the volatility of boric acid formed part of a study of the system $\text{B}_2\text{O}_3\text{-H}_2\text{O}$, and were the first quantitative work on

⁵ An investigation of the solubility of B(OH)_3 in saturated and superheated water vapor between 1–200 atm (M. A. Styrikovich, D. G. Tschiraschwilli, and D. P. Nelierdize, *Doklady Akad. Nauk. S.S.S.R.* **134**, 615 (1960); D. G. Tschiraschwilli and D. P. Nelierdize, *Doklady Akad. Nauk. S.S.R.* **23**, 695 (1959), showed that B(OH)_3 molecules go from the saturated solution into the vapor.

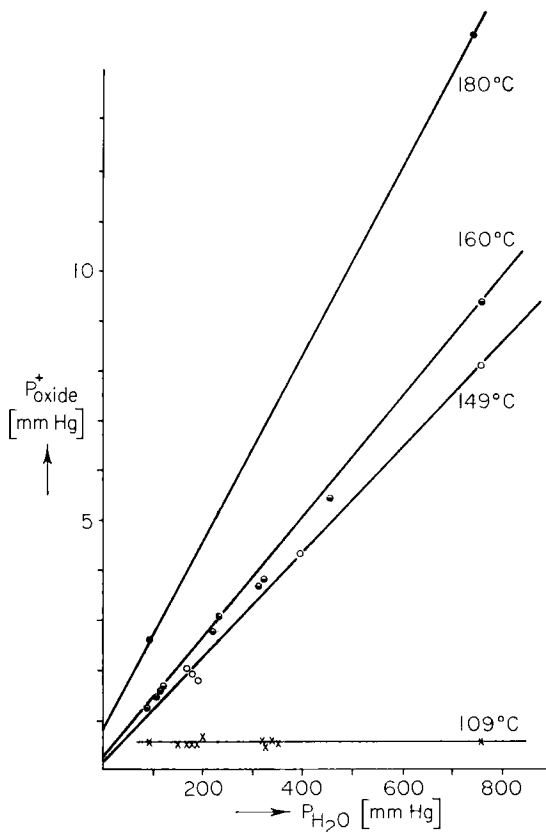


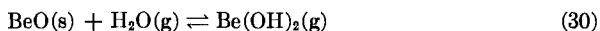
FIG. 8. Volatility of $\text{B}(\text{OH})_3$ at various temperatures as a function of vapor partial pressure.

the formation of gaseous compounds starting from oxide and water. It is noteworthy that even in this investigation the method of determining association numbers was explored and discussed in order to establish the stoichiometry of the reaction (the authors actually used the expression "degree of hydration"). von Stackelberg *et al.*, considered that water vapor could be regarded as a "gaseous solvent" and were thus able to formulate variations in its concentration very simply. The conclusions drawn by the authors from their studies of the system $\text{B}_2\text{O}_3\text{-H}_2\text{O}$, and particularly those relating to the existence of $\text{BOOH}(\text{g})$, are not incompatible with later experimental findings as outlined in the earlier part of this section.

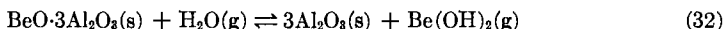
b. Gaseous Beryllium Hydroxide. If the interaction between oxide and water vapor is considered more from the preparative and technical point of view, the main interest centers on the phenomenon of the apparent increase in the vapor pressure of the oxide under the influence of water

vapor i.e., the increase in volatility. The system BeO-H₂O is a striking example of this. Malm and Hutchison (39, 39a) made preparative studies on the purification of BeO. They found that they could obtain a separation of BeO by allowing it to react with water vapor at higher temperatures, when it was carried over in the vapor form and recondensed as a solid. Separation from impurities which were not volatile under these conditions was thus achieved. In order to explain the reaction the authors assumed the existence of a gaseous product formed from BeO and H₂O. This conclusion agrees with the work of Berkmann and Simon (5), who likewise studied the volatility of BeO in water vapor. Hutchinson and Malm established that the volatility of BeO at a given temperature increases with the water vapor pressure. Von Wartenberg (83) concluded from their observations that a gaseous beryllium hydroxide was formed and this result was then confirmed by Grossweiner and Seifert (35) and firmly established by further measurements.

These authors worked with the transfer method in the temperature range 1200–1400°C. They found an association number of unity and formulated the reaction as



on the assumption of monomeric gaseous species. Technical aspects of the subject were also involved in the work of Young (88), who studied the reaction of water vapor with beryllium, chrysoberyl, and BeO·3Al₂O₃. The objective was to reduce the chemical potential of beryllium oxide in order to reduce complications associated with the use of BeO in reactor technique as a result of the volatility of the oxide in presence of water vapor. The transfer method was used and the results were evaluated on the assumption of a monomeric gaseous reaction product Be(OH)₂. The reactions



were investigated in addition to the reaction with BeO as the solid phase. The thermodynamic data from this investigation are collected in Table X together with values from the work of Grossweiner and Seifert. From Young's work it was found that the equilibrium pressure $p_{\text{Be(OH)}_2}$ over BeO·3Al₂O₃ at 1600°C was $\frac{1}{2}$ to $\frac{2}{3}$ of the value measured over pure BeO as the solid phase. This is agreement with formation of mixed crystals and ideal behavior. The resulting reduction in the volatility of beryllium was thought not to be sufficient to overcome health risks and corrosion defects which occur when moist gases are used in cooling BeO moderators in high temperature reactors.

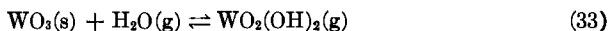
c. Gaseous Molybdenum and Tungsten Hydroxides. Some time ago

TABLE X
THERMODYNAMIC DATA FOR SOME REACTIONS LEADING TO THE FORMATION OF $\text{Be}(\text{OH})_2(\text{g})$, ACCORDING TO YOUNG

		Temperature range T' (°K)	$\Delta H_{T'}$ (kcal/mole)	$\Delta S_{T'}$ (e.u.)	ΔG_{1823} (kcal/mole)	Reference
$\text{BeO}(\text{s})$	$+ \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Be}(\text{OH})_2(\text{g})$	1462–1823	41.5	7.4	27.9	(35)
$\text{BeO}(\text{s})$	$+ \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Be}(\text{OH})_2(\text{g})$	1576–1839	42.5	8.8	26.4	(88)
$\frac{3}{2}\text{BeO} \cdot \text{Al}_2\text{O}_3(\text{s})$	$+ \text{H}_2\text{O}(\text{g}) \rightleftharpoons \frac{1}{2}\text{BeO} \cdot 3\text{Al}_2\text{O}_3(\text{s}) + \text{Be}(\text{OH})_2(\text{g})$	1604–1848	49.4	11.2	29.0	(88)
$\text{BeO} \cdot 3\text{Al}_2\text{O}_3(\text{s})$	$+ \text{H}_2\text{O}(\text{g}) \rightleftharpoons 3\text{Al}_2\text{O}_3(\text{s}) + \text{Be}(\text{OH})_2(\text{g})$	1626–1832	43.2	7.1	30.3	(88)

Millner and Neugebauer (51) found that there was a considerable loss in weight by WO_3 , W_4O_{11} , WO_2 , and MoO_3 in presence of water vapor or water vapor + hydrogen (for lower tungsten oxides) at 1000° (for all tungsten oxides) and at $600\text{--}700^\circ\text{C}$ (for molybdenum oxide). They were able to show from this investigation that the cause of the corrosion phenomena in tungsten wire incandescent lamps must lie in the volatility of tungsten oxide in presence of water vapor. Brewer and Elliott (12) suggested that earlier determinations of the vapor pressure of WO_3 had probably been influenced by the formation of gaseous hydroxide as a result of the presence of water vapor. According to Ruff and Grieger (63) the vapor pressure of WO_3 at 1393°K is 10 mm Hg, but later measurements with the mass spectrometer (6) give 4.1×10^{-3} mm Hg.⁶

Newer measurements have now provided more information about the formation of a gaseous tungsten hydroxide (31, 32). Figure 6 shows that there is association number $m = 1$ for the reaction between $\text{WO}_3(\text{s})$ and $\text{H}_2\text{O}(\text{g})$. From this, assuming that monomeric species are formed, it follows from the thermodynamic data that the equilibrium involved is



A representative temperature dependence of the equilibrium constants for other systems is shown in Fig. 9. The enthalpy of reaction, ΔH_T° , for the heterogeneous reaction (33) was found to be 39.9 kcal/mole ($T = 900\text{--}1100^\circ\text{C}$).

A fuller discussion of the results, based on the assumption that monomeric species are formed in the reaction, is given in the following section. It may be mentioned at this point that mass-spectrographic reexamination (18) of the system $\text{WO}_3\text{--H}_2\text{O}$ has shown that at higher temperatures the reaction product is correctly formulated as $\text{WO}_2(\text{OH})_2$. More highly aggregated species were not observed by the mass-spectrographic method. The findings and general considerations on the occurrence of a monomeric gaseous tungsten hydroxide can certainly be applied to the corresponding molybdenum compound. It is thus possible to formulate the reaction for which Glemser and von Haeseler found an association number $m = 1$ as:



The authors found an enthalpy $\Delta H_T^\circ = 35.5$ kcal/mole for this reaction at $T = 600\text{--}690^\circ\text{C}$.

⁶ This explanation agrees with newer measurements (31). It seems from this that Ruff and Grieger determined the vapor pressure of WO_3 in a water vapor atmosphere ($p_{\text{H}_2\text{O}} \approx 760$ mm Hg), which is unlikely. It is therefore not known what caused the discrepancy in Ruff and Grieger's measurements. The matter cannot be checked since the statement by the authors (in "Landolt-Bornstein Tabellen," Suppl. II, Ergänzungsband Part 2, p. 1301) is based on a private communication.

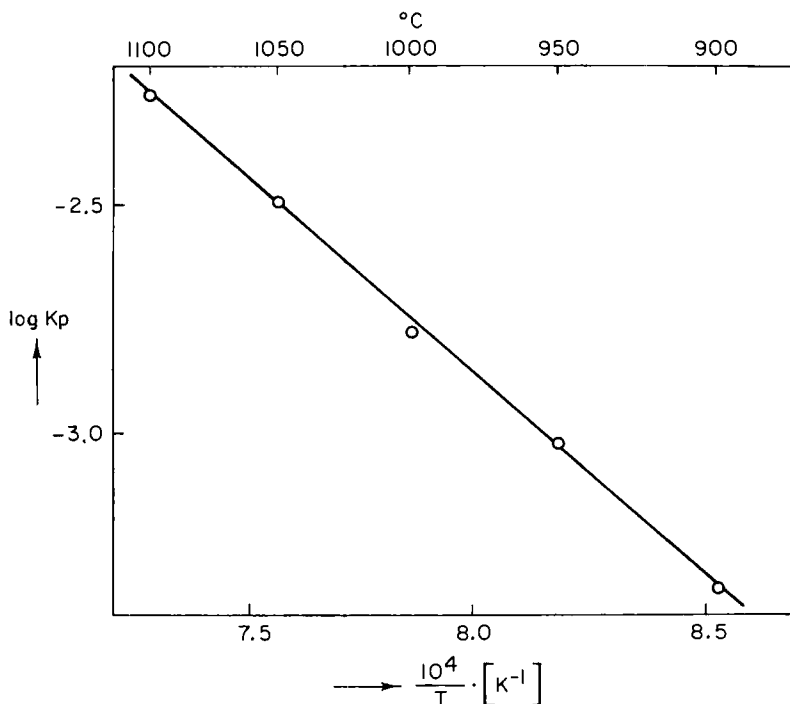
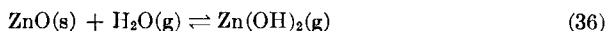
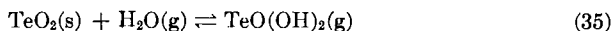


FIG. 9. Temperature dependence of the equilibrium constant for reaction (33).

Glemser and Wendlandt (33) also studied the system WO_3/MoO_3-H_2O from the preparative viewpoint. For a composition of the mixed solid phase WO_3/MoO_3 with a mole fraction $x_{MoO_3} < 0.1$, the results at 600° to 700°C and with $p_{H_2O} \approx 760$ mm Hg are compatible with mixed crystal formation.

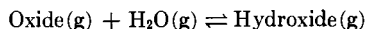
d. *Gaseous Tellurium Oxide Hydroxide and Zinc Hydroxide.* In further investigations by the transfer method the reactions between $TeO_2(s)$ and $H_2O(g)$ and between $ZnO(s)$ and $H_2O(g)$ were examined. In both cases proportionality between p_{H_2O} and p_{oxide}^+ was established. Using the experimentally determined association number $m = 1$ and assuming monomeric gaseous reaction products, the reactions may be formulated as:



The reaction with TeO_2 was studied at 600–700°C and that with ZnO at 1300–1350°C.⁷

⁷ Compare also J. Kasarnowsky, *Z. physik. Chem.* **109**, 289 (1924). The demonstration of the formula $TeO(OH)_2$ given in this work is incorrect.

Finally, let us consider Table XI, in which are collected enthalpy values of interest in discussing gaseous hydroxides in the homogeneous reaction



The values have been determined (except for the value for the reaction of B_2O_3 which, as⁸ described previously, was determined directly) from the enthalpy of the heterogeneous reaction (cf. Table VIII) and the sublima-

TABLE XI
ENTHALPIES OF REACTIONS $\text{OXIDE(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{HYDROXIDE(g)}$

Oxide	Gaseous product	Sublimation (vaporization) enthalpy of pure oxide (kcal/mole)	Enthalpy of heterogeneous reaction ^a $\Delta H_{T'}$ (kcal/mole)	Enthalpy of homogeneous reaction ^b $\Delta H_{T'}$ (kcal/mole)	Temperature range T' (°K)
B_2O_3	BOOH		42.3	-1.4	1060-1450
Li_2O	LiOH	98.5	79.0	-19.5	1100-1400
BeO	Be(OH)_2	150.0	41.5	-108.5	1673
ZnO	Zn(OH)_2	117.2	102.2	-15.0	1573-1623
MoO_3	$\text{MoO}_2(\text{OH})_2$	102.0 ^c	35.3	-66.7	873-963
WO_3	$\text{WO}_2(\text{OH})_2$	127.0 ^c	39.9	-87.1	1173-1373
TeO_2	TeO(OH)_2	54.9	33.4	-21.5	923-973

^a $\text{Oxide(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{Hydroxide(g)}$.

^b $\text{Oxide(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{Hydroxide(g)}$.

^c See Footnote 8.

tion (vaporization) enthalpy of the pure oxide. These data are also included in Table XI. The enthalpies of sublimation of MoO_3 and WO_3 are given for the equilibrium $\text{MeO}_3(\text{s}) \rightleftharpoons \text{MeO}_3(\text{g})$ ($\text{Me} = \text{W}, \text{Mo}$).⁸ The value for the reaction of B_2O_3 with $\text{H}_2\text{O(g)}$ clearly differs from those for the other reactions. It is not possible, however, to conclude from this that there is any essential difference in the formulation of the reaction products, for the system $\text{B}_2\text{O}_3\text{-H}_2\text{O}$ has been studied in detail by various authors.

5. Discussion of Results

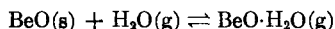
Among the compounds which result from the reaction equilibrium $I/2$, we are best informed about lithium hydroxide and the various boron hydroxides. For them we know the molecular weights and, in part, the molecular structures in addition to the thermodynamic data. For all of the

⁸ This value ($=\Delta H_1$) follows from the measured enthalpy of the reaction $3\text{MeO}_3(\text{s}) \rightleftharpoons (\text{MeO}_3)_3(\text{g})$ ($=\Delta H_2$) and the enthalpy of depolymerization $(\text{MoO}_3)_3(\text{g}) \rightleftharpoons 3\text{MoO}_3(\text{g})$ ($=\Delta H_3$) as $\Delta H_1 = 1/3 (\Delta H_2 + \Delta H_3)$. Values of ΔH_2 are well known for both oxides: cf. (7), (8). The value of ΔH_3 is from the work of R. P. Burns, G. De Maria, J. Drowart and R. T. Grimley, *J. Chem. Phys.* **32**, 1363 (1960).

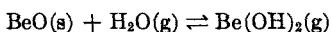
oxides, including the less studied oxides of beryllium, zinc, tungsten, and tellurium, there is no doubt that a strong interaction with water vapor can be observed at higher temperatures. By analogy with Li_2O and B_2O_3 , which react with water vapor to form gaseous hydroxides, and on the basis of thermodynamic data and the small and definite association number of unity, it is very probable, therefore, that interaction of the other oxides and water vapor at higher temperatures also leads to the formation of gaseous hydroxides.

In this connection, if we start from the fact that, for example, in the system $\text{BeO-H}_2\text{O}$ a solid hydroxide $\text{Be}(\text{OH})_2$ exists which decomposes at 180°C to $\text{BeO}(\text{s})$ and $\text{H}_2\text{O}(\text{g})$, it is possible to understand the apparent difficulty that the same solid oxide at 1300°C again reacts to form a gaseous hydroxide of the same stoichiometric composition. Let us first of all consider the occurrence of the gaseous compound. Here it must first be remembered, as Brewer (11) emphasized recently, that thermodynamic calculations, which serve to determine the behavior of the system in the higher temperature range, do not suffice to describe the behavior at lower temperatures. Calculations based on the compounds known at lower temperatures become unreliable if new species are formed with increasing temperature. In other words, it is doubtful whether the comparison of solid beryllium hydroxide with gaseous beryllium hydroxide is justifiable if all gaseous hydroxides of the type under discussion are considered. In the case of the gaseous hydroxides of molybdenum, tungsten, and tellurium we already know from investigations which are now going on that such a comparison is not possible. Molybdenum and tungsten in the solid state do not form hydroxides [apart from compounds such as $\text{H}_6(\text{H}_2\text{W}_{12}\text{O}_{40})$, which are prepared under special conditions] but only oxide-hydrates (69, 69a), while for tellurium the facts known so far justify only the formulation $\text{TeO}_2(\text{aq})$, i.e., an oxide-hydrate. For molybdenum, tungsten, and tellurium, therefore, the gaseous hydroxides formed from the oxides and water vapor must be considered as separate compounds which are distinct from the oxide-hydrates of those elements occurring in the solid state. If we assume this to be so in the case of lithium, beryllium, and zinc, it must be a matter of chance that the formula for the gaseous hydroxides (the stoichiometric ratio $\text{Be}:\text{OH} = 1:2$) is the same as that for the solid compound.

Which data then, apart from the enthalpy of formation, must be considered in describing the thermodynamic stability? For the reaction of $\text{BeO}(\text{s})$ and $\text{H}_2\text{O}(\text{s})$ an enthalpy change of about 108 kcal was found. As Grossweiner and Seifert mentioned, this is too large for a simple molecular association corresponding to the equation:



and the observed values of ΔH° , ΔG° , and ΔS° accord better with the formation of a gaseous hydroxide.



The value for the Be—OH bond energy supports this view. This conclusion may in all probability be extended to the other reactions studied. It is supported by the examples of the reactions of B_2O_3 and Li_2O with H_2O , which have already been described and for which mass-spectrographic and infrared methods have brought about a notable widening of the experimental basis of the subject.

Some further comments may be made on the possible formulation of the gaseous hydroxides. As has been explained several times, polynuclear oxides have been detected in the vapor over solid BeO , MoO_3 , and WO_3 . Figure 10 gives the proposed structural formulas for these gaseous hydroxides.

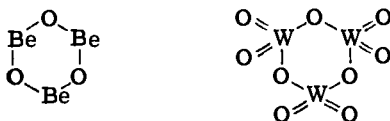
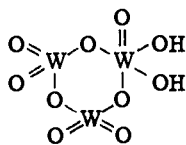
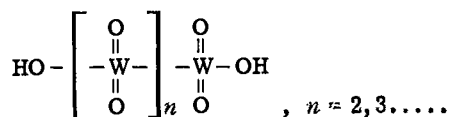


FIG. 10. Structure of gaseous oxides of beryllium and tungsten.

It will be seen that the metal atom in the trimeric gaseous molecule has an increased coordination number compared with that in the monomer. In these essentially covalent compounds between metal and oxygen, however, an increase in coordination number is associated with increase in the volatility of the molecule. In the gaseous state coordination numbers of 2 and 4 are favored by beryllium and tungsten respectively. If we allow BeO(s) to react with $\text{H}_2\text{O(g)}$ the possible species with a coordination number of two are HO—Be—OH or the polynuclear compound $\text{HO—[Be—O]}_n\text{—BeOH}$ ($n = 2, 3, \dots$), the formula of which would certainly not be linear. The latter is not very likely. In the reaction of $\text{WO}_3\text{(s)}$ with $\text{H}_2\text{O(g)}$ it would be possible to have a ring structure (A) with a coordination number of five for the tungsten atom or a nonlinear chain formula (B), with a coordination number of four.

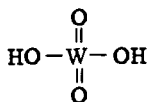


(A)



(B)

On the other hand a coordination number of four for all the tungsten atoms is attained in the monomer $\text{WO}_2(\text{OH})_2$, and this represents the most



probable formulation. As already mentioned, its existence has been established mass-spectrographically (18).

B. REACTIONS AT HIGHER PRESSURES OF WATER VAPOR

In addition to reactions of an oxide with water vapor at a total pressure of one atmosphere, experiments have been made at water vapor pressures substantially greater than this value and mostly above the critical pressure of water. A formal relationship between measurements in the two pressure regions may be demonstrated only when the experimental methods are considered.

The experimental method most frequently used with higher water vapor pressures may be compared with the transfer method. In the latter we determine the amount of solid material carried by a known volume of the transfer medium, i.e., we determine the (apparent) increase in the vapor pressure of the oxide [see Eq. (13)] or the "solubility" of the solid oxide in the transport medium. This is exactly the objective in investigating the reaction of oxides at higher pressures of water vapor.

Two experimental approaches may be mentioned. In one method (53) a sample is taken from the reaction space and the content of dissolved substance is determined. The other method gives the solubility indirectly from the loss in weight of the oxide. In investigating the solubility of quartz the loss in weight is derived in a highly original way from the change in frequency of a quartz plate set up to act as an oscillator (44).

Questions on the behavior of oxides in the supercritical region of water, or in superheated steam at higher pressures, have arisen earlier, especially in connection with geochemical, technological, and preparative problems.⁹ The system $\text{SiO}_2\text{-H}_2\text{O}$ has been prominent in this connection. van Nieuwenburg and Blumendal (78) and van Nieuwenburg and van Zon (79) demonstrated the transport of SiO_2 through the gas phase, and this result was confirmed later by other authors and put on a quantitative basis.

⁹ cf. C. W. Correns, *Einführung in die Mineralogie*, Springer, Berlin-Göttingen-Heidelberg, 1949, p. 189 *et seq.*, See also P. Niggli, *Das Magma und seine Produkte*, Akademische Verlagsges. Leipzig, 1937; O. Fuchs, *Z. Elektrochemie*, **47**, 101, 1941; R. Nacken, *Chemiker-Zeitung*, **74**, 745 (1950). See also Booth and Bidwell (9), Morey (52) and Franck (27, 27a).

Today we know from a great number of investigations how the system $\text{SiO}_2\text{-H}_2\text{O}$ behaves if the water component is varied over a wide range. There are a number of possible ways of presenting the results; we will consider here only those which link up with the thermodynamic considerations of the previous section.

A first method of presentation, which is generally applicable, is to consider the dependence of solubility on the water pressure; this is done in Fig. 11, which gives the results of Morey and Hesselgesser (53). This gives qualitatively the relationship between the increase in solubility and the increase in pressure.

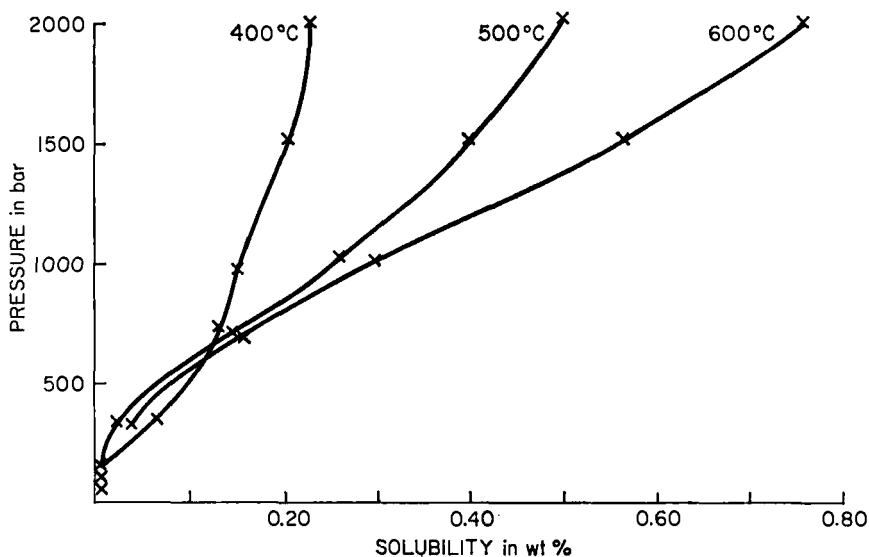


FIG. 11. The dependence of the solubility of quartz in water vapor on the pressure at various temperatures.

Kennedy (44) introduced the density d or the reciprocal volume as a measure of the water concentration. He was then able to represent results up to a pressure of 1000 bar in the form

$$S = -Af(T) \log \frac{1}{d} \quad \begin{array}{l} S = \text{Solubility} \\ A = \text{Constant} \end{array} \quad (37)$$

Jasmund (42) showed that the solubility of SiO_2 in water at high pressures and temperatures could be described by the general expression

$$L = \text{constant} \times D^n \quad (38)$$

where L stands for the solubility isotherm, D is the density, and n denotes an association number. Finally, Mosebach (54, 54a) discussed the solubility

of SiO_2 as a heterogeneous gas reaction and gave a relationship equivalent to that above in the form

$$\log L = m \cdot \log D + b \quad (39)$$

where L = solubility expressed as g of SiO_2/kg of H_2O ; D = density of the vapor phase, m = association number; b = a temperature-dependent constant. Figure 12 shows the solubility isotherms for SiO_2 in compressed water vapor. From the slope of the lines an association number $m = 2$ is derived [cf. Eq. (14)].

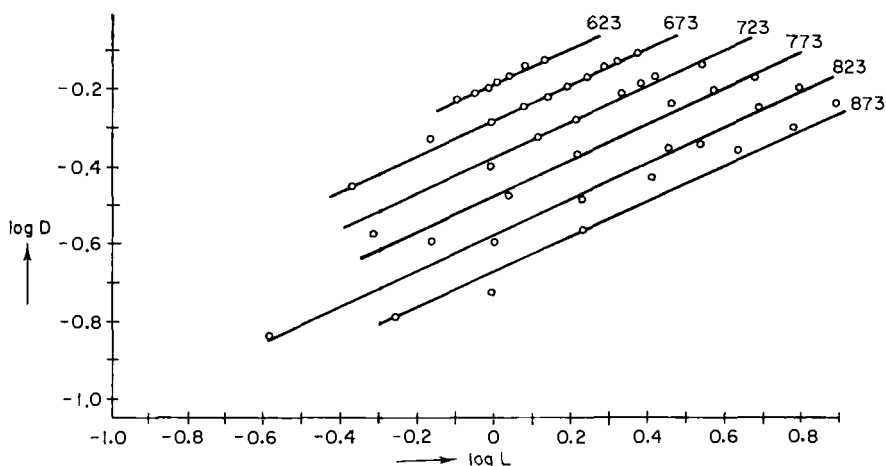


FIG. 12. Solubility isotherms for SiO_2 in compressed water vapor at different temperatures.

Mosebach expressed the temperature dependence of the solubility in the form

$$\log L = m \log D - \frac{A}{T} + B \quad (40)$$

which, putting $\log L - m \log D = -(A/T) + B = \log K_n$, corresponds formally with Eq. (17). Evaluating all experimental results then available, Mosebach determined the constants for the solubility of quartz as $A = +2.071$ and $B = +3.68$. Experimental results may be expressed by this empirical relationship with an accuracy of $\pm 10\%$. Bearing in mind the difficulties associated with the measurements, this agreement may be regarded as very satisfactory.

Mosebach and Franck (27, 27a) and Wasserburg (85) find a mean association number of $m = 2$; Wood (87) also finds $m \approx 2$ at 460°C and 700 bar. The most plausible formulation with $m = 2$ is $\text{SiO}_2 + 2\text{H}_2\text{O} \rightleftharpoons$

Si(OH)_4 , i.e., volatile Si(OH)_4 is formed. According to Mosebach, this reaction with quartz has an enthalpy of association of 9.47 kcal/mole in the temperature range 200–600°C and up to a pressure of 2000 atm.

Possibly, polynuclear hydroxides are formed at higher pressures.¹⁰ Franck (26) considers that the assumption of a partial dissociation of Si(OH)_4 into H^+ and SiO(OH)_3^- ions which has been discussed (54, 54a) is not very probable because conductivity measurements in the system $\text{SiO}_2\text{-H}_2\text{O}$ at about 600°C and 1000–1500 atm pressure show no difference from pure water.

In interpreting this reaction of SiO_2 with H_2O there is a point of resemblance to the experiments at atmospheric pressure in that, in both cases, the increase in vapor pressure of the solid may readily be detected but it is difficult to elucidate the nature of the products. It must not be overlooked, however, in this connection that, depending on the technique used, a wide range of results may be obtained in the determination of molecular weights, the identification of reaction products, and the investigation of the thermodynamics of equilibria, for reactions at atmospheric pressure. The experimental difficulties in the high pressure region are greater, especially if it is a question of determining the criteria just mentioned. It may be expected, however, that further investigation will lead to progress in this case too.

The solubility of solids in highly compressed gases has been known since the work of Hannay and Hogarth (36) and has been put on a sound theoretical basis.¹¹ The inclusion of the system water-oxide (solid) in these studies occurred relatively late, not least because of the considerable experimental difficulties of working with water under the reaction conditions already described. The measured increase in vapor pressure (volatilization or solubility) of the oxide in compressed water vapor cannot be explained by a purely hydrostatic action; in the case of SiO_2 this effect is negligibly small. Interaction of the molecules in the water vapor with the solid is the decisive factor in increasing the vapor pressure. Naturally, such effects

¹⁰ A similar interpretation which is difficult to understand [that Si(OH)_4 exists at higher and $\text{Si}_2\text{O(OH)}_6$ at lower pressures] is due to E. L. Brady, *J. Phys. Chem.* **57**, 706 (1953). It seems rather unlikely that the conclusions of G. R. B. Elliott (Univ. of Calif. Thesis 952, UCRL-1831), that the product of the action of water vapor under pressure on silica is $\text{SiO}\cdot 4\text{H}_2\text{O}$, can be correct. Wood (84) postulated the formation of higher aggregation products such as $(\text{H}_4\text{SiO}_4)_2$, $(\text{H}_4\text{SiO}_4)_3$ etc. at high pressures, but these formulas are, naturally, not proved.

¹¹ An introductory treatment is given by Denbigh (23). Booth and Bidwell (9) have collected solubility measurements. Morey (52) considers theoretical aspects of the solubility of solids in gases and reports new measurements. Franck (28) reviews and extends the theoretical treatment, and particularly discusses the role of water as a strongly polar gaseous solvent with reference to his own measurements.

generally depend on the specific interaction between gas and solid. According to Franck, the relationship

$$\ln \frac{x_2}{x_2^\circ} = \frac{V_{2F} \cdot P}{RT} + m \ln \frac{k_m}{V} \quad (41)$$

holds in the limiting case of high densities and strong interaction. (x_2 = mole fraction of solute; x_2° = mole fraction of the solute under its own vapor pressure; V_{2F} = molar volume of the solid; P = total pressure; m = association number; $1/V$ = total density; k_m = constant.)

If the Poynting effect [the first of the two terms in Eq. (41)] is neglected, this expression agrees with the Eq. (39) used for the expression of the solubility relationships in the system SiO_2 -water. Let us now return to Eq. (39), which Mosebach postulated on the assumption of a heterogeneous gas reaction. Such an interpretation would be understandable for the supercritical region on the basis that there is here yet another phase which may be considered as a gas phase. It cannot be overlooked in this discussion that, as Franck showed, the supercritical phase becomes more and more like a liquid as the density is increased, since formation of association complexes and electrolytic dissociation occur, as in liquid water. The heterogeneous reaction model therefore cannot be used without reservations in the interpretation of experimental data. This is evident if the hydrothermal solubility data for BeO given in Table XII are compared with those obtained by extrapolation of data for the equilibrium $\text{BeO(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{Be(OH)}_2\text{(g)}$; the results differ by two or three orders of magnitude.

TABLE XII
SOLUBILITY OF OXIDES IN WATER VAPOR AT 500°C AND 1050 ATM

Oxide	Solubility (ppm)	Oxide	Solubility (ppm)
BeO	120	SnO_2	3.0
Al_2O_3	1.8	Nb_2O_5	28.0
VO_2	0.2	Ta_2O_5	30.0
SiO_2	2600	Fe_2O_3	90.0
GeO_2	8700	NiO	20.0 (at 2100 atm)

Studies on the solubility of oxides in the supercritical region of water have not been confined to SiO_2 . Morey and Hesselgesser and Morey and Chen [see Morey (52)] have studied the solubility of a series of other oxides in water vapor at 510°C and 1050 atm. A summary of their results is given in Table XII. According to Franck and Tötheide (28) the formation of

gaseous $\text{CO}(\text{OH})_2$ from CO_2 and H_2O at 600°C and 900–1600 atm is not established.

It would be of great interest in the investigation of volatile compounds in oxide-water systems if the solubility of the oxides in Table XII and of further oxides in highly compressed water vapor at various pressures and temperatures could be determined. This would enable association numbers to be determined and formulas for the volatile compounds to be discussed, as in the systems $\text{SiO}_2\text{--H}_2\text{O}$.

Investigation of the action of water on oxides which, like MoO_3 , react at atmospheric pressure at higher temperatures, is of special interest. If different compounds are formed at higher pressures, it can be established whether they are related to those obtained at lower pressures or to the poly-anions formed in aqueous solution at ordinary pressures. The discussion of such relationships is also of interest for the $\text{SiO}_2\text{--H}_2\text{O}$ system. We will conclude with a discussion of these questions.

Let us suppose the system



is investigated at various temperatures and pressures. As already discussed in detail in Section III,A, analysis shows how much oxide, m_{oxide} , is transported under equilibrium conditions for a given quantity of water, $m_{\text{H}_2\text{O}}$. Since $n_{\text{H}_2\text{O}} \gg n_{\text{oxide}}^+$, $P_{\text{total}} \approx P_{\text{H}_2\text{O}}$,

$$x_{\text{oxide}}^+ = \frac{n_{\text{oxide}}^+}{n_{\text{H}_2\text{O}}} \quad (43)$$

and since the influence of the saturation vapor pressure can be neglected it follows that

$$x_{\text{hyd}} = \frac{n_{\text{hyd}}}{n_{\text{H}_2\text{O}}} \quad (44)$$

We will now evaluate m , the association number. In order to do this we must express x_{hyd} as a function of the concentration of water in the gas phase, and in doing so the character of the gas or supercritical phase as well as the pressure dependence of the chemical potential of the solid phase must be taken into account.

We assume that there is no appreciable interaction between molecules of the compound which is formed or between these molecules and water molecules. Since the fugacity coefficients of the compound formed are unknown, we will present the results of the measurements as a function of the experimentally determined PVT data for water (38a), represented by the density.

We define

$$C_{\text{hyd}} = \frac{n_{\text{hyd}}}{V} \quad C_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{V} \quad (45)$$

with

$$V \approx V_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}}; \quad V_{\text{hyd}} \ll V_{\text{H}_2\text{O}} \quad (46)$$

We then obtain

$$K_c = \frac{C_{\text{hyd}}}{C_{\text{H}_2\text{O}}^m} = \frac{n_{\text{hyd}}}{n_{\text{H}_2\text{O}}^m} \cdot \frac{\rho_{\text{H}_2\text{O}}^m}{\rho_{\text{H}_2\text{O}}} \quad (47)$$

or
$$K_c = x_{\text{hyd}} \cdot \frac{1}{\rho_{\text{H}_2\text{O}}^{m-1}} \quad \text{where } \rho = \text{density} \quad (48)$$

The pressure dependence of the chemical potential of the solid phase is given by

$$\frac{d\mu_{\text{SiO}_2}}{dp} = V_{\text{SiO}_2} \quad \text{where } V_{\text{SiO}_2} = \text{molar volume} \quad (49)$$

Integrating from a pressure $p^1 = 1$ atm to the reaction pressure P , and assuming the pressure dependence of the molar volume, it follows that

$$\mu_{\text{SiO}_2}^P - \mu_{\text{SiO}_2}^0 \cong P \cdot V_{\text{SiO}_2} \quad (50)$$

From this

$$\log a = \frac{V_{\text{SiO}_2}}{4.574} \cdot \frac{P}{T} \quad (51)$$

The experimental data may then be represented by the equations

$$K_c^a = \frac{x_{\text{hyd}}}{a_{\text{SiO}_2}^x \cdot \rho_{\text{H}_2\text{O}}^{m-1}} \quad (52)$$

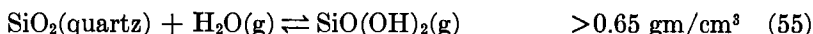
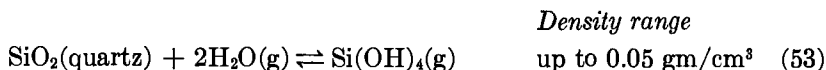
$$\log \frac{x_{\text{hyd}}}{a_{\text{SiO}_2}^x} = (m-1) \log \rho_{\text{H}_2\text{O}} + K_c^a \quad (52a)$$

Equation (52a) may be evaluated for a reaction of type (42). Since, however, the investigation extends over a large range of densities, e.g., from 0.08 gm/cm³ to 0.8 gm/cm³, the possibility that several reactions may occur must be taken into account. It may be assumed that there are ranges of density corresponding with the existence of separate species, though the existence of transition regions in which more than one species can occur is not excluded. With this proviso, Eq. (52a) becomes the equation for the

tangent for the curve corresponding with the existence of the i th species and enables us to determine the i th association number and the i th equilibrium constant. The experimentally determined relationships are in fact simpler and the curves corresponding with the existence of the separate species are good approximations to straight lines.

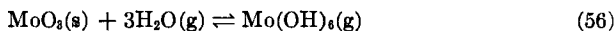
Results will first be evaluated using an estimated value of x . The determination of the association number is not affected, though the equilibrium constant is uncertain by the factor x . This first approximation shows whether there are several reactions leading to different species in the density range under examination. If this is so the evaluation is repeated with the most probable value for x .

Consider now the results obtained in using Eq. (52a) to evaluate the measurements of G. C. Kennedy (44) and G. W. Morey and J. M. Hesselgesser (53). Three association numbers are found. At low densities $m = 2$, at densities around 0.05 gm/cm³ $m = 3$ and at high densities $m = 1$. The solubility increases with increasing density. These findings may be interpreted stoichiometrically and the following equations are proposed:

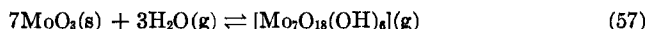


The density ranges shown are only a rough indication of the limits for the separate regions and do not define them precisely. The compound $\text{SiO}(\text{OH})_2$ is probably not a monomer, though further experimental work is needed to clarify this problem.

In the case of the system $\text{MoO}_3\text{—H}_2\text{O}$ it is already known that the gaseous hydroxide $\text{MoO}_2(\text{OH})_2$ occurs at higher temperatures. The highest water vapor pressure used hitherto in investigations to determine the association number was 1 atm. When the water vapor pressure is increased, no change in the association number is found up to about 160 atm. The only reaction up to this pressure is the heterogeneous gas reaction with an association number of unity. From 160 atm a reaction between $\text{MoO}_3(\text{s})$ and $\text{H}_2\text{O}(\text{g})$ is found which has an association number $m = 3$. In this there is a considerable increase in the solubility of the MoO_3 . Its formulation as



is therefore excluded on stoichiometrical grounds. The formulation



can however be reconciled with an association number of three and with the experimental results. At still higher pressures, from about 330 atm, it seems that there is another reaction with an association number of two.

When the reaction product in Eq. (57) is compared with the polyanions known in aqueous solution we see that the compositions are similar. It is now known that the only ions to occur in acidified molybdate solutions are $[\text{Mo}_7\text{O}_{24}]^{6-}$ and $[\text{Mo}_8\text{O}_{26}]^{4-}$. In our experiments on the action of water on MoO_3 at high densities and temperatures (33) we observed that the reaction product formed at >160 atm shows in the expanded aqueous phase behavior like that of the polymolybdate ion $[\text{Mo}_7\text{O}_{24}]^{6-}$. A further analogy may be shown to exist between the results of investigations of the heterogeneous reaction and observations on molybdate ions in aqueous solution. There is a limiting concentration which must be exceeded if polymolybdate ions are to be formed in aqueous solution. It is about $2 \cdot 10^{-4}$ g-atom molybdenum/1 (68a). In the reaction between $\text{MoO}_3(\text{s})$ and $\text{H}_2\text{O}(\text{g})$ with an association number of unity this concentration is not exceeded when the concentration of the gaseous hydroxide is expressed in the units referred to. The limiting concentration is, however, exceeded in the case of the reaction with an association number $m = 3$.

The results of the foregoing investigations show, as has been mentioned already, that the specific interaction between oxide and water determines the magnitude of the effect which, in the last examples, may be explained in terms of solvation. A simple solvation model is, however, unsatisfactory. The change in the dielectric constant of water with pressure at a given temperature runs somewhat parallel to the observed increase in the molar fraction x_{hyd} with density. It is not surprising, therefore, that compounds occur at higher pressures and temperatures which are already known in aqueous solution. From the experimental point of view this relationship suggests the possibility of using measurements at different pressures as an approach to the study of the interesting field of polyanion chemistry.

ACKNOWLEDGMENT

We thank Dr. E. Schwarzmann and Dr. H. K. Hofmeister for active support and stimulating discussion.

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THE BORAZINES

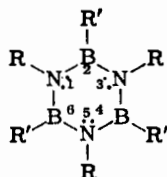
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I. Introduction

The borazines are one of several compound types that are isoelectronic with benzene, and consequently they have attracted considerable attention since the parent compound borazine (I, $R = R' = H$) was first isolated and



(I)

characterized by Stock and Pohland (164). These investigators suggested a cyclic structure for borazine on the basis of chemical evidence, and this

was later substantiated by direct structural investigations (see Section V,A). It appears possible that Gustavson (57) prepared a borazine derivative in 1870 by allowing BCl_3 to condense with ethylamine (cf. ref. 174), and Rideal (138) almost certainly did so in 1889 when he studied the reaction of BCl_3 with aniline. In 1939 Jones and Kinney (82) demonstrated that the latter reaction does indeed yield a borazine. The hydrogen atoms in the parent compound can be replaced by a variety of groups, and recently described methods for the preparation of several unsymmetrically-substituted derivatives suggest interesting possibilities for the study of isomeric borazines.

Borazole, the name given to I, $\text{R} = \text{R}' = \text{H}$, by Wiberg and Bolz (186) on the basis of its similarity to benzene (benzol), is no longer acceptable according to the Ring Index (128); the systematic name *s*-triazatriborine is preferred. However, I($\text{R} = \text{R}' = \text{H}$) and its derivatives undergo reaction predominantly at the boron sites, and it would appear advantageous to choose a name for this compound which emphasizes the boron atoms rather than the nitrogen atoms. The name borazine has been favored by investigators active in the field and is the name used in this review. Generally, line formulas or names derived from the atom on which substitution occurs are used. For example, $\text{Me}_3\text{B}_3\text{N}_3\text{H}_3$ or *B*-trimethylborazine is used in place of the systematic name 2,4,6-trimethyl-*s*-triazatriborine (75, 128).

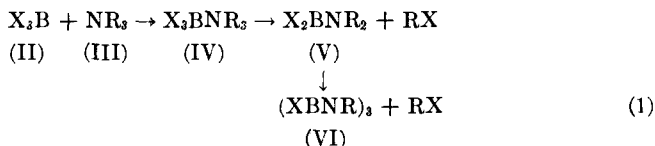
An attempt has been made in this review to cover the pertinent papers in the literature through May, 1962. Previous reviews have appeared in which the physical properties of borazines are compared with those of the analogous benzene derivatives (185) and which are chiefly concerned with the reactions and syntheses of borazines (46, 72, 105, 159).

II. Synthesis of the Borazine Ring

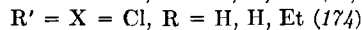
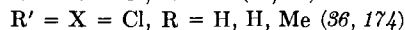
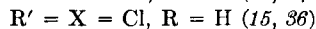
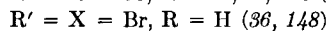
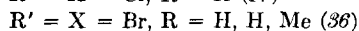
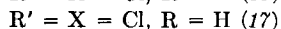
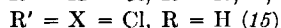
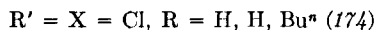
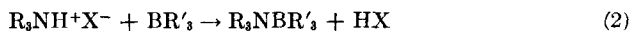
The most satisfactory method available for the synthesis of borazines involves the condensation of amines with boranes. The majority of these reactions lead to symmetrically-substituted borazine rings, although some unsymmetrically-substituted borazines have been prepared using these methods. In general, it is possible to prepare borazines that are symmetrically substituted with respect to both the boron and the nitrogen atoms [cf. (I)] or to prepare borazines carrying the same substituents on all atoms (I , $\text{R}' = \text{R}$) by a judicious choice of reactants. A second method for the preparation of borazines carrying different substituents on the nitrogen and boron atoms proceeds in two steps: (a) the formation of a borazine ring carrying a portion of the required substituents by a condensation reaction, followed by (b) a substitution reaction. This second route to the borazines is limited to replacement of substituents (usually halogen) on the boron positions in the ring; substitution reactions on the nitrogen atoms in the borazine ring have not been observed often.

A. CONDENSATION REACTIONS

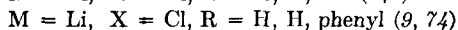
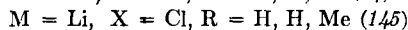
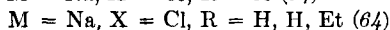
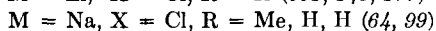
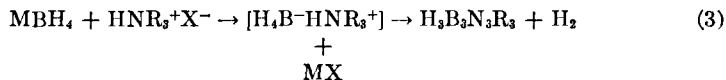
Condensation reactions between boranes and amines may be visualized as occurring via the formation of a borane-amine addition compound (IV),



which then loses substituents (one from boron and one from nitrogen) in two successive steps to form the borazine ring (9). The aminoborane intermediate (V) (84, 168, 188) and compound (IV) (9, 13, 29, 71, 82, 85, 121, 124, 170, 174, 188) have been isolated prior to their conversion into the corresponding borazine in several instances. The addition compound (IV) may be formed by direct combination of an amine with a borane (2, 49, 85, 121, 143, 194), by the displacement of hydrogen halide from ammonium salts [Eq. (2)], or by the elimination of hydrogen in the reaction of a



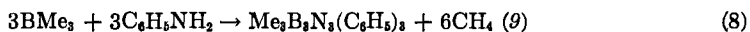
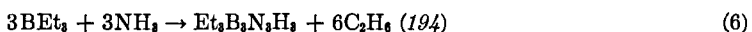
borohydride with an ammonium salt. The maximum yield for the preparation of borazine using the latter reaction occurs at a 2:1 mole ratio of LiBH_4 to NH_4Cl (111). The reaction of a borohydride with an ammonium salt at elevated temperatures (200–250°) usually proceeds directly to the corresponding borazine with the elimination of two moles of hydrogen.



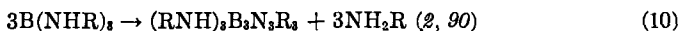
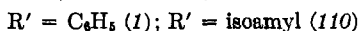
Borazines have been prepared at lower temperatures by substituting hydrazine salts for ammonium salts in reaction (3); no *N*-aminoborazines were formed in this process (36).

Conversion of the borane-amine adduct (IV) into the borazine (VI) occurs most readily when RX is a hydrogen halide. Adducts formed from boron halides and mono-alkyl- or -aryl-substituted amines lose hydrogen halides upon pyrolysis (9, 15, 146, 170), refluxing in a solvent such as C_6H_6 , C_6H_5Br , C_6H_5Cl , or diglyme (17, 49, 55, 64, 68, 71, 82, 148), or upon treatment with a strong base like triethylamine (106, 121, 145). Triethylamine aids in the removal of hydrogen halides by the formation of insoluble triethylammonium halides. Pyrolytic reactions carried out in the presence of a specially prepared cobalt catalyst gave an increased yield of the borazine (36).

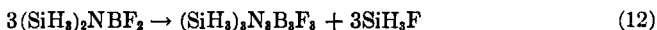
Vigorous pyrolytic conditions (e.g., temperatures up to 450°) have been employed to remove the elements of more complex compounds from the adduct.



Pyrolysis of di- or tri-aminoboranes also leads to the formation of a borazine ring.



It is interesting to note in this connection that silyl fluoride is eliminated from silylaminoborondifluorides under milder conditions (168).

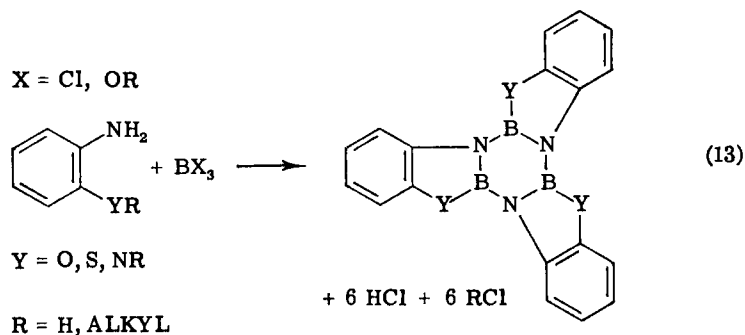


If the adduct (IV) contains the elements of only one mole of hydrogen halide, the reaction stops at the intermediate aminoborane (V) unless drastic pyrolytic conditions are applied (190, 191). Refluxing amine-borane adducts (IV, $X = \text{H}$, $R = \text{H}$, H , alkyl) or amine adducts of higher boron hydrides (151, 164, 165) in a solvent (67, 68) or pyrolysis of the adducts (9, 149, 151, 165, 171, 186, 188) yields borazines and hydrogen. Borazine itself has been prepared from the diammoniate of diborane by pyrolysis of this compound (186) or by treatment with sodium acetylide (155). In the case of some borane adducts the intermediate aminoboranes (IV,

X = H, R = H and alkyl) are trimeric (13, 171) and can be considered as analogs of cyclohexane.

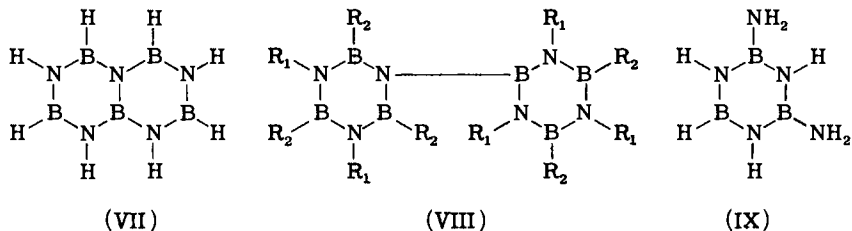
Unsymmetrically-substituted borazines have been prepared by the copyrolysis of mixtures of adducts. *B*-Methyl-, *B*-dimethyl-, and *B*-trimethyl-borazine are obtained in low yield upon heating a mixture of methyl-diboranes and ammonia (149). *N*-Methyl- and *N*-dimethyl-borazine have been prepared in a similar manner (150), but also in poor yield. The copyrolysis of a mixture of ammonia-trimethylborane and methylamine-trimethylborane at 380° in an autoclave yielded *B*-trimethylborazine (5%), *N*-methyl-*B*-trimethylborazine (17%), *N*-dimethyl-*B*-trimethylborazine (13.5%), and hexamethylborazine (2.8%) (178). Unsymmetrically-substituted *B*-chloroborazines were obtained from the pyrolysis of borazine with *B*-trichloroborazine (148).

The borazine ring has been incorporated in polycyclic systems by allowing alkyl borates or boron trichloride to react in refluxing xylene with ortho-substituted anilines (16, 142); this reaction occurred at lower temperatures in the presence of 2,6-lutidine.



B. POLYBORAZINES AND FUSED BORAZINE RINGS

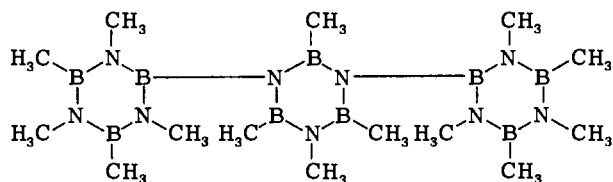
The controlled pyrolysis of gaseous borazine at 380° in a dynamic system yields hydrogen and a mixture of compounds from which can be separated the B—N analogs of naphthalene (VII) and biphenyl (VIII, R₁ = R₂ = H), a compound formulated as *B*-diaminoborazine (IX), and



derivatives of VII, VIII ($R_1 = R_2 = H$), and IX (93, 113). These structural assignments were made on the basis of chemical analyses, mass spectral data, infrared spectra, and nuclear magnetic resonance spectra. Similar results were obtained when gaseous borazine was allowed to decompose for $3\frac{1}{2}$ months at ambient temperatures (101, 192a), although borazine has previously been reported to be stable in the gas phase (148). Pyrolysis of borazine in a static system (93, 113, 164, 185) yields a nonvolatile solid with the empirical composition BNH_x . The nature of the products depends upon the temperature of pyrolysis. This polymeric material constantly loses hydrogen upon heating, and it was suggested that the end-product is boron nitride (185). The presence of IX as an intermediate in the pyrolysis of boron nitride (92) is consistent with the observation (91) that *B*-tri-aminoborazines evolve amines at 300° to form first polyborazines bridged by alkylimine groups and finally cross-linked polymers (2, 90, 91).

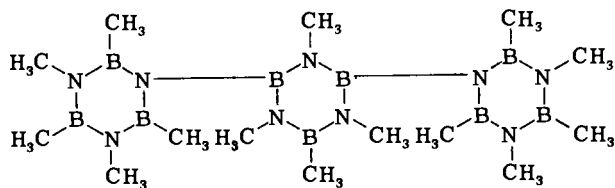
In contrast to the pyrolysis of borazine, pyrolysis of an equimolar mixture of isomeric pentamethylborazines gave only a trace of (VII) ($R_1 = R_2 = CH_3$) (179). Upon independent pyrolysis of the isomeric pentamethylborazines most of the starting material is recovered unchanged together with small amounts of tri-, tetra-, and hexa-methylborazines. The latter disproportionation products could arise either by a depolymerization reaction followed by random polymerization (cf. Section III,B,2,a) or through a bridged transition state (cf. Section III,B,1,b).

The discovery of *N*-lithioborazines presents a new and perhaps more specific synthetic route to the polyborazines (179). Decamethyl-*N*-*B'*-biborazyl (VIII, $R_1 = R_2 = Me$) was prepared by the elimination of lithium chloride from an equimolar mixture of *N*-lithiopentamethylborazine and *B*-chloropentamethylborazine. This type of reaction has been extended to combinations of *N*-mono-, -di-, and -tri-lithioborazine with *B*-mono-, -di-, and -tri-chloroborazine which yielded X, XI, XII, and the polymeric substance XIII.

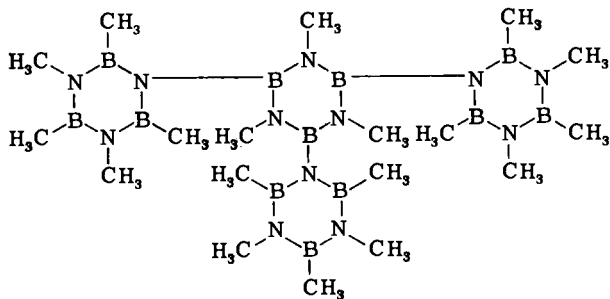


(X)

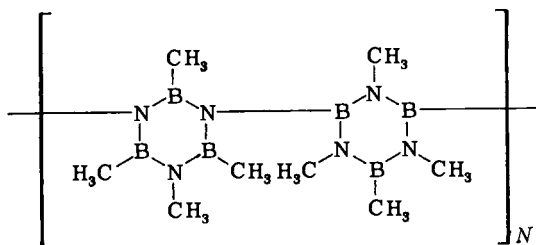
Attempts to dehydrohalogenate mixtures of *N*-dimethyl-*B*-trimethylborazine and *B*-chloropentamethylborazine using tertiary amines did not yield the desired product.



(XI)



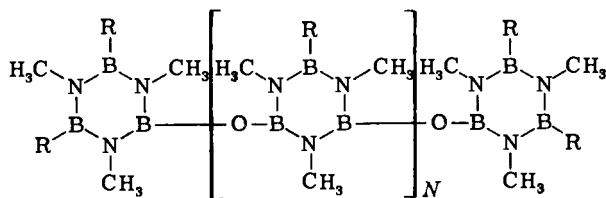
(XII)



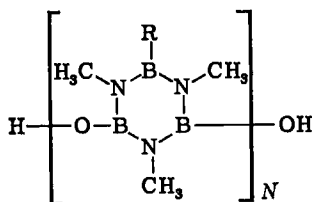
(XIII)

C. POLYBORAZINES WITH BRIDGING GROUPS

Polycondensation of borazine rings joined together through an oxygen atom was effected by the controlled hydrolysis of mixtures of *B*-mono- and *B*-di-halogenoborazines (XIV, $n = 0 - 3$); hydrolysis of dihalogeno-



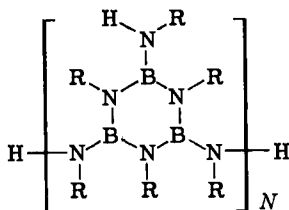
(XIV)



(XV)

borazines alone produced a glassy polymer (XV, $n = \sim 23$) (179). A compound similar to XIV [$n = 0$, $\text{R} = \text{CH}_2\text{Si}(\text{CH}_3)_3$] was obtained as a by-product of the reaction between *B*-trichloroborazine and $(\text{CH}_3)_3\text{SiCH}_2\text{MgCl}$ (153).

Polyborazines (XVI, $\text{R} = \text{Et}$) crosslinked with alkylimino groups have been prepared by the pyrolysis (600°) of *N*-trialkylaminoborazines;



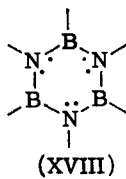
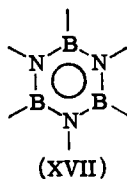
(XVI)

pyrolysis at lower temperatures yielded the condensation dimer XVI ($\text{R} = \text{Et}$, $n = 2$) (2, 90, 91). A short report has appeared describing the condensation of *B*-trialkylborazines with hexamethylene diisocyanate (87). No details are given, but it appears unlikely that the formation of these polymeric substances occurred by attack on the nitrogen sites in view of the noticeable lack of reactivity of these positions in the borazine ring.

Incorporation of the borazine ring into polycyclic systems is described in Section II,A.

III. Reactions of the Borazine Ring

Borazine rings can be formulated either as aromatic systems (XVII) in which three electron pairs are distributed in a π -type orbital extending over the whole molecule or as cyclic triamines (XVIII).



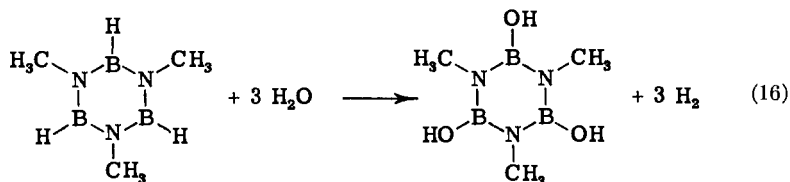
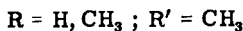
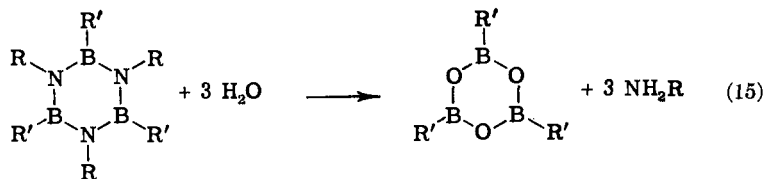
A. ADDITION REACTIONS

$$\text{R}'_3\text{B}_3\text{N}_3\text{R}_3 + 3\text{R}''\text{X} \rightarrow (\text{R}'_3\text{X}_3)\text{B}_3\text{N}_3(\text{R}_3\text{R}''_3) \rightarrow \text{X}_3\text{B}_3\text{N}_3\text{R}''_3 + 3\text{R}'\text{R} \quad (14)$$

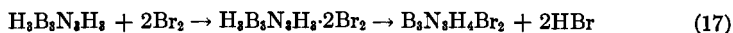
(XIX)
(XX)

R = *p*-anisyl, R' = Cl (85).

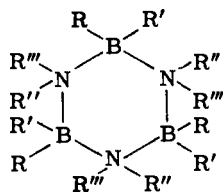
It is interesting to note that the addition compound between bromine and borazine contains only two moles of bromine (185, 186), that alcohols other than methanol do not yield either adducts of type XIX or form the borazine XX (14, 65), and that silyl-substituted borazines undergo ring cleavage upon reaction with halogens (25, 153). Several compounds of the type XIX have been prepared from borazine itself, but no direct evidence is available concerning the structures of these particular compounds. In several instances the substituted borazine (XX) has been obtained from the addition compound XIX [$R' = R = H$, $R''X = MeOH$ (65); $R' = R = Me$, $R''X = HCl$ (187); $R' = R = H$, $R''X = HCl$, HBr



(186)] while in others (XIX) has been postulated as an intermediate (82, 84, 85, 187). The adduct formed between bromine and borazine decomposes to give a disubstituted compound (186).



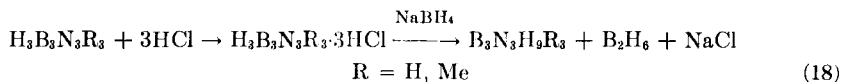
X-Ray diffraction studies of the compound $\text{B}_3\text{N}_3\text{Me}_6\text{H}_6$ indicate that it has a cyclic structure (XXI; $\text{R} = \text{R}'' = \text{H}$, $\text{R}' = \text{R}''' = \text{Me}$) and exists in the chair configuration (171); the hydrogen hyperfine splitting in the B^{11}



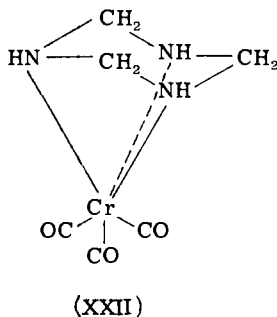
(XXI)

nuclear magnetic resonance spectrum of this compound and of hexahydroborazine (XXI; $\text{R} = \text{R}' = \text{R}'' = \text{R}''' = \text{H}$) (27) also supports this formulation (19). Compounds of this type can be considered as the boron-nitrogen analogs of cyclohexane or as "saturated" borazines. Presumably the compound $\text{B}_3\text{N}_3\text{H}_9\text{Me}_3$ (XXI; $\text{R} = \text{R}' = \text{R}'' = \text{H}$, $\text{R}''' = \text{Me}$), which loses hydrogen at 200° to form a borazine and which has been resolved into two isomers (44), and $(\text{R}\cdot\text{C}=\text{H}\cdot\text{NBRH})_3$ (69) also have a cyclic structure. Borazine has not been hydrogenated using conventional techniques; treatment of borazine with hydrogen in the presence of a catalyst causes an evolution of hydrogen and the formation of a polymeric material of indefi-

nite composition (186). An indirect hydrogenation of borazine (27) and of *N*-trimethylborazine (44) was accomplished by the reaction of the borazine-HCl adducts [(XXI), $R = R'' = R''' = H$, $R' = Cl$; (XXI), $R = R'' = H$, $R''' = Me$, $R' = Cl$] with sodium borohydride [Eq. (18)]. Hexahydroborazine [(XXI), $R = R' = R'' = R''' = H$] is converted into borazine by pyrolysis at 200°.



Theoretically, borazines could form addition compounds with electron-pair acceptors (Lewis acids) if (a) the “ π ” electrons are localized on the nitrogen atoms or (b) the “ π ” electrons are delocalized as in benzene. In the former case the borazine could be considered as a cyclic amine and might act as a Lewis base. On the other hand, a delocalized π system in the borazine ring could be capable of forming “sandwich”-type compounds similar to dibenzenechromium. Although sandwich compounds containing borazine rings have not yet been formed, charge-transfer complexes between hexamethylborazine and tetracyanoethylene (21), chloranil (21), and iodine (103) have been observed in solution. Charge-transfer complexes are well known for benzenoid systems, but the charge-transfer spectrum observed with the borazine ring does not necessarily mean that a delocalized π system of electrons is present in this ring because amines have been reported to give charge-transfer complexes with I_2 also (86, 193). Indeed, the isolation of a sandwich compound or a molecular-addition compound containing the borazine ring could not be taken as evidence that an aromatic system is involved, for if the “ π ” electrons are localized initially or become so under the influence of the acceptor (cf. dibenzene-chromium, ref. 80) the borazine could be considered as a tridentate cyclic amine. Cyclic triamines can act as tridentate ligands as exemplified by the reaction of hexahydro-*s*-triazine with chromium hexacarbonyl to form $Cr(CO)_3(C_3N_3H_6)$. The latter compound has been formulated as XXII (98). In view of these considerations,



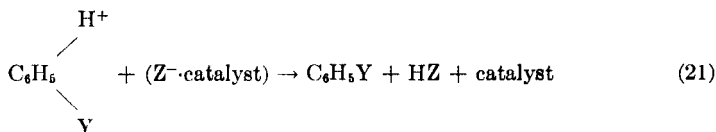
it may be difficult to establish the bond nature of any complex compound of this type containing borazine which may be prepared even if a complete structure determination is made. The structures of the halogen-borazine adducts ($\text{H}_3\text{B}_3\text{N}_3\text{H}_3 \cdot 3\text{Cl}_2$, $\text{H}_3\text{B}_3\text{N}_3\text{H}_3 \cdot 2\text{Br}_2$) are of interest in this respect since trimethylamine-iodine adducts (60, 167) are known to contain iodine associated with the nitrogen atom (presumably through the lone pair electrons) in a linear N—I—I arrangement; this situation occurs even with γ -picoline in which the I—I axis is in the plane of the ring (61). Apparently the electronic charge is more available for bond formation from the nitrogen lone pair electrons than from the aromatic π cloud. On the other hand, the halogen-benzene adducts $\text{C}_6\text{H}_6 \cdot \text{I}_2$ (41), $\text{C}_6\text{H}_6 \cdot \text{Br}_2$ (62), and $\text{C}_6\text{H}_6 \cdot \text{Cl}_2$ (63) contain the halogen atom associated with the entire benzene ring. When they are determined, the structures of the borazine-halogen complexes may clarify the disposition of the lone pair electrons in the borazine ring.

Partial localization of the π electrons on the nitrogen atom could lead to the borazine ring acting as an acceptor of electrons at the boron atom sites. Presumably the addition of polar molecules, HX (X = halogen) (186, 187), occurs because the electrophilic fragment (H^+) adds to the nitrogen atom while the nucleophilic moiety adds to the boron atom, since pyrolysis of the adduct yields *B*-halogeno-substituted borazines (186, 187). In view of this apparent electron-pair donating and accepting ability of the borazine ring an interesting possibility arises for the formation of addition compounds with the transition metals. If the " π " electrons are partially localized on the nitrogen atoms of the borazine ring, it can behave as a tridentate ligand, donating its electrons to available vacant *d* orbitals of a suitable transition metal atom, and it can also accept electron pairs at the boron sites from filled *d* orbitals of the transition metal. A compound formed in this manner might be difficult to distinguish from a "sandwich compound" resulting from interaction of delocalized " π " electrons on the borazine ring.

No addition compounds containing the borazine ring as an electron acceptor have been characterized; borazine was found to react slowly with amines and dimethyl ether to yield products that are apparently polymers (186) and not to be affected by di-*n*-butyl ether (148).

B. SUBSTITUTION REACTIONS

Borazine rings undergo substitution reactions primarily on the boron positions and very rarely on the nitrogen positions, the majority of the former reactions having been reported for *B*-halogenoborazines. Benzenoid systems are most readily substituted by electrophilic reagents, and generally a catalyst is required to aid in the formation of the attacking group.

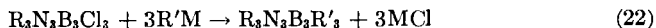


The intermediate carbonium ion [Eq. (20)] decomposes to give a substituted aromatic system because the latter has a much lower energy content than the former. By contrast, substitution reactions occur on the borazine ring without a catalyst. In view of the mode of addition of polar reagents to borazines and the fact that *B*-substitution occurs more readily than *N*-substitution, it would appear that most of the substitution reactions occur via attack of a nucleophilic species at the electron-deficient boron atoms, followed by either addition of the electrophilic portion of the reagent to the ring nitrogen atoms or elimination of a group from the boron position.

1. Substitution of Chlorine Attached to Boron

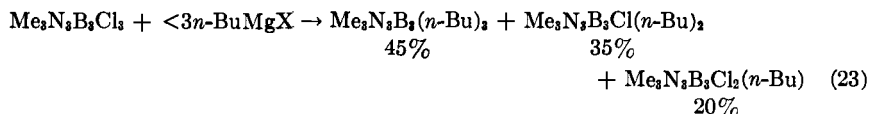
Perhaps the most convenient method for the preparation of borazines involves the condensation of boron trichloride with an appropriately-substituted ammonium salt to form symmetrically-*N*-substituted *B*-trichloroborazines. These compounds can react with a variety of reagents to yield tri-*N*-substituted tri-*B*-substituted borazines.

a. Substitution by Alkyl or Aryl Groups. Alkyl and aryl Grignard reagents ($M = \text{MgX}$) (9, 37, 55, 66, 144, 153), alkyl- and aryl-lithium reagents ($M = \text{Li}$) (5, 55, 114), and triphenylsilyl-potassium (25) or -lithium (153) react with *B*-trichloroborazines to form the corresponding *B*-tri-alkyl-, -aryl-, or -silyl-borazines [Eq. (22)]. An attempt to prepare



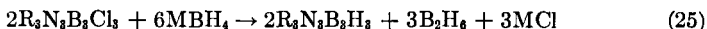
B-perfluoroalkylborazines by the reaction of heptafluoro-*n*-propyl-lithium on *B*-trichloro-*N*-triphenylborazine was unsuccessful (89).

Usually sufficient Grignard or lithium reagent is added to substitute all the chlorine atoms on the borazine, but if a deficiency of reagent is employed [Eq. (23)] a mixture of products is obtained (144). Reaction (23)

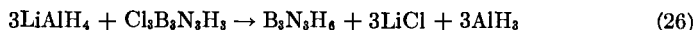


apparently proceeds by the consecutive substitution of alkyl groups in a statistical manner, since the presence of one alkyl group does not markedly affect the rate of substitution of subsequent alkyl groups (144). This conclusion is not supported, however, by the distribution of products observed in the reaction of Grignard or lithium reagents with B—H bonds (158). Some investigators have indicated that it is difficult to separate *B*-alkyl- or -aryl-borazines from ether in high yield, however addition of tertiary amines to the reaction mixture increases the yield markedly (37).

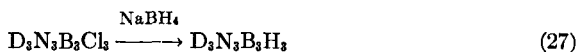
b. Substitution by Hydrogen. Lithium aluminum hydride (148, 158), sodium borohydride (29, 71, 186), and lithium borohydride (148) have been used to substitute hydrogen for chlorine on the boron sites in borazines [Eqs. (24) and (25)]. The reaction of LiAlH_4 with *B*-trichloroborazine (148)



apparently gives a poorer yield of the corresponding dehalogenated borazine than does the reaction with *B*-trichloro-*N*-triphenylborazine (158), which may be the result of a different mode of reaction. Aluminum hydride is reported to be one of the products in the reaction of LiAlH_4 with *B*-trichloroborazine [Eq. (26)], whereas all of the hydrogen atoms on the reducing agent are replaced on reaction with *B*-trichloro-*N*-triphenylborazine.



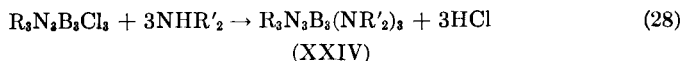
An interaction appears to occur between AlH_3 and borazine since the addition of AlH_3 to an ethereal solution of borazine prevents the recovery of borazine from the mixture (148). Lithium hydride (177) and sodium trisopropoxyborohydride (94) have also been employed to effect hydrogen substitution for chlorine atoms. The reaction between a borazine and sodium borohydride probably does not affect the substituent on nitrogen because *B*-trichloro-*N*-trideutero borazine reacts with NaBH_4 to yield *N*-trideutero borazine (184). These results lend indirect support to the



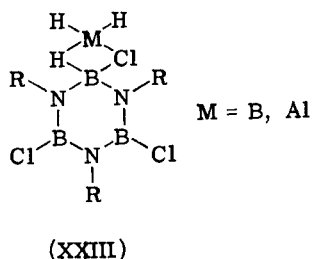
suggestion (154) that the borazine forms a bridged complex (XXIII) upon reaction with reducing agents. A complex of this type has also been

suggested as the intermediate in the exchange of alkyl groups between $\text{Cl}_2\text{EtB}_3\text{N}_3\text{Me}_3$, $\text{ClEt}_2\text{B}_3\text{N}_3\text{Me}_3$, and $\text{Et}_3\text{B}_3\text{N}_3\text{Me}_3$ (144) and in the exchange of alkyl groups during the pyrolysis of certain isomeric alkylborazines (179).

c. *Substitution by Amino, Hydroxyl, or Alkoxy Groups.* *B*-Trichloroborazines react with secondary amines (47, 121, 158) or their salts (121) to form *B*-triaminoborazines (XXIV); the reaction of ammonia with *B*-tri-



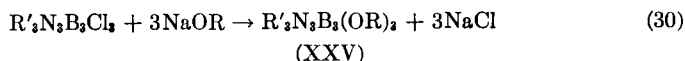
chloroborazine is reported to yield *B*-triaminoborazine (XXIV, $\text{R} = \text{R}' = \text{H}$) (54) as well as a polymeric material (47).



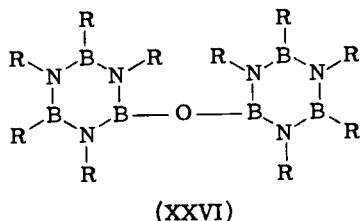
Hydroxyl groups have been substituted for chlorine atoms on the boron sites in the borazine ring by reaction with water (82, 85), and the reverse



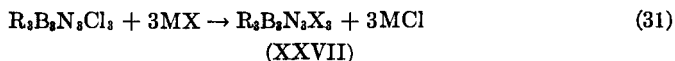
of this conversion can be accomplished by treating the *B*-trihydroxyborazine with SOCl_2 (5). Alkoxyborazines have been prepared from *B*-trichloroborazines using sodium alkoxides (14, 65), and *B*-trisiloxyborazines (XXV, $\text{R} = \text{OSiMe}_3$) can be prepared in a similar manner (153). An interesting



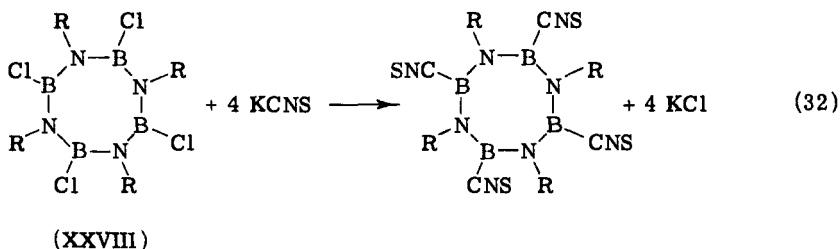
series of polyborazines are obtained from the reaction of *B*-monochloroborazines or *B*-dichloroborazines with water in the presence of triethylamine. The former compounds yield (XXVI), while the latter yield a polymeric substance (179).



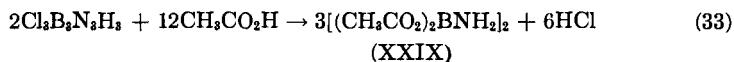
d. *Substitution by Miscellaneous Reagents.* Several other reagents can replace chlorine atoms on the boron sites in borazines. The reaction [Eq. (31)] of potassium thiocyanate or silver cyanide with *B*-trichloroborazine



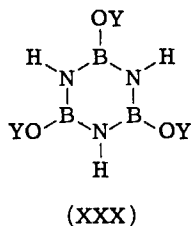
in acetonitrile yields compounds which correspond to *B*-trithiocyanatoborazine [(XXVII); R = H, X = SCN] and *B*-tricyanoborazine [(XXVII); R = H, X = CN], respectively (15). Difficulty was encountered in freeing the latter compound of silver, and this may have been due to complex formation (see above). Reaction with silver nitrite and silver nitrate yielded precipitates of silver chloride under the same conditions, although the corresponding borazine [(XXVII); R = H, X = NO₂ or NO₃] could not be isolated (15). The reaction of silver perchlorate with *B*-trichloro-*N*-trimethylborazine yielded a solid, the stoichiometry of which corresponded to that expected for *B*-triperchlorato-*N*-trimethylborazine [(XXVII); R = Me, X = ClO₄] (100). This compound explodes violently when treated with water or when placed in a flame and should be treated with extreme caution. Similar observations have been reported concerning the stability of the reaction products of *B*-trichloroborazine with silver nitrite (15). The tetrameric borazynes (XXVIII), R = *t*-butyl, the boron-nitrogen analog of cyclooctatetraene, has been reported, and substitution of the chlorine atom attached to boron can be effected by treatment with potassium isothiocyanate (175).



Anhydrous acetic acid reacts with borazine to form a 1:3 adduct (cf. Section III,A), but it attacks *B*-trichloroborazine by cleaving the ring with the concomitant liberation of hydrogen chloride and the formation of the dimeric aminoborane (XXIX) (15). Esters of phosphoric acid react with

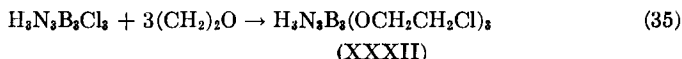
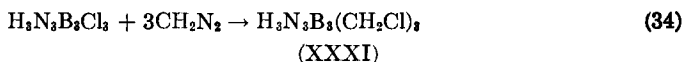


B-trichloroborazine to form compounds of type (XXX) [Y = P(O)(OR)₂] (119), while esters of phosphorus acid in the presence of aldehydes form



phosphinyl-substituted alkoxyborazines [(XXX); $\text{Y} = \text{—CHRP(OR)}_2$] (12). *B*-Trichloroborazine is reported to undergo reaction with benzene in boiling chlorobenzene containing AlCl_3 to give *B*-triphenylborazine in about 24% yield (118). If the mechanism of this reaction is similar to that proposed for a Friedel-Crafts type reaction, it would appear that the borazine ring can act as an electrophile under the influence of AlCl_3 since the complex AlCl_3 forms with benzene is not considered to be essential in the mechanism of the normal Friedel-Crafts process (141).

Diazomethane (173) and ethylene oxide (123) react with *B*-trichloroborazine. The product (XXXII) of the latter reaction is identical with

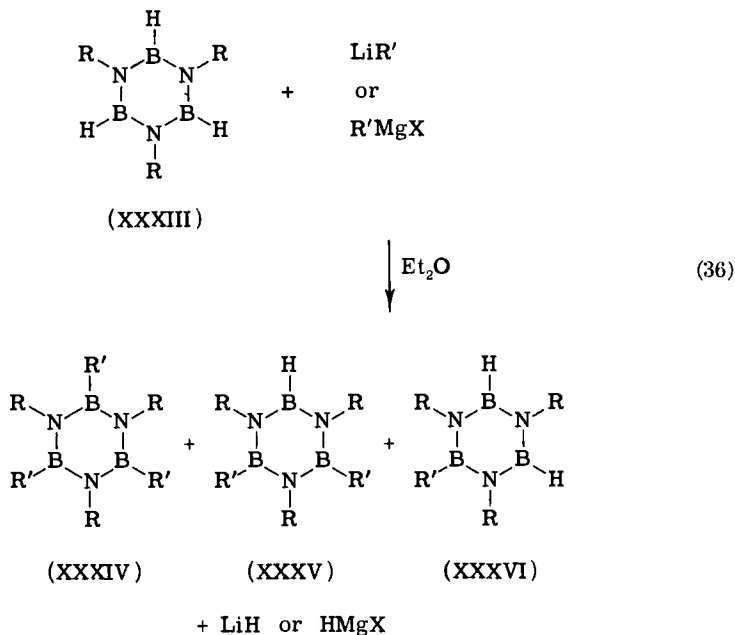


that obtained from the reaction of the appropriate chlorinated alcohol with *B*-triaminoborazine. The former reaction yields the only known halogenomethylborazine (XXXI); this type of reaction is also observed with *N*-triarylborazines (163).

2. Substitution of Hydrogen or Alkyl Groups Attached to Boron

Many of the substitution reactions observed with chlorine attached to boron also occur with hydrogen attached to boron, although these substitution reactions have not been as extensively investigated. Deuterium, diborane- d_6 , and sodium borodeuteride undergo exchange reactions with borazine at the boron sites only (28), which in the case of the last two named compounds appears to be consistent with the suggestion (154) that a bridged intermediate is involved [cf. (XXIII)].

a. Substitution by Alkyl or Aryl Groups. The reaction of *N*-triphenylborazine or *N*-trimethylborazine with Grignard reagents or alkyl- or aryllithium reagents supports the suggestion that the hydrogen atoms in these compounds are hydridic or pseudo-halogen in nature (158). *B*-mono- (XXXVI) and -di-substituted borazines (XXXV) were obtained in good yield upon alkylation of *N*-triphenylborazine [(XXXIII), $\text{R} = \text{C}_6\text{H}_5$];

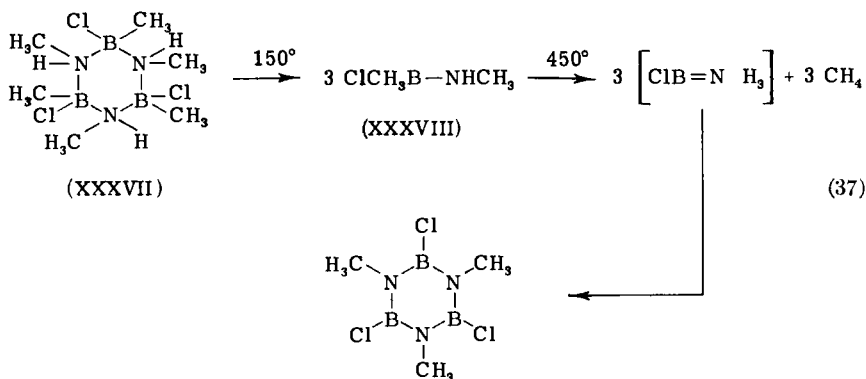


only one product was obtained in each case. In contrast to this behavior, *N*-trimethylborazine yielded appreciable amounts of all possible substitution products [(XXXIV), (XXV), and (XXXVI), R = Me] under the same conditions. A statistical distribution of products is not obtained upon alkylation or arylation of *N*-triphenylborazine indicating that the introduction of a substituent on the boron atom alters the reactivity of the remaining B—H sites (contrast with reaction of *B*-trichloroborazine, Section III,B,1,a). In the case of *N*-triphenylborazines, both methyl and phenyl groups substituted on boron sites decrease the rate at which further substitution occurs; the order of the reactivity of the compounds in this series appears to be unsubstituted > monosubstituted > disubstituted. Substitution of alkyl groups deactivates the borazine ring to a lesser degree in *N*-trimethylborazine than in *N*-triphenylborazine (158).

Trimethylborane reacts with borazine at 100° to yield a mixture of all the possible *B*-substituted derivatives, although *B*-trimethylborazine is the major product (150). No nitrogen sites were substituted, which is in keeping with the results observed with other alkylating reagents.

b. Substitution by Halogen Atoms. *B*-Halogenoborazines can be prepared by the action of a hydrogen halide (164, 165, 178, 185, 186, 187, 188) or a halogen (185, 186) on the corresponding borazine (164, 185, 186) or trialkylborazine (187, 188) at elevated temperatures. As is discussed in Section III,A this reaction proceeds through the formation of an intermediate

addition compound. Alkyl groups or hydrogen atoms on the boron atom are eliminated as alkanes or molecular hydrogen, respectively; alkyl groups on the nitrogen sites are retained during the pyrolysis reaction. If these reactions are conducted in the presence of excess (over a 3:1 molar ratio) hydrogen halide, complete ring cleavage results (187). It has been suggested (185, 186) that the elimination of alkanes is not a simple molecular displacement, but proceeds through formation of the 1:3 adduct (XXXVII), which in turn dissociates into the corresponding aminoborane (XXXVIII); (XXXVIII) eliminates methane and recombines to form a borazine [Eq. (37)].



(37)]. The high temperature reaction of borazine with NH_4Cl to yield small amounts of *B*-trichloroborazine (146) can be considered as an extension of the reaction between borazine and HCl under the same conditions.

Boron trihalides react with borazine at room temperature to yield a mixture of mono- and di-substituted borazines as well as hydrogen and unidentified nonvolatile products (146).

c. Substitution by Miscellaneous Reagents. The hydridic character of the hydrogen atoms on boron sites is also exemplified by the stepwise reaction of diazomethane with *N*-triarylborazines to form *B*-mono-, *B*-di-, and *B*-tri-methyl-*N*-triarylborazines (163). The stepwise course of this reaction is consistent with the results obtained for the successive replacement of the hydrogen atoms in *N*-triarylborazines by alkyl groups using Grignard reagents (cf. Section III,B,2,a).

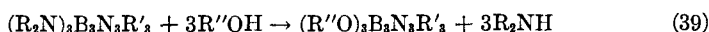
3. Substitution of Amino Groups Attached to Boron

Amino groups attached at the boron sites in borazines can be replaced by other amino groups [Eq. (38)] (38, 39, 47, 124, 187), but in some instances polycondensation competes with the transamination reaction (47).



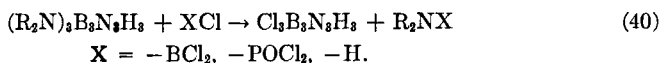
Unsymmetrically-substituted *B*-triaminoborazines have been prepared by reacting symmetrically-substituted *B*-triaminoborazines with the appropriate amine in equimolar proportions (91). Hydrazine and unsymmetrical-dimethylhydrazine have also been employed in this type of reaction [Eq. (38)] to obtain *B*-trihydrazinoborazines (124, 187).

B-Triaminoborazines react with an excess of an alcohol or perhalogenoalcohol to yield *B*-trialkoxyborazines [Eq. (39)] (124, 187); *B*-mono- and -di-alkoxyborazines can be prepared by using stoichiometric amounts of the reagents (91). All amino or alkylamino groups attached to the boron



sites are easily replaced by alcohols, and the order of replacement is $NH_2 \geq N_2H_3 > NHR > NR_2$ (187).

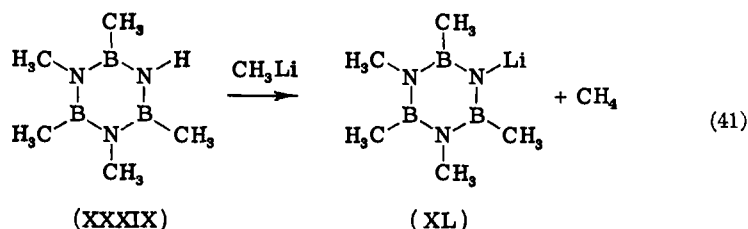
Boron trichloride (47, 124), phosphonyl chloride (124), and HCl (47) displace $-NR_2$ groups from the boron sites of borazine rings to form *B*-trichloroborazines [cf. Eq. (40)].



4. Substitution on the Nitrogen Atom

Although substitution on the nitrogen sites in the borazine ring is not commonly observed, ND_3 , DCl , and DCN were found to exchange with hydrogen attached to nitrogen atoms at a rate which is comparable to that with which these substances add to the borazine (28). The results of the exchange experiments between DCl and borazine indicate that the adduct $B_3N_3H_6 \cdot 3DCl$ does not decompose into borazine nor does the adduct exchange with borazine.

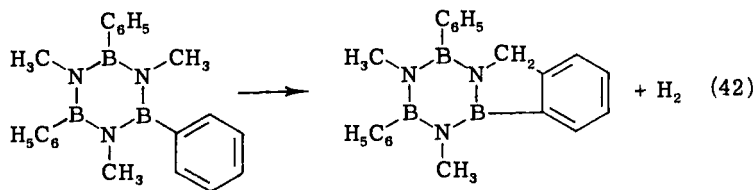
Hydrogen atoms attached to nitrogen positions in the borazine ring can be replaced by lithium [Eq. (41)] using methyl-lithium (178, 179).



A nearly quantitative yield of *N*-lithio-pentamethylborazine (XL) can be obtained from *B*-trimethyl-*N*-dimethylborazine (XXXIX), but the reaction of *B*-trimethylborazine with methyl-lithium in a 1:1 mole ratio gives predominantly *N*-monolithio-*B*-trimethylborazine with lesser amounts of

the *N*-di- and -tri-lithio derivatives. This reaction has been used to prepare a variety of unsymmetrically-substituted borazines (178) as well as polymeric borazines. A similar replacement of hydrogen atoms on the nitrogen sites has been observed with Grignard reagents (59).

The pyrolysis of *B*-triphenyl-*N*-trimethylborazine proceeds by the elimination of hydrogen from the methyl group and the ortho position of the benzene ring [Eq. (42)] with the concomitant formation of a five-membered ring.



IV. Commercial Uses of Borazines

Borazines have been used in proportional counters for neutron detection (58, 114), as gasoline additives (122, 152), and as polymerization catalysts (81). Although attempts to make borazine polymers have been successful (see, for example, refs. 87, 131, and 179 and Sections II,C and II,B), no commercially important polymers have been reported.

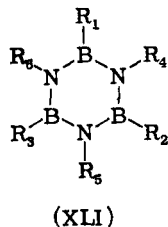
V. Physical Properties of Borazines

The similarity of the physical properties of borazine (Table I) and benzene has often been cited to support the statement that the former can be looked upon as "inorganic benzene," in spite of the apparent difference in the chemistry of these ring systems. When compared with a series of benzene derivatives, those properties of the analogous borazines that are dependent upon structural similarities vary in a predictable manner. For example, the ratio of the boiling points (expressed in °K) of methyl borazines to the boiling points of the analogous benzene derivatives is approximately 0.93 (187). The physical properties of borazine appear to be those expected for an unassociated liquid, although it has been suggested (154) that the temperature dependence of viscosity for borazine (34) indicates association at low temperatures in contrast with benzene. On the other hand, Trouton's constant, Eötvös' constant, and the value of the product of the viscosity (η) and molar volume (V_m) indicate that borazine is not associated to any appreciable extent. The product ηV_m for borazine is about half the corresponding value for benzene at normal temperatures, but associated liquids exhibit a ηV_m value of about 100 times that of unassociated liquids (115).

TABLE I
 THE PHYSICAL PROPERTIES OF BORAZINE

Boiling point	55.0° (186)
Melting point	-56.2° (34)
$\log P_{mm} = -1828.2/T + 8.6829$	(-55°C to -15°) (186)
$\log P_{mm} = -1565.5/T + 7.6616$	(-15°C to +20°) (186)
$\log P_{mm} = -1538.0/T + 7.5668$	(+20°C to +50°) (186, see also ref. 164)
D (gm/cm ³) = 1.1551 - 0.001074 <i>T</i>	(<i>T</i> = 238.2 to 313.9) (34)
D (gm/cm ³) = 0.8613 - 0.00097 <i>t</i>	(<i>t</i> = -40 to +10) (74, 186)
$n_D^{20} = 1.3821$	(34, 74)
Molar refraction at 20°	= 22.26 (74)
Molar volume at 0°	= 93.5 (74)
Trouton's constant	= 21.1 (74), 21.4 (186)
ΔH_v	= 7034 cal/mole (74, 186)
Critical temperature	= 252° (186)
η (poise) = 47.3(10 ⁻⁵) $D^{1/2}e^{665.5D/T}$	(34)
γ (dynes/cm) = 58.3 - 0.1207($D^{2/3}$)	(34, see also ref. 186).
γ (at m.p.)	= 31.09 dynes/cm (186)
Parachor	= 207.7 (186)
Molecular surface tension	= 503 - 2.0 <i>t</i> (186)
Diamagnetic anisotropy	= -49.6 × 10 ⁻⁶ e.m.u. (180)
Dipole moment: gas phase, 0.67 Debye	(186); benzene solution, 0.50 Debye (96)

The physical properties that have been reported for substituted borazines are summarized in Table II, and borazines that have not been characterized other than by their elemental analysis or their reactions appear in Table III. The compounds in these tables are listed according to the boron substituents and the nitrogen substituents which have been arbitrarily numbered according to (XLI).

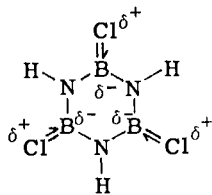


A. MOLECULAR STRUCTURE

X-ray data on borazine were reported by Stock, but the Debye-Scherrer pattern proved too complex for analysis at the time (164). The similarity between electron diffraction photographs of borazine and benzene led to an assignment of D_{3h} symmetry to the former (166), and this symmetry group has been assumed in the analysis of electron diffraction data on *N*-trimethylborazine and *B*-trichloroborazine (22). Structural parameters for several borazines and for one cyclohexane-type derivative [(XXXVIII); $R = R' = H$, $R'' = R''' = Me$] are given in Table IV. Electron diffraction

data indicate that all atoms in the borazine ring are coplanar to within 0.1 Å (6). Preliminary X-ray studies conducted on microcrystals of borazine and benzene (40, 139) indicate a similar arrangement of molecules in the unit cell.

The structural parameters obtained from X-ray crystallographic data for $\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$ (24) indicate that the ring atoms are coplanar to less than 0.01 Å and that the molecule has D_{3h} symmetry within experimental error. The larger intermolecular H—H' and Cl—Cl' distances and the smaller Cl—H' distances observed in *B*-trichloroborazine as compared with the corresponding distance in *s*-trichlorobenzene suggest that a greater charge exists on the chlorine and hydrogen atoms in the former compound (XLII). Because of significant contributions of (XLII) to the structure, there is less aromatic character in *B*-trichloroborazine than in the analogous benzene derivative (95). This observation is in agreement with trends established from diamagnetic anisotropy data (Section V,F).



(XLII)

The molecular structure of $\text{B}_3\text{N}_3\text{H}_6\text{Me}_6$ has been elucidated from X-ray data, although the crystallographic space group was not unequivocally assigned. This molecule is in the chair form with C_{3v} symmetry within experimental error, and it is interesting to note that no sterically satisfactory, fixed arrangement of the methyl hydrogens could be found (172). The B—N bond distance observed in this compound approaches that expected for a single bond (45).

An "equivalent" C—C bond length (1.406 Å) has been calculated using an empirical relationship for the B—N bond in $\text{H}_3\text{B}_3\text{N}_3\text{H}_3$ and an estimated bond order of 1.58 derived (160). A bond order of 1.20 for the B—N bond in $\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$ has been estimated from Gordy's formula (51) assuming 1.45 Å for the B—N single bond length and 1.281 Å for the B—N double bond length (154). The value for the B—N double bond length is taken from the equilibrium bond distance for the lower $^3\Pi$ state of the diatomic molecule BN (33). A comparison of the C—C distance in the species C_2 (1.31 Å) and C_2H_4 (1.35 Å) (169) suggests that the value for the BN double bond distance in the $^3\Pi$ state is about 0.04 Å too small for the hypothetical species $\text{H}_2\text{B}=\text{NH}_2$. If the empirical correction is made, the calculated B—N

TABLE II^a
THE PHYSICAL PROPERTIES OF BORAZINES

<i>B</i> -Substituents			<i>N</i> -Substituents			Reference	m.p.	b.p./mm.	Other properties
R ₁	R ₂	R ₃	R ₄	R ₅	R ₆				
H	Me	Me	H	H	Me	(150)		139	$\log P = -1965/T + 7.652$; $\Delta H_v = 8916$; $T = 21.6$
H	Me	Me	H	H	H	(149)	-48	107	$\log P = -2019/T + 8.200$; $\Delta H_v = 9230$; $T = 24.3$
H	Me	Me	Me	Me	Me		32.8 (178)	187 (158)	$D/t = 0.87/35$, IR (178)
H	Me	Me	Ph	Ph	Ph	(163)	205-7	101.2/38 (178)	
H	Me	Me	$\leftarrow 4\text{-BrC}_6\text{H}_4 \rightarrow$ ^{b,c}			(163)	211-3		
H	Me	Et	Ph	Ph	Ph	(158)	128		
H	Ph	Ph	Ph	Ph	Ph	(158)	207		
H	Br	Br	H	H	H	(146)	49.5-50.0	167.1	$\log P = -2849/T + 9.352$; $\Delta H_v = 13037$; $T = 29.6$
H	Cl	Cl	H	H	H	(146)	33.0-33.5	151.9	$\log P = -1994/T + 7.572$; $\Delta H_v = 9125$; $T = 21.5$
H	Cl	Cl	$\leftarrow 2,6\text{-Me}_2\text{C}_6\text{H}_3 \rightarrow$			(173)			IR; NMR
H	NH ₂	NH ₂	H	H	H	(101, 103)			MS
H	H	Me	H	H	Me	(150)		124	$\log P = -1732/T + 7.245$; $\Delta H_v = 8013$; $T = 20.2$
H	H	Me	H	H	H	(149)	-59	87	$\log P = -1800/T + 7.880$; $\Delta H_v = 8230$; $T = 22.8$
H	H	Me	Me	Me	Me	(178)	-14.5	162 (158)	$D/t = 0.85/25$, IR (178)
								76.2/38 (158)	
H	H	Me	Ph	Ph	Ph		140-2 (158)		
							138-41 (163)		
H	H	Me	$\leftarrow 4\text{-MeC}_6\text{H}_4 \rightarrow$			(163)	150-1		
H	H	Me	$\leftarrow 3\text{-MeC}_6\text{H}_4 \rightarrow$			(163)	137-8		
H	H	Ph	H	H	H	(112)	73.5-75		
H	H	Ph	Ph	Ph	Ph	(158)	215		
H	H	Br	H	H	H	(146)	34.8	122.3	$\log P = -2172/T + 8.373$; $\Delta H_v = 9939$; $T = 25.1$
H	H	Cl	H	H	H	(146)	-34.6	109.5	$\log P = -1846/T + 7.703$; $\Delta H_v = 8445$; $T = 22.1$
H	H	H	H	H	H		See Table I		X (164); NMR (77, 132); IR (26, 183); R (26), UV (133); See also Table I
H	H	H	H	H	Me	(150)		84	$\log P = -1713/T + 7.669$; $\Delta H_v = 7975$; $T = 22.3$
H	H	H	H	Me	Me	(150)		108	$\log P = -1832/T + 7.685$; $\Delta H_v = 8375$; $T = 21.9$
H	H	H	Me	Me	Me		-7.8 (71)	133 (74)	$\log P = -2009/T + 7.812$ (74, 150, 188); $\Delta H_v = 9200$ (74); $T = 22.9$ (74) $D/t = 0.8699/0$ (74); $n/t = 1.4404/20$ (74); MR = 37.98 (74); $\chi_m = -78.6$ (180) IR (64, 178); UV (137); ED (22); R (182); NMR (78, 132)

H	H	H	Et	Et	Et	(74)	-49.1 (71)	184	$\log P = -2012.4/T + 7.238$; $\Delta H_v = 9210$; $T = 20.2$; MR = 50.90; $D/t = 0.8604/0$ $n = 1.4380/20$; IR (11)
H	H	H	Pr ⁿ	Pr ⁿ	Pr ⁿ	(74)		225	$\log P = -2190.4/T + 7.2793$; $\Delta H_v = 1002$; $T = 20.2$; MR = 66.39; $D/t = 0.8485/0$; $n = 1.4484/20$
H	H	H	Pr ⁱ	Pr ⁱ	Pr ⁱ	(74)	-6.7 (6)	203	$\log P = -2249.0/T - 7.6001$; $\Delta H_v = 1029$; $T = 21.6$; MR = 64.66; $D/t = 0.8648/0$; $n = 1.4434/20$
H	H	H	Bu ⁿ	Bu ⁿ	Bu ⁿ	(107)		109-11/3.5	$n = 1.4524/20$
H	H	H	Bu ⁱ	Bu ⁱ	Bu ⁱ	(107)		92/3	$D/t = 0.8245/20$; $n = 1.4466/20$
H	H	H	C ₆ H ₁₁	C ₆ H ₁₁	C ₆ H ₁₁	(71)	98.9		
H	H	H	Ph	Ph	Ph		157-8 (71)		IR (9), UV (10)
							154-5 (9)		
H	H	H	←4-BrC ₆ H ₄ →			(163)	234-5		
H	H	H	←3-BrC ₆ H ₄ →			(163)	125-5.4		
H	H	H	←4-MeC ₆ H ₄ →				149-50 (71)		
							150-2 (9)		
H	H	H	←3-MeC ₆ H ₄ →			(163)	165.5-6.5		
H	H	H	←4-MeOC ₆ H ₄ →				137-8 (71)		
							139-40 (163)		
CN	CN	CN	H	H	H	(16)	$d > 200$		
Me	Et	Pr ⁿ	Ph	Ph	Ph	(168)	131		
Me	Br	Br	Me	Me	Me	(178)	127-9		IR
Me	Cl	Cl	Me	Me	Me	(178)	145-6		IR
Me	Me	Bu ⁿ	Ph	Ph	Ph	(168)	113		
Me	Me	Br	Me	Me	Me	(178)	127-9		IR
Me	Me	Me	H	Me	Me	(178)		187-6	IR; $D/t = 0.88/25$
Me	Me	Me	H	H	Me	(160)		158	$\log P = -2294/T + 8.207$; $\Delta H_v = 10440$; $T = 24.5$; $D/t = 0.86/25$; IR (178)
Me	Me	Me	H	H	H		31.5 (149)	129 (149)	$\log P = -2199/T + 8.3779$; $\Delta H_v = 10060$ (149, 188); $\log P = -3258/T + 11.8488$; $\Delta H_v = 14900$ (188); $T = 23.3$ (149); $D/t = 0.84/35$ (178); IR (178); X (188); R (53); UV (137)
Me	Me	Me	Me	Me	Me		99 (158)	221 (187)	$\log P = -2523.7/T + 7.9871$; $\Delta H_v = 11540$; $T = 23.4$ (187); MR = 50.0; $\chi_m = -119$ (180)
							97.1 (187)		DM = 0.76 (181); NMR (78); IR (178, 183)
Me	Me	Me	Et	Et	Et	(78)			NMR
Me	Me	Me	Pr ⁱ	Pr ⁱ	Pr ⁱ	(152)	68-70	101	

TABLE II (Continued)

B-Substituents			N-Substituents			Reference	m.p.	b.p./mm	Other properties
R ₁	R ₂	R ₃	R ₄	R ₅	R ₆				
Me	Me	Me	Ph	Ph	Ph		267-9 (55)		MR = 108.5 (181); χ_m = -234 (180); DM = 0.18 (181); IR (9, 183); NMR (78); UV (10)
CH ₂ Cl	CH ₂ Cl	CH ₂ Cl	H	H	H	(173)	117-8		IR
Et	Et	Et	H	H	H	(66)	-46.4	173	log P = -2167/T + 7.746; ΔH_v = 9880; T = 22.1; D/t = 0.886/20; IR; ϵ /20 = 1.48 (194)
Et	Et	Et	Me	Me	Me		1-2 (144)	98/1.8 (144)	MR = 63.9 (181); χ_m = -146 (180); DM = 0.83 (181); n = 1.4791/22.5 (144); IR (144); NMR (78)
Et	Et	Et	Et	Et	Et		88.5-9.5 (66)		MR = 77.7; DM = 0.37 (181); χ_m = -189 (180); NMR (78); IR (181, 183); UV (181)
Et	Et	Et	Ph	Ph	Ph		169-71 (55)		NMR (78); IR (183); MR = 122.3 (181); χ_m = -264 (180); DM = 0.47 (181)
C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	Ph	Ph	Ph	(130, 131)	187-9		
C ₆ H ₄ Cl	C ₆ H ₄ Cl	C ₆ H ₄ Cl	H	H	H	(143)	127-8.5		
Pr ⁿ	Pr ⁿ	Pr ⁿ	H	H	H			108/9 (67)	UV (68); IR (68); NMR (68)
Pr ⁿ	Pr ⁿ	Pr ⁿ	Ph	Ph	Ph	(55)	169-71		
Pr ⁱ	Pr ⁱ	Pr ⁱ	H	H	H			70/0.5 (67)	IR (68); UV (68); NMR (68)
Pr ⁱ	Pr ⁱ	Pr ⁱ	Ph	Ph	Ph	(147)	197-8		
C ₃ H ₇	C ₃ H ₇	C ₃ H ₇	Me	Me	Me	(144)	-(37-9)	110-12/13	n = 1.5047/22.5; IR
C ₃ H ₇	C ₃ H ₇	C ₃ H ₇	Ph	Ph	Ph	(56, 131)	98-9		
Bu ⁿ	Bu ⁿ	Bu ⁿ	Me	Me	Me	(144)	-(4-6)	101/1.1	n = 1.4876/22.5; IR
Bu ⁿ	Bu ⁿ	Cl	Me	Me	Me	(144)		122/1.13	n = 1.4807/22.5; IR
Bu ⁿ	Bu ⁿ	Bu ⁿ	H	H	H			110/0.6 (67)	n = 1.4494/25 (67); UV (68); NMR (68)
Bu ⁿ	Bu ⁿ	Bu ⁿ	Me	Me	Me	(144)	-(18-7)	140/1.1	n = 1.4759/22.5; IR (144, 153)
Bu ⁿ	Bu ⁿ	Bu ⁿ	Bu ⁿ	Bu ⁿ	Bu ⁿ	(143)		90-8/0.1	
Bu ⁿ	Bu ⁿ	Bu ⁿ	Ph	Ph	Ph	(147)	129-32		IR (183)
Bu ^s	Bu ^s	Bu ^s	H	H	H	(67)		94/0.7	IR (68); NMR (68); UV (68)
Bu ⁱ	Bu ⁱ	Bu ⁱ	H	H	H	(68)		72.1/0.03	IR; NMR; UV
Bu ⁱ	Bu ⁱ	Bu ⁱ	Ph	Ph	Ph	(55)	185-7		
Bu ⁱ	Bu ⁱ	Bu ⁱ	H	H	H	(68)		60/0.10	IR; NMR; UV
Ph ⁿ	Ph ⁿ	Ph ⁿ	H	H	H	(68)		125/0.07	IR; NMR; UV
← Me ₂ CHCH ₂ CH ₃ →			H	H	H	(110)		114-15.5/0.1	D/t = 0.8485/20; n = 1.4538/20

\longleftrightarrow	$\text{Me}_2\text{CHCH}_2\text{CH}_2$	\longleftrightarrow	Et	Et	Et	(110)	43-5	113-4/0.06	
\longleftrightarrow	$\text{Me}_2\text{CHCH}_2\text{CH}_2$	\longleftrightarrow	Bu ^t	Bu ^t	Bu ^t	(110)	53-5	126-8/0.06	
\longleftrightarrow	$\text{Me}_2\text{CHCH}_2\text{CH}_2$	\longleftrightarrow	Ph	Ph	Ph	(110)	93.5-5.5	180-1/0.06	
H _X ⁿ	H _X ⁿ	H _X ⁿ	H	H	H	(68)		140/0.05	UV (68); IR (68); NMR (68)
Ph	Ph	Ph	H	H	H		183-5 (9, 32)		IR (9, 117); UV (10, 125)
							181-182.5 (108)		
							175-6 (118)		
							179-82 (37)		
Ph	Ph	Ph	Me	Me	Me		261-7 (117)		IR (9, 20, 117); UV (10)
							249 (9)		
							270 (158)		
Ph	Ph	Ph	Et	Et	Et	(106, 108)	205-6		
						(109)			
Ph	Ph	Ph	Ph	Ph	Ph		413-5 (55)		IR (183)
\longleftrightarrow	4-MeC ₆ H ₄	\longleftrightarrow	H	H	H	(108, 109)	189-90		
\longleftrightarrow	4-MeC ₆ H ₄	\longleftrightarrow	Et	Et	Et	(109)	222-5		
\longleftrightarrow	4-MeC ₆ H ₄	\longleftrightarrow	Ph	Ph	Ph	(109)	282-4		
\longleftrightarrow	4-BrC ₆ H ₄	\longleftrightarrow	H	H	H	(109)	292-3		
\longleftrightarrow	4-ClC ₆ H ₄	\longleftrightarrow	H	H	H	(109)	269-70		UV (125)
Bz	Bz	Bz	H	H	H	(68)			UV; IR; NMR
\longleftrightarrow	terphenyl	\longleftrightarrow	Me	Me	Me	(20)			IR
\longleftrightarrow	1-C ₁₀ H ₇	\longleftrightarrow	H	H	H	(108)	185-7		
\longleftrightarrow	1-C ₁₀ H ₇	\longleftrightarrow	Et	Et	Et	(108)	269-71		
2Py	2Py	2Py	Me	Me	Me	(20)			IR
\longleftrightarrow	Me ₃ SiCH ₂	\longleftrightarrow	Me	Me	Me	(153)	64		IR
\longleftrightarrow	EtMe ₂ SiCH ₂	\longleftrightarrow	Me	Me	Me	(153)		183-4/1.0	D/t = 0.8977/24; n = 1.4875/25
\longleftrightarrow	Bu ⁿ Me ₂ SiCH ₂	\longleftrightarrow	Me	Me	Me	(153)		213-4/0.9	D/t = 0.8855/25; n = 1.4845/25
\longleftrightarrow	Me ₃ SiOSi(Me) ₂ CH ₂	\longleftrightarrow	Me	Me	Me	(153)		175-6/0.55	D/t = 0.9158/25; n = 1.4517/25; IR
Br	Br	Br	H	H	H		128-9 (36)		
							126-8 (148)		
Br	Br	Br	Et	Et	Et	(71)	78-84		
Cl	Cl	Cl	H	H	H	(15, 17, 181)	83.9-84.5		log P = -2497/T + 8.25; ΔH _v = 12300 (17); log P = -3743/T + 11.73, ΔH _v = 17000 (17); D/t = 1.5/25; NMR (78, 116, 156); IR (3, 183, 184); UV (73); X (24); DM = 0.56 (181)
Cl	Cl	Cl	Me	Me	Me		162-4 (71)		MR = 50.8; DM = 0.47 (181); NMR (78); IR (178, 183)
Cl	Cl	Cl	Et	Et	Et		57-9 (71)		NMR (78); IR (183)
Cl	Cl	Cl	Bu ⁿ	Bu ⁿ	Bu ⁿ	(174)	30	115-20/0.5	IR (183)

TABLE II (Continued)

B-Substituents			N-Substituents			Reference	m.p.	b.p./mm	Other properties
R ₁	R ₂	R ₃	R ₄	R ₅	R ₆				
Cl	Cl	Cl	C ₆ H ₁₁	C ₆ H ₁₁	C ₆ H ₁₁	(71)	217-9		
Cl	Cl	Cl	Ph	Ph	Ph		273-5 (71)		IR (9, 183)
Cl	Cl	Cl	$\leftarrow 4\text{-MeC}_6\text{H}_4 \rightarrow$			(71)	307-9		
Cl	Cl	Cl	$\leftarrow 4\text{-MeOC}_6\text{H}_4 \rightarrow$			(71)	233-8		
F	F	F	Me	Me	Me		85 (189)	224 (189)	$\log P = 3165.2/T + 10.8256$; $\Delta H_v = 14500$ (168)
NHMe	NHMe	NHMe	H	H	H	(54)	85-105		
NHMe	NHMe	NHMe	Me	Me	Me	(2)		110/0.1	IR (3); $D/t = 1.016/20$; $n = 1.5082/20$; MR = 61.7
NHEt	NHEt	NHEt	Et	Et	Et	(2)		145-50/0.1	IR (3); $D/t = 0.933/20$; $n = 1.4826/20$; MR = 89.8
NHPr ⁱ	NHPr ⁱ	NHPr ⁱ	Pr ⁱ	Pr ⁱ	Pr ⁱ	(2)		106/0.03	IR (3); $D/t = 0.8220/20$; $n = 1.4628/20$; MR = 118.0
NHBu ⁿ	NHBu ⁿ	NHBu ⁿ	Bu ⁿ	Bu ⁿ	Bu ⁿ	(2)		158/0.005	IR (3); $D/t = 0.900/20$; $n = 1.4730/20$; MR = 144.3
NHBu ^s	NHBu ^s	NHBu ^s	Bu ^s	Bu ^s	Bu ^s	(2)		135/0.01	IR (3); $D/t = 0.892/20$; $n = 1.4695/20$; MR = 144.2
NHBu ^t	NHBu ^t	NHBu ^t	Bu ^t	Bu ^t	Bu ^t	(2)		103/0.04	IR (3); $D/t = 0.883/20$; $n = 1.4631/20$; MR = 144.0
$\leftarrow \text{NHC}_6\text{H}_{11} \rightarrow$			C ₆ H ₁₁	C ₆ H ₁₁	C ₆ H ₁₁	(2)		52-5	
NHPh	NHPh	NHPh	Ph	Ph	Ph	(2)		152-5	IR (3)
$\leftarrow \text{NH}(\text{CH}_2\text{C}_6\text{H}_5) \rightarrow$			Bz	Bz	Bz	(2)		> 250/0.05	IR (3); $D/t = 1.156/20$; $n = 1.642/20$; MR = 208.1
N ₂ HMe ₂	N ₂ HMe ₂	N ₂ HMe ₂	Me	Me	Me	(124)	55-9	134/3	IR
N ₂ HMe ₂	N ₂ HMe ₂	N ₂ HMe ₂	Et	Et	Et	(124)		140/3	IR
NH ₂	NH ₂	NH ₂	H	H	H	(47)			IR
NH ₂	NH ₂	NH ₂	Et	Et	Et	(124)	54	138-40/5	IR
NMe ₂	NMe ₂	NMe ₂	H	H	H	(34)	112-3		IR (48, 50)
NMe ₂	NMe ₂	NMe ₂	Me	Me	Me	(124)	66	122-4/3	
NMe ₂	NMe ₂	NMe ₂	Et	Et	Et	(124)	61	102-4/3	
NMe ₂	NMe ₂	NMe ₂	Pr ⁱ	Pr ⁱ	Pr ⁱ	(152)		128-32/1.6	
NMePh	NMePh	NMePh	H	H	H	(48)	128-32		IR (48, 50)
NEt ₂	NEt ₂	NEt ₂	H	H	H			120/2 (54)	IR (47, 48, 50); $D/t = 0.9160/20$ (47); $n = 1.4728/20$ (47)
NEt ₂	NEt ₂	NEt ₂	Me	Me	Me	(124)		138/5	
NEt ₂	NEt ₂	NEt ₂	Et	Et	Et	(124)		133-5/5	
NEtPh	NEtPh	NEtPh	H	H	H		85-7 (48)		IR (50)
NPr ₂ ⁿ	NPr ₂ ⁿ	NPr ₂ ⁿ	H	H	H		32-5 (47)	170-2 (47)	IR (48, 50)
NPr ₂ ⁱ	NPr ₂ ⁱ	NPr ₂ ⁱ	H	H	H		138-43 (47)		IR (48, 50)
NBu ₂ ⁿ	NBu ₂ ⁿ	NBu ₂ ⁿ	H	H	H	(47)		200/0.05	IR (48, 50); $D/t = 0.8986/20$; $n = 1.4720/20$
NBu ⁿ Ph	NBu ⁿ Ph	NBu ⁿ Ph	H	H	H		79-81 (48)		IR (48, 50)
NBu ₂ ⁱ	NBu ₂ ⁱ	NBu ₂ ⁱ	H	H	H	(47)		167/0.3	IR (48, 50); $n = 1.4690/20$
$\leftarrow \text{N}(\text{C}_6\text{H}_{11})_2 \rightarrow$			H	H	H	(48)		> 300	IR (50)
NPh ₂	NPh ₂	NPh ₂	H	H	H	(47)		> 325	IR (49, 50)
NBz ₂	NBz ₂	NBz ₂	H	H	H	(50)	148-50		IR

←NH·C ₆ H ₁₁ →			Et	Et	Et	(121)		94-6/3	
OH	OH	OH	Ph	Ph	Ph	(82)	130		
OH	OH	OH	←4-MeOC ₆ H ₄ →			(84)	112-120		
OMe	OMe	OMe	H	H	H	(65)	110-111		
OMe	OMe	OMe	Me	Me	Me	(14)		62-5/0.07	IR (3); n = 1.4610/23
OMe	OMe	OMe	Et	Et	Et	(124)		93-6/3	IR
OEt	OEt	OEt	H	H	H	(65)	53-4		
OEt	OEt	OEt	Me	Me	Me	(14)		79.5/80.5/0.10	IR (3); n = 1.4540/22.5
OEt	OEt	OEt	Et	Et	Et	(124)		133-6/3	IR
OPr ^a	OPr ^a	OPr ^a	Me	Me	Me	(14)		101-3/0.015	IR (3); n = 1.4561/22
OPr ⁱ	OPr ⁱ	OPr ⁱ	Me	Me	Me	(14)		85-7/0.10	IR (3); n = 1.4460/23
OBu ^a	OBu ^a	OBu ^a	H	H	H	(47)			IR
OBu ^a	OBu ^a	OBu ^a	Me	Me	Me	(14)		130-4/0.30	IR (3); n = 1.4572/23
OBu ^a	OBu ^a	OBu ^a	Et	Et	Et	(90)		153-6/0.4	IR (3); D/t = 0.9311/20; n = 1.4544/20
OBu ^t	OBu ^t	OBu ^t	Me	Me	Me	(14)	84-7	120-5/0.52	IR (3)
OPh	OPh	OPh	Me	Me	Me	(14)	81-4	185-7/0.07	IR (3)
←Me ₂ SiO→			Me	Me	Me	(153)	22-3	130/0.85	IR
SCN	SCN	SCN	H	H	H	(15)	147-50		
SiPh ₃	SiPh ₃	SiPh ₃	Me	Me	Me		248-51 (153)		IR (25, 153)
SiPh ₃	SiPh ₃	SiPh ₃	Ph	Ph	Ph	(25)	55-8		IR

^a The following abbreviations have been used throughout this table.

m.p. = melting point

b.p. = boiling point

D/t = density in gm/cm³ at temperature t .

p = pressure in mm of mercury.

T = Trouton's constant

ΔH_v = heat of vaporization, calories/mole

ΔH_s = heat of sublimation, calories/mole

MR = molar refraction, ml.

η/t = viscosity, centistokes, at temperature t

χ_m = diamagnetic anisotropy $\times 10^6$, emu

DM = dipole moment (measured in benzene at 25°), debyes

MS = mass spectra

IR = infrared spectra

UV = ultraviolet spectra

NMR = nuclear magnetic resonance

R = Raman spectra

X = X-ray

ED = electron diffraction

Functional derivatives: Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl; Ph, phenyl; Hx, hexyl; Bz, benzyl; Py, pyridyl; n, normal; i, iso; s, secondary; t, tertiary.

^b This type of designation indicates that the same substituent occurs on all the positions.

^c Substituted benzene rings are numbered with respect to their point of attachment to either boron or nitrogen. Thus, 4-BrC₆H₄ indicates that the benzene ring attached to a boron or nitrogen is substituted with bromine in the 4-position.

TABLE III
 BORAZINES NOT CHARACTERIZED BY THEIR PHYSICAL PROPERTIES

B-Substituents			N-Substituents			References
R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	
H	Me	Me	←4-ClC ₆ H ₄ → ^{a, b}			(163)
H	Me	Me	←3,4-(MeO) ₂ C ₆ H ₃ →			(163)
H	Me	Me	←2-C ₁₀ H ₇ →			(163)
H	OH	OH	←2,6-(CH ₃) ₂ C ₆ H ₃ →			(5)
H	H	Me	←4-ClC ₆ H ₄ →			(163)
H	H	Me	←4-MeOC ₆ H ₄ →			(163)
Me	Me	Me	H	Li	Li	(178)
Me	Me	Me	H	H	Li	(178)
Me	Me	Me	Me	Li	Li	(178)
Me	Me	Me	Me	Me	Li	(178)
C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	Et	Et	Et	(130)
C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	C ₆ H ₁₁	C ₆ H ₁₁	C ₆ H ₁₁	(130)
C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	Bz	Bz	Bz	(130)
C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	←4-MeC ₆ H ₄ →			(130)
C ₃ H ₅	C ₃ H ₅	C ₃ H ₅	Et	Et	Et	(56)
C ₃ H ₅	C ₃ H ₅	C ₃ H ₅	C ₆ H ₁₁	C ₆ H ₁₁	C ₆ H ₁₁	(56)
C ₃ H ₅	C ₃ H ₅	C ₃ H ₅	Bz	Bz	Bz	(56)
C ₃ H ₅	C ₃ H ₅	C ₃ H ₅	←4-MeC ₆ H ₄ →			(56)
←4-PhC ₆ H ₄ →			Me	Me	Me	(114)
←4-PhC ₆ H ₄ →			Ph	Ph	Ph	(20)
←1-C ₁₀ H ₇ →			Me	Me	Me	(114)
Br	Br	Br	Me	Me	Me	(36)
Cl	Cl	Cl	Pr ⁱ	Pr ⁱ	Pr ⁱ	(152)
Cl	Cl	Cl	←4-BrC ₆ H ₄ →			(49)
F	F	F	SiH ₃	SiH ₃	SiH ₃	(168)
NHEt	NHEt	NHEt	H	H	H	(91)
NHEt	NEt ₂	NEt ₂	Et	Et	Et	(91)
N ₂ H ₅	N ₂ H ₅	N ₂ H ₅	H	H	H	(120, 123)
NEt ₂	OBu ^t	OBu ^t	H	H	H	(91)
NCS	NCS	NCS	Bu ^t	Bu ^t	Bu ^t	(175)
NO ₂	NO ₂	NO ₂	H	H	H	(15)
←O-CH ₂ CH ₂ Cl→			H	H	H	(123)
OBu ⁿ	NHEt	NHEt	Et	Et	Et	(91)
OBu ^t	OBu ^t	OBu ^t	H	H	H	(91)
ONO	ONO	ONO	H	H	H	(15)

^a This type of designation indicates that the same substituent occurs on all the positions.

^b Substituted benzene rings are numbered with respect to their point of attachment to either boron or nitrogen. Thus, 4-BrC₆H₄ indicates that the benzene ring attached to a boron or nitrogen is substituted with bromine in the 4-position.

TABLE IV
 BOND DISTANCES AND BOND ANGLES IN BORAZINE AND ITS DERIVATIVES

Parameter	Compound	Value	Method ^a	Reference
B—N	H ₆ B ₃ N ₃ Me ₆	1.59 ± 0.027 Å	X	(172)
	H ₃ B ₃ N ₃ H ₃	1.44 ± 0.02 Å	E	(6)
	H ₃ B ₃ N ₃ Me ₃	1.42 ± 0.02 Å	E	(22)
	Cl ₃ B ₃ N ₃ H ₃	1.413 ± 0.010 Å	X	(24)
N—C	H ₆ B ₃ N ₃ Me ₆	1.49 ± 0.040 Å	X	(172)
	H ₃ B ₃ N ₃ Me ₃	1.48 ± 0.03 Å	E	(22)
B—Cl	Cl ₃ B ₃ N ₃ H ₃	1.760 ± 0.015 Å	X	(24)
∠BNB	Cl ₃ B ₃ N ₃ H ₃	121 ± 1°	X	(24)
	H ₆ B ₃ N ₃ Me ₆	113 ± 1°	X	(172)
∠NBN	Cl ₃ B ₃ N ₃ H ₃	119 ± 1°	X	(24)
	H ₆ B ₃ N ₃ Me ₆	114 ± 2°	X	(172)
∠CNC	H ₆ B ₃ N ₃ Me ₆	104 ± 2.5°	X	(172)
∠BNC	H ₆ B ₃ N ₃ Me ₆	109.5 ± 3.5°	X	(172)

^a E, electron diffraction; X, X-ray diffraction.

bond orders for H₃B₃N₃H₃, H₃B₃N₃Me₃, and Cl₃B₃N₃H₃ are 1.48, 1.56, and 1.58, respectively.

Two isomers have been predicted for borazine on the basis of a "general stereochemical law" (134), but this suggestion is not supported by any of the present structural evidence. Apparently, delocalization of the nitrogen *p* electrons was not taken into account in the formulation of this law.

B. DIPOLE MOMENTS

A dipole moment of 0.67 Debye is reported for borazine in the gas phase, but the questionable purity of the sample makes the results tentative (136). A more recent value of 0.50 Debye for the dipole moment of H₃B₃N₃H₃ in benzene solution has been reported together with values in the range 0.18–0.72 Debye for seven borazine derivatives. The existence of these moments was attributed either to deviations from planarity (cf. Section V,A) or to low frequency molecular vibrations which accounted for a large atomic polarization (181). However, apparent dipole moments of several symmetrical benzene derivatives have been found illusionary by measuring the dielectric constant and dielectric loss of solutions of these compounds as a function of frequency in the anomalous dispersion region (32). The existence of appreciable dipole moments for borazine and its derivatives is by no means completely established. It has been suggested on the basis of atomic and orientation polarization data that Cl₄B₄N₄Bu₄' has no dipole moment and is in a boat configuration (175).

C. NUCLEAR RESONANCE SPECTRA

1. Nuclear Magnetic Resonance

a. ^{11}B Resonance. The nuclear magnetic resonance spectrum of borazine and its derivatives is consistent with a cyclic structure. An estimation of the fractional s character in the bonding of BH_3 adducts with amines and ethers has been made from the magnitude of the B—H spin coupling constants by assuming that the boron atoms in borazine and *N*-trimethylborazine are in an sp^2 hybridized state (132). ^{11}B chemical shifts and the B—H spin coupling constants for several borazines are given in Table V.

TABLE V
 ^{11}B CHEMICAL SHIFTS AND B—H SPIN COUPLING CONSTANTS
FOR CYCLIC BORON-NITROGEN SYSTEMS

Compound	Chemical shift (ppm) ^a	$J_{\text{B-H}}$ (cps)	References
$\text{Cl}_4\text{B}_4\text{N}_4\text{Bu}^t_4$	-30.1		(175)
$\text{Br}_4\text{B}_4\text{N}_4\text{Bu}^t_4$	-30.3		(175)
$\text{H}_3\text{B}_3\text{N}_3\text{H}_3$	-30.4	136	(132)
		140	(76)
$\text{Cl}_3\text{B}_3\text{N}_3\text{Me}_3$	-31.3		(102)
	-33.5		(175)
$\text{H}_3\text{B}_3\text{N}_3\text{Me}_3^b$	-32.4	134	(132)
$\text{R}_3\text{B}_3\text{N}_3\text{H}_3$	-34.9 to -36.1		(68)
$\text{Me}_3\text{B}_3\text{N}_3\text{Me}_3$	-36.2		(102)
	-36.5		(42)
$\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$	-36.5		(175)
$\text{Me}_3\text{B}_3\text{N}_3\text{Ph}_3$	-36.5		(42)
$\text{Ph}_3\text{B}_3\text{N}_3\text{Me}_3$	-38.5		(42)

^a Chemical shifts are presented relative to the $\text{BF}_3\text{—Et}_2\text{O}$ adduct.

^b R = alkyl. These data represent nine *B*-trialkylborazines.

^{11}B chemical shifts for $\text{Cl}_3\text{B}_3\text{N}_3\text{Me}_3$ and $\text{Me}_3\text{B}_3\text{N}_3\text{Me}_3$ are unaltered when tetracyanoethylene or I_2 is added to a solution of either of these borazines, although color changes, indicative of complex formation, occur (102).

b. ^1H Resonance. Proton chemical shifts and coupling constants which have been reported are collected in Table VI. The difference in chemical shifts between methyl protons and methylene protons in ethyl-substituted borazines was used to estimate the electronegativity of the boron atom (1.7) and of the nitrogen atom (3.4–3.5) in the borazine ring. The marked deviation from usually accepted values is explained on the basis of partial double bonding in the ring (78, 125a). The B—H and N—H chemical shifts in *B*-trichloroborazine and *N*-trimethylborazine are essentially the same as

TABLE VI
 PROTON CHEMICAL SHIFTS AND SPIN COUPLING CONSTANTS

Type of proton	Compound	Chemical shift, (ppm) ^a	Spin coupling constant (cps)	Reference
B—CH ₃	Me ₃ B ₃ N ₃ Ph ₃	0.00		(78)
	Me ₃ B ₃ N ₃ Me ₃	-0.60		(78)
		-0.62		(42)
B—CH ₂ CH ₃	Me ₃ B ₃ N ₃ Et ₃	-0.67		(78)
	Et ₃ B ₃ N ₃ Ph ₃	-0.55 ^b		(78)
	Et ₃ B ₃ N ₃ Et ₃	-1.08 ^b		(78)
	Et ₃ B ₃ N ₃ Me ₃	-1.15 ^b		(78)
N—CH ₂ —CH ₃ (methyl)	Me ₃ B ₃ N ₃ Et ₃	-1.20	$J_{H-H} = 7.2$	(78)
	Et ₃ B ₃ N ₃ Et ₃	-1.20	$J_{H-H} = 8.1$	(78)
	Cl ₃ B ₃ N ₃ Et ₃	-1.22	$J_{H-H} = 8.0$	(78)
N—CH ₃	Ph ₃ B ₃ N ₃ Me ₃	-2.71		(42)
	Me ₃ B ₃ N ₃ Me ₃	-2.98		(42)
		-3.18		(78)
	Et ₃ B ₃ N ₃ Me ₃	-3.10	$J_{N-H} = 3.0^c$	(78)
	H ₃ B ₃ N ₃ Me ₃	-3.20		(78)
	Cl ₃ B ₃ N ₃ Me ₃	-3.28		(42)
		-3.35		(78)
N—CH ₂ —CH ₃ (methylene)	Me ₃ B ₃ N ₃ Et ₃	-3.58	$J_{H-H} = 7.2$	(78)
	Et ₃ B ₃ N ₃ Et ₃	-3.77	$J_{H-H} = 8.1$	(78)
	Cl ₃ B ₃ N ₃ Et ₃	-3.80	$J_{H-H} = 8.0$	(78)
B—H	H ₃ B ₃ N ₃ Me ₃	-4.65	$J^{11}B-H = 125$	(78)
	H ₃ B ₃ N ₃ H ₃	-4.67	$J^{11}B-H = 138$	(77)
			$J^{10}B-H = 48^c$	(77)
N—H phenyl	Cl ₃ B ₃ N ₃ H ₃	-5.53 ^b		(78)
	H ₃ B ₃ N ₃ H ₃	-5.65	$J_{N-H} = 56$	(77)
	Me ₃ B ₃ N ₃ Ph ₃	-7.35 ^b		(78)
	Et ₃ B ₃ N ₃ Ph ₃	-7.35 ^b		(78)
	Ph ₃ B ₃ N ₃ Me ₃	-7.42 ^b		(42)

^a All shifts reported relative to Si(CH₃)₄.^b Unresolved.^c Estimated.

for borazine. These shifts are apparently insensitive to the substituent effects, reflected in the electronic spectra (Section V,D), and, after correction for the effect of the ring current, correspond to the proton in —C=CH—C—. The latter correlation has been used to support the partial double-bond character of the B—N bonds in borazines (78). Incidentally, the presence of a ring current is the basis for one definition of aromaticity (35).

Alkyl proton shifts in nine *B*-trialkylborazines indicated that no alkyl isomerism had occurred during synthesis (68).

The proton magnetic resonance spectrum of $B_3N_3H_{12}$ could not be recorded (27), but the spectrum of $B_3N_3H_6Me_6$ consists of a quartet (B—H) superimposed on a strong single resonance (N—CH₃) (19). It can be inferred from the reported spacing of the B—H quartet (2 ppm) that the spin coupling constant, $J_{\text{B—H}}$, for this compound is approximately 80 cps, indicating an sp^3 hybridized state for the boron atom (132), which is consistent with the suggestion that this compound is the boron-nitrogen analog of cyclohexane.

2. Nuclear Quadrupole Resonance

An estimate of 68% double-bond character in *N*-trimethylborazine was obtained from the ^{11}B quadrupole coupling constant for this compound (88), while approximately 80% double-bond character was obtained from line-width measurements on *B*-trichloroborazine (88, 156). In contrast, the double-bond contribution to the B—N bond in boron nitride is 45% (156).

The frequency of the ^{35}Cl resonance line for *B*-trichloroborazine is lower than that observed for boron trichloride, and this is taken as evidence for some degree of aromaticity for the borazine ring (156). The ^{35}Cl resonance line in *B*-trichloro-*N*-trimethylborazine or *B*-trichloro-*N*-triphenylborazine (116) was not observed.

D. ELECTRONIC SPECTRA

The ultraviolet absorption bands for borazine and for substituted borazines are summarized in Tables VII and VIII, respectively. Several *B*-trialkylborazines show only a weak end absorption (68), and this observa-

TABLE VII
ULTRAVIOLET ABSORPTION BANDS AND THEIR ASSIGNMENTS FOR BORAZINE

Bands observed		Reference	Assignment	Corresponding benzene transition	Calculated band energy (ev)		
(Å)	(ev)				(140)	(126)	(30)
			$^1A'_1 \rightarrow ^3A'_1$	$^1A_{1g} \rightarrow ^3B_{1u}$	5.9		
			$^1A'_1 \rightarrow ^3E'$	$^1A_{1g} \rightarrow ^3E_u^-$	6.4		
1995	6.2	(79, 133)	$^1A'_1 \rightarrow ^1A'_2$	$^1A_{1g} \rightarrow ^1B_{2u}$	6.5	6.50	5.7
1962	6.3						
1928	6.4						
1895	6.5						
			$^1A'_1 \rightarrow ^3A'_2$	$^1A_{1g} \rightarrow ^3B_{2u}$	6.9		
1852 ^a	6.7	(137)	$^1A'_1 \rightarrow ^1A'_1$	$^1A_{1g} \rightarrow ^1B_{1u}$	7.2	6.80	6.1
1710 ^b	7.2	(137)	$^1A'_1 \rightarrow ^1E'$	$^1A_{1g} \rightarrow ^1E_u^-$	7.7	7.98	8.8

^a Estimated.

^b Gas phase.

tion is in agreement with the data given in Table VIII. The borazine bands at 6.2–6.5 electron volts are assigned to the ${}^1A'_2$ transitions (79) instead of to the ${}^1A'_1$ transitions (133) on the basis of the assumption that the latter are hidden by the intense ${}^1E'$ band; no bands were found at wavelengths greater than 2000 Å.

TABLE VIII
THE ULTRAVIOLET ABSORPTION SPECTRA OF SOME BORAZINES (137)

Compound	Band		Extinction coefficient	Assignment
	(Å)	(ev)		
$\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$	1901	6.5	$\sim 2000^b$	${}^1A'_1 \rightarrow {}^1A'_2$
	1852 ^a	6.7 ^a	—	${}^1A'_1 \rightarrow {}^1A'_1$
	1783	7.0	8000	${}^1A'_1 \rightarrow {}^1E'$
$\text{Me}_3\text{B}_3\text{N}_3\text{H}_3$	1908	6.5	$\sim 2000^b$	${}^1A'_1 \rightarrow {}^1A'_2$
	1852 ^a	6.7 ^a	—	${}^1A'_1 \rightarrow {}^1A'_1$
	1761	7.1	6000	${}^1A'_1 \rightarrow {}^1E'$
$\text{H}_3\text{B}_3\text{N}_3\text{Me}_3$	2278	5.4	1200	${}^1A'_1 \rightarrow {}^1A'_2$
	2242	5.5		
	2198	5.6		
	2174 ^a	5.7 ^a	—	${}^1A'_1 \rightarrow {}^1A'_1$
	1942	6.4	28000	${}^1A'_1 \rightarrow {}^1E'$
	1901	6.5		
	1859	6.7		

^a Estimated.

^b Diffuse.

Of the three molecular orbital treatments concerned with the structure of borazine which have appeared, two are semi-empirical (126, 140), and the other is a self-consistent calculation which includes the donation of p electrons from the nitrogen atom to the boron atom (30). Parameters included in the latter treatment are used to explain the bathochromic shift observed with N -trisubstituted borazines (137); a B—N bond order of 0.663 and a B—N bond distance of 1.42 Å have been calculated from this model (cf. Section V,A). The spectral energies calculated from all treatments are summarized in Table VII.

The salient feature of the spectra of the substituted borazines is the bathochromic shift observed for N -trimethylborazine. Oscillator strengths have been calculated for several of the transitions, and it has been suggested that the frequency spread between the ${}^1A'_2$ and ${}^1E'$ transitions reflects the amount of double-bond character in borazine derivatives. The relative chemical effects of substituents that exert an *ortho-para* directing influence in benzene have been related to the effects of these substituents on the electronic spectra of borazines (137).

A comparison of the absorption bands due to the benzene ring in the spectra of *N*-triphenylborazine and *B*-triphenylborazine with those in aniline, toluene, and several substituted biphenyls indicates that there is significant conjugative interaction between the borazine ring and the phenyl substituents together with some delocalization of the "nitrogen π " electrons (10). The absence of conjugation in $\text{Me}_3\text{B}_3\text{N}_3\text{Ph}_3$ and $\text{Ph}_3\text{B}_3\text{N}_3\text{Me}_3$ is attributed to the loss of planarity due to steric hindrance. The spectra of two phenyl-substituted borazines are similar to the spectrum of 1,3,5-triphenylbenzene (125).

A stable π complex was predicted between 1,3,5-trinitrobenzene and $\text{Me}_3\text{B}_3\text{N}_3\text{Me}_3$ (154), and, although no report concerning this particular complex has appeared, complexes between hexamethylborazine and tetracyanoethylene (TCNE) and between hexamethylborazine and chloranil have been characterized by charge transfer bands appearing in the ultraviolet region of the spectrum (21). As expected, the stability constant of the hexamethylborazine-TCNE complex (0.7 ± 0.3 liter-mole⁻¹) is lower than that of the corresponding hexamethylbenzene-TCNE complex measured under equivalent conditions; values of 263 (104) and 27.6 ± 0.5 have been reported for the stability constant of the latter complex. Ionization potentials for hexamethylborazine estimated from the wavelengths of the charge transfer bands are 8.5 eV from the $\text{Me}_3\text{B}_3\text{N}_3\text{Me}_3$ -TCNE complex and 8.7 eV from the $\text{Me}_3\text{B}_3\text{N}_3\text{Me}_3$ -chloranil complex; the calculated ionization potential for hexamethylbenzene is 8.15 eV (42a, 43).

A preliminary report has appeared concerning fluorescence studies on aryl-substituted borazines; gamma rays and neutrons were used as the exciting radiation (114).

E. INFRARED AND RAMAN SPECTRA

Electron diffraction studies (cf. Section V,A) have established that borazine belongs to symmetry point group D_{3h} . A nonlinear, 12-atom molecule has 30 normal modes of vibration, but, in this case, symmetry considerations show that 20 of these modes constitute 10 doubly degenerate pairs. The distribution of the 20 fundamental frequencies expected is shown in Table IX.

The infrared and Raman spectra of borazine have been recorded and the fundamental frequencies assigned (26), but the assignment was hampered by the absence of a number of the E' fundamentals in the Raman spectrum. In 1950 a more complete gas phase infrared spectrum of borazine in the 500–7000 cm⁻¹ region was reported (135), and the fundamentals and overtones were assigned. A more recent study (184) of the gas phase infrared spectrum of *N*-trideuteroborazine indicates that the assignments of the out-of-plane B—H and N—H bending frequencies (A''_2) should be revised.

A normal coordinate treatment on borazine was carried out assuming a simple valence force potential (26); the application of a Urey-Bradley force field gave unsatisfactory results. This treatment is one of the first published examples of Wilson's method for the approximate separation of low and high frequency vibrations in factoring secular equations (192). Deviations of the calculated A''_2 frequencies from experimentally obtained frequencies were ascribed to interactions between bonds in the meta position, and, although recalculation of these frequencies on this basis

TABLE IX
FUNDAMENTAL FREQUENCY DISTRIBUTION OF BORAZINE

Symmetry of species	Type ^a	Number of frequencies
$A'_1{}^b$	IR inactive Raman active (P)	4
$A''_1{}^b$		0
$A'_2{}^b$	IR inactive Raman inactive	3
$A''_2{}^b$	IR active Raman inactive	3
E'^c	IR active Raman active (D)	7
E''^c	IR inactive Raman active (D)	3

^a Planar vibrations are denoted by a single prime, nonplanar vibrations by a double prime. (P) and (D) represent Raman polarized and Raman depolarized, respectively.

^b Nondegenerate.

^c Degenerate.

(162, 183) improved the agreement, the difficulty seems to have been an incorrect assignment (184). The distribution of potential energy among normal coordinates for borazine has also been calculated (183), but these calculations were made prior to the reassignment of the A''_2 frequencies. The stronger lines in the spectrum of *B*-trichloroborazine have been assigned on the basis of a calculation of the distribution of potential energy among normal coordinates (183) and by a comparison with the infrared spectrum of *B*-trichloro-*N*-trideuteroborazine (184). A normal coordinate treatment of *N*-trimethylborazine assuming D_{3h} symmetry and that methyl groups are point masses (11) was attempted using infrared spectra which appear in the literature (135). The Raman spectra in the literature for this compound are in agreement (11, 182), but the infrared spectra are inconsistent (135, 182). The force constants that have been estimated for various vibrations in borazine and in *N*-trimethylborazine are summarized in Table X. It should be noted that the force constant for the

TABLE X
 FORCE CONSTANTS FOR BORAZINE AND *N*-TRIMETHYLBORAZINE

Vibration	Borazine, 10 ⁵ dyne/cm	Reference	<i>N</i> -Trimethylborazine, 10 ⁵ dyne/cm	Reference
B—N stretch	6.300	(26)	6.4005	(11)
B—H stretch	3.423	(26)	3.3756	(11)
N—X stretch	6.524	(26)	3.1072	(11)
Planar ring distortion	0.525	(26)	0.640	(11)
Planar B—H bend	0.35	(26)		
Planar N—H bend	0.65	(26)		
Nonplanar B—H bend	0.28	(184)	0.383	(11)
Nonplanar N—H bend	0.245	(184)	0.472	(11)
B—N torsion	0.098	(184)	0.006	(11)

 TABLE XI
 B—N STRETCHING FREQUENCIES OF BORAZINE DERIVATIVES^a

Derivative ^b	Frequency range, (cm ⁻¹)	Number of compounds studied	References
(NR ₂) ₃ B ₃ N ₃ X ₃ (R = H, alkyl, aryl)	1285–1517	22	(3, 46, 47, 48, 50)
R ₃ B ₃ N ₃ X ₃ (R = aryl)	1368–1479	5	(9, 20, 46, 117, 183)
Me ₃ B ₃ N ₃ X ₃	1376–1477	7	(9, 46, 53, 178, 183)
R ₃ B ₃ N ₃ X ₃ (R = alkyl)	1382–1475	18	(20, 46, 68, 144, 153, 183)
H ₃ B ₃ N ₃ X ₃	1401–1465	4	(9, 26, 135, 178, 182, 183, 184)
(RO) ₃ B ₃ N ₃ X ₃ (R = alkyl, aryl, SiMe ₃)	1407–1450	11	(3, 14, 153, 183)
Cl ₃ B ₃ N ₃ X ₃	1378–1445	9	(9, 14, 46, 178, 183, 184)
X ₃ B ₃ N ₃ H ₃	1441–1517	25	(9, 26, 46, 48, 50, 53, 93, 124, 135, 173, 178, 184)
X ₃ B ₃ N ₃ Me ₃	1370–1513	21	(3, 9, 14, 20, 46, 117, 124, 144, 153, 178)
X ₃ B ₃ N ₃ R ₃ (R = alkyl)	1414–1497	12	(3, 46, 124, 183)
X ₃ B ₃ N ₃ D ₃	1410–1436	2	(184)
X ₃ B ₃ N ₃ R ₃ (R = aryl)	1285–1404	12	(9, 46, 183)
Polyborazines	1410–1470	15	(46, 59, 93, 96, 101, 179)

^a The strong band in the spectrum of Cl₃B₃N₃Me₃ at 1458 cm⁻¹ has been assigned to the B—N stretching mode (14), but it is more likely that this mode should be assigned to the band at 1395 cm⁻¹.

^b X represents any substituent.

B—N stretching frequency in the borazine ring is less than that of a B—N single bond (52), and, using this type of data, the B—N bond in borazine has been estimated to have 25–28% double-bond character (53, 162).

Partial and complete infrared spectra have been reported for approximately 85 borazine derivatives, and the characteristic frequencies are summarized in Tables XI and XII. The bands reported for *B*-tri-*n*-butoxyborazine (179) are not included in these tables since this compound was not isolated and characterized, but was identified by its spectrum.

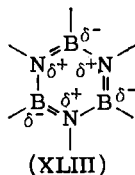
TABLE XII
RING SUBSTITUENT STRETCHING FREQUENCIES IN BORAZINES

Vibration	Frequency range, (cm ⁻¹)	Number of compounds studied	References
N—H stretch X ₃ B ₃ N ₃ H ₃	3390–3509	23	(26, 47, 48, 59, 68, 93, 135, 173, 178, 183, 184)
N—H stretch (NHR) ₃ B ₃ N ₃ X ₃	3425–3448	8	(3)
N—D stretch	2570–2632	3	(28, 184)
B—H stretch	2475–2556	8	(5, 9, 26, 93, 135, 178, 182, 184)
B—D stretch	1887	2	(28)
B—O stretch	1280–1330	10	(3, 14, 46, 124)
B—Cl stretch ^b	833–987 ^a	6	(14, 46, 178, 183, 184)
B—Me stretch	858–891	10	(178, 183)

^a An associated band appears at 1032–1155 cm⁻¹ (14).

^b The assignment for this vibration has been recently disputed.

A strong band, usually with a shoulder on the high-frequency side, occurs near 1400 cm⁻¹ in the infrared spectra of most borazines and is assigned to the B—N stretching mode (183); Gordy's rule (122) indicates that this frequency should occur at 1471 cm⁻¹. The fact that this band is generally the strongest in the spectrum indicates considerable polarity in the B—N bond (135), suggesting that (XLIII) is an important canonical structure. Assignment of the 1400 cm⁻¹ band is complicated in the



N-trimethylborazines because the *N*-methyl deformation frequencies occur in the same region (3). The absence of this band has been used to establish

that *B*-tri(terphenyl)-*N*-trimethylborazine is not planar (20). However, other spectra reported in this reference (20) are not in agreement with those recorded by other workers (117, 144); physical properties are not given for the polyphenyl borazines studied. The B—N stretching frequency is also absent from one of the —B—O—B—linked polymers reported (179), although it is present in similar compounds.

Attempts have been made to relate the B—N frequency to the identity of ring substituents (see, e.g., references 9, 46, 48, 153) but an examination of Table XI shows only that the B—N stretching frequency is more sensitive to nitrogen substitution than to boron substitution. This conclusion is in agreement with the data from electronic spectra (cf. Section V,D).

The intensity of the N—H band in borazine (135) and in *B*-trichloroborazine (48) indicates a polar bond in these compounds; however, the intensity of this band is much lower for *B*-tris(dialkylamino)borazines (48). Several reports of the preparation of *B*-triaminoborazine have appeared (47, 54, 101, 120, 123), but there is some disagreement concerning its properties. The positions of the N—H bands reported for this compound are not in agreement (47, 124). The appearance of a band at 3045 cm^{-1} in *B*-trihydrazinoborazines has been used to support the structural assignment of these compounds (124). On the basis of the electron-donating ability of the amino group, the N—H frequencies of *B*-triaminoborazines decrease in the order *B*-tris(dialkylamino)- > *B*-tri(alkylarylamino)- > *B*-tris(diaryl-amino)-borazine (48).

The intensity of the B—H stretching band is much greater in borazine than in *N*-trimethylborazine, the intensity of this band for the former compound being about equal to that for AlBH_4 (135).

The band assigned to the B—O stretching mode occurs at a lower frequency than the corresponding band for compounds of the type B(OR)_3 , and this has been attributed to a decrease in B—O double-bond character due to double bonding in the ring (3, 46). A band in the 1100 cm^{-1} region has been assigned to the B—Cl stretching mode since it disappears on substitution of another group for the chlorine atom (46). This assignment is complicated in *B*-trichloro-*N*-trimethylborazine since a strong band due to an *N*-methyl rocking vibration is expected in the same region (183).

Arguments leading to a tentative assignment of strong bands at $920\text{--}1238\text{ cm}^{-1}$ in the spectra of *B*-triaminoborazines to the N—H in-plane deformation mode are based on the incorrect assignment of D_{6h} symmetry to borazine (48). Several investigators have observed bands (usually doublets) in the 700 cm^{-1} region (3, 48), and these are considered to be characteristic of substituted borazines in which substituents on the ring can conjugate with the borazine ring.

Extensive assignments of frequencies due to the C—H stretching and

deformation modes in *B*-triaminoborazines have been made (50) but are not included in this review.

F. DIAMAGNETIC ANISOTROPY

An attempt was made, using a self-consistent molecular-orbital approach, to calculate the diamagnetic anisotropy of borazine, but the validity of this approach could not be ascertained because of a lack of precise experimental data (31). The same method gave satisfactory results for benzene. An estimate of molecular parameters for borazine has been made from its diamagnetic anisotropy, with the conclusion that the B—N bonds in borazine have 24% double-bond character (180). Measured diamagnetic anisotropies for borazines and several benzenoid systems (for comparison) are listed in Table XIII.

TABLE XIII
DIAMAGNETIC ANISOTROPIES

Compound	Value $\times 10^6$ emu/mole	Reference
$\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$	-18	(96)
$\text{H}_3\text{B}_3\text{N}_3\text{H}_3$	-36	(180)
$\text{Me}_3\text{B}_3\text{N}_3\text{Me}_3$	-37	(180)
$\text{Et}_3\text{B}_3\text{N}_3\text{Et}_3$	-40	(180)
sym- $\text{C}_6\text{H}_3\text{Br}_3$	-47	(96)
C_6H_6	-59.7	(73)

The mean diamagnetic susceptibilities of seven borazine derivatives were measured and diamagnetic anisotropies for three of them calculated using a value for χ_{11} estimated from that of benzene. The validity of this procedure is supported by a calculation of the value of χ_{11} for borazine using Pascal's rule (180), although the use of Pascal constants for this purpose has been criticized (31). The diamagnetic anisotropy for *B*-trichloroborazine was calculated using crystal susceptibilities and Pascal constants, and it is suggested that the diamagnetic anisotropy is a measure of aromatic character (96).

G. THERMOCHEMICAL DATA

References to values reported for the heats of vaporization and sublimation for various borazines obtained from vapor pressure measurements are given in Table II.

The entropy, free energy function, and heat capacity for borazine have been calculated from infrared spectroscopic data (26) which were later revised (Section V,E), and equations for the entropy (26) and heat capacity (161) have been derived. The heats of formation of gaseous and liquid

borazine have been calculated from the heat of combustion (83). Earlier values for the B—N bond strength in *B*-trichloroborazine (45, 157, 176) have been revised (23), and a value of 106.5 kcal is now accepted.

H. MASS SPECTROSCOPY

The mass spectra of borazine, *B*-trichloroborazine, *B*-trimethylborazine (97), and of three deuterated borazines (28) have been reported. Data for borazine itself suggests that the B—H bond in this compound is more easily cleaved than the C—H bond in benzene.

Products from the pyrolysis of borazine have been investigated using mass spectrometric techniques (93, 101), and these data indicate that ring cleavage occurs with borazine to a greater extent than with benzene (4).

VI. Conclusion

The results of various types of physical-chemical investigations indicate that there is partial delocalization of the three pairs of electrons originally associated with the nitrogen atoms in the borazine ring, although the delocalization is not as extensive as in benzene and its derivatives. This conclusion is in general agreement with the chemical properties of the borazine ring.

ACKNOWLEDGMENT

The authors gratefully acknowledge the support of a fellowship from The University of Texas (E.K.M.) and a grant from the Robert A. Welch Foundation (J.J.L.).

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DECABORANE-14 AND ITS DERIVATIVES

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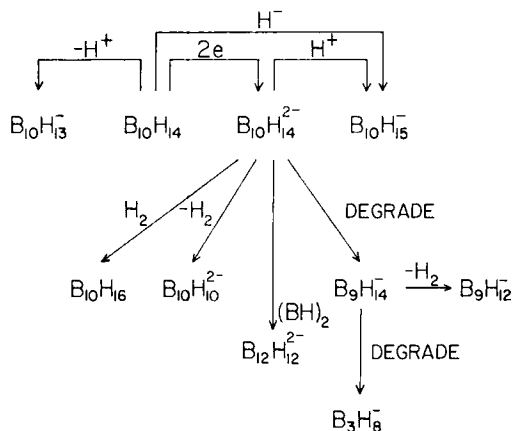
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I. Introduction

Among the many boron hydrides characterized by Alfred Stock and his co-workers (76) was a remarkably versatile material, $B_{10}H_{14}$. Decaborane-14 may be prepared by the pyrolysis of diborane and today this material is commercially available to the chemical investigator. This availability is a relatively new condition since decaborane-14 was virtually unavailable prior to 1950. During the last decade the boron hydrides, as a class, have been extensively investigated as candidate reaction motor fuels. This impetus has extended the frontiers of boron hydride chemistry to such an extent that boron hydride chemistry might someday become a truly major area of chemical technology. It seems unlikely, however, that boron hydride chemistry will ever challenge the chemistry of carbon hydrides in popularity or general usefulness. In any event it is likely that decaborane-14 will play a prominent role in the future as an easily handled starting material for synthetic, structural, and mechanistic studies.

The present article will be devoted to the discussion of decaborane-14 and compounds which may be obtained from this hydride by relatively simple reactions. Any discussion of decaborane-14 chemistry would be incomplete if the newly discovered and characterized (21, 22) decaborane-16 were not included. Figure 1 represents the interrelationships of the various derivatives of decaborane. This outline will be followed as closely as possible in the present discussion. It is seen that this organizational outline is formally based upon proton, hydride ion and electron transfer reactions. Particular compounds, where possible, will be treated as derivatives of the parent hydrides shown in Fig. 1.

The reader is referred to an excellent review by Lipscomb (43) for a discussion of the principles which support current ideas regarding the

FIG. 1. Interrelationship of $\text{B}_{10}\text{H}_{14}$ derivatives.

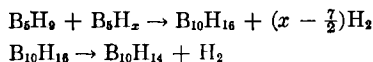
bonding and structure of the boron hydrides. Indeed, the topological method of Lipscomb and co-workers and their treatment of electron-deficient bonding have made boron-hydride chemistry truly comprehensible for the first time. Jumbled facts have fallen into place and accurate chemical predictions based on these principles are now well known to the chemical public.

II. The Preparation and Structure of Decaborane-14

A. PREPARATION OF $\text{B}_{10}\text{H}_{14}$

The preparation of decaborane-14 is based upon the pyrolysis of diborane-6 at temperatures near 100° (76). Under these conditions the crystalline $\text{B}_{10}\text{H}_{14}$ (m.p. 100°) is accompanied by varying amounts of the lower hydrides (B_4H_{10} , B_5H_9 , B_5H_{11} , B_6H_{10} , etc.) and chalky $(\text{BH})_x$ polymer of uncertain structure. The hydride products are easily separated from one another by distillation and sublimation or recrystallization from hydrocarbon solvents. The fact that $\text{B}_{10}\text{H}_{14}$ is commercially available attests to the efficiency of existing preparative methods.

The mechanism of the pyrolysis reaction which leads to the formation of $\text{B}_{10}\text{H}_{14}$ is presently unclear. A recent review (43) indicates the complexity of the over-all reaction sequence which appears to involve the formation of key B_5 intermediates by combination of smaller fragments. It has been suggested (21) that $\text{B}_{10}\text{H}_{14}$ results from the thermal degradation of the newly discovered $\text{B}_{10}\text{H}_{16}$. The over-all sequence might then be the following in which an unidentified B_5 hydride, B_5H_x , reacts with B_5H_9 to form $\text{B}_{10}\text{H}_{16}$.



The chemistry of $B_{10}H_{16}$ and its observed rearrangement to $B_{10}H_{14}$ and $B_{10}H_{14}$ derivatives (21) will be discussed below. That two B_5H_9 molecules do not combine to form $B_{10}H_{16}$ and one mole of hydrogen is shown by the work of Hillman *et al.* (34) who observed that the reaction of isotopically normal B_5H_9 with $B_2^{10}H_6$ produced decaborane-14 which contained five B^{10} labeled atoms per molecule. Thus, for the above scheme to be correct, B_5H_x must arise from the pyrolysis of diborane-6 alone.

B. STRUCTURE OF $B_{10}H_{14}$

The structure of $B_{10}H_{14}$ was first elucidated from the single crystal X-ray diffraction studies of Kasper *et al.* (38). Later, least squares refinement of the original data by Moore *et al.* (52) has produced the structure and B—B distances to a high degree of certainty. The geometrical arrangement of boron atoms in the $B_{10}H_{14}$ molecule is that of an icosahedron with two nearest neighbor atoms removed. Figure 2 presents the structure of deca-

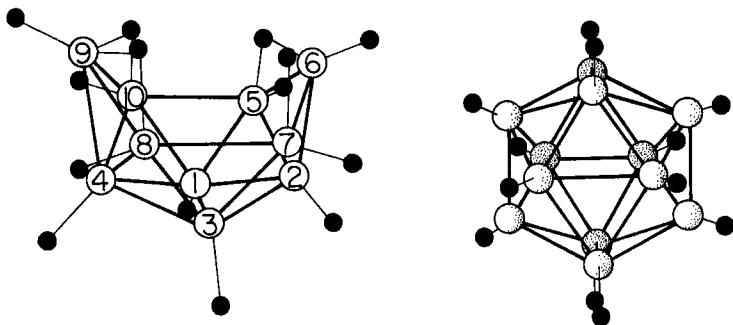


FIG. 2. $B_{10}H_{14}$ and the icosahedral $B_{12}H_{12}^{2-}$ ion.

borane-14 and the icosahedron from which it is formally derived. The numbering system commonly employed throughout $B_{10}H_{14}$ chemistry is shown in Fig. 2. Accurate B—H distances are not available but the observed B—H distances average about 1.30 Å. That the B—H—B bridge is unsymmetrical with respect to the hydrogen position is seen in the refined data (52). The B_6 —H bridge distance varies from 1.43 to 1.50 Å while the B_5 —H bridge distance varies from 1.25 to 1.39 Å.

C. BONDING IN $B_{10}H_{14}$

Decaborane-14, in common with all other boron hydrides, is "electron-deficient." Each boron atom contributes four atomic orbitals, $2s$, $2p_x$, $2p_y$, and $2p_z$ which might be hybridized sp , sp^2 , and sp^3 . Each boron atom contributes three valence electrons which may be used for bonding to hydrogen or other boron atoms. The fourteen hydrogen atoms each con-

tribute a $1s$ orbital and one electron. Thus a total of 54 atomic orbitals and 22 electron pairs are available for bonding in $B_{10}H_{14}$. Assuming that each of the four bridge hydrogen atoms utilizes one orbital from each of its neighbor boron atoms as well as its own $1s$ orbital a total of 18 of the 40 boron orbitals available are employed in bonding to hydrogen. The four 3-center hydrogen bridge bonds consume a total of four electron pairs and the ten B—H two-center bonds consume a total of ten electron pairs. Arithmetic thus shows that 22 boron atomic orbitals remain to hold the eight remaining electron pairs which furnish bonding in all existing boron-boron interactions. These eight electron pairs may be fully utilized only if they occupy six B—B—B 3-center orbitals (one pair each) and two 2-center orbitals. Thus the bonding in decaborane-14 may be described as ten B—H 2-center bonds, four B—H—B 3-center bonds, two B—B 2-center bonds and six B—B—B 3-center bonds. Arguments similar to those presented above have been employed by Eberhardt *et al.* (12) to establish a set of topological rules which rationalize the bonding arrangements in the boron hydrides and their derivatives. These topological rules will be referred to throughout this article and the reader is referred to a recent review (43) for a critical examination of their basis. Using the topological language of Dickerson and Lipscomb (6), the known decaborane-14 is described as 4620 (s, t, y, x).

The parameters s , t , y , and x have been previously defined (12) to describe the number and types of bonds in possibly existent boron hydrides and their derivatives. Thus, s refers to the number of B—H—B bridge arrays, t is the number of B—B—B 3-center bonds ("open" or "closed" types), y is the number of B—B 2-center bonds and x is the number of $-BH_2$ groups present in a given molecule. These four parameters are interrelated by the three equations: $s + x = q$, $s + t = p$, and $p = t + y + q/2$. Code symbols are given in the order s , t , y , and x .

Other, as yet unknown, decaborane-14 molecules may be envisaged (43) (3711 and 2802).

The valence bond structure for decaborane preferred by Lipscomb (43), on the basis of molecular geometry and interrelationships with other boron hydrides, is that shown in Fig. 3. In this model boron atoms 2 and 4 are trigonally hybridized sp^2 and all other boron atoms are tetrahedrally hybridized sp^3 . The two B—B 2-center bonds required in the $B_{10}H_{14}$ topology are between boron atoms 2—6 and 4—9. The $2p_z$ orbital of boron atoms 2 and 4 overlap with sp^3 orbitals from boron atoms 5 and 7 and 8 and 10, respectively.

The localized valence-bond structure of $B_{10}H_{14}$ shown in Fig. 3 is, in common with all such representations, an overly simplified description since some delocalization of the framework electrons probably exists. Therefore, Moore *et al.* (53) have undertaken a molecular orbital approach to the $B_{10}H_{14}$ molecule in order to more accurately predict the charge densities

present in this molecule. Localized bonds predict (12) charges of $-\frac{2}{3}e$ on boron atoms 2 and 4, zero charge on boron atoms 1, 3, 6 and 9 and $+\frac{1}{3}e$ on boron atoms 5, 7, 8, and 10. These charge densities predict a dipole moment of 6.6 Debyes for decaborane-14. The molecular orbital approach, in which a $-0.2e$ charge is assigned to each bridge hydrogen atom, yields the following results (53): $-0.254e$ on boron atoms 2 and 4, $+0.046e$ on boron atoms 1 and 3, $+0.069e$ on boron atoms 5, 7, 8, and 10, and $+0.468e$ on boron atoms 6 and 9. Without correction for the $-0.2e$ charge present on

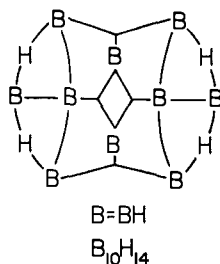


FIG. 3. Topological drawing of $B_{10}H_{14}$.

each bridge hydrogen atom, a dipole moment of 3.6 Debyes was calculated (53). This is in agreement with the observed dipole moment of 3.52 Debyes (42). It is seen from these results that the localized valence bond structure for $B_{10}H_{14}$ qualitatively fits the known facts although the molecular orbital treatment gives much closer agreement. It might be concluded that in molecules of low symmetry, such as $B_{10}H_{14}$, the localized bond picture is adequate for purposes of chemical discussion. About the same degree of success could be expected in boron hydride molecules as is obtained in organic molecules when using this simplified approach.

D. NUCLEAR MAGNETIC RESONANCE ASSIGNMENTS FOR $B_{10}H_{14}$

Perhaps the most economical structural tool available to the boron hydride chemist is the nuclear magnetic resonance spectrometer. B^{11} probes are available (ca. 12.8 Mc at 10,000 gauss) and yield the most useful spectra. During the last decade a considerable number of workers have employed H^1 and B^{11} spectra in the solution of structural problems. Decaborane-14 and its derivatives have been examined in detail and these spectra will be referred to throughout this review.

Figure 4 presents the H^1 NMR spectrum of $B_{10}H_{14}$ obtained at 40 Mc and Fig. 5 is the B^{11} NMR spectrum of isotopically normal $B_{10}H_{14}$ obtained at 12.8 Mc. Figure 4 also presents the H^1 NMR spectrum of bridge deuterated decaborane in which only the terminal protons are observed. The resonance peaks labeled (a) are due to protons at the 2 and 4 positions and

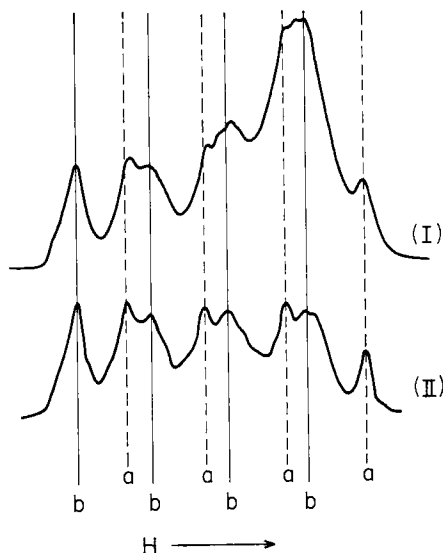


FIG. 4. (I) H^1 nuclear magnetic resonance spectra of $B_{10}H_{14}$; and (II, bridge deuterated) $B_{10}H_{10}D_4$; a = apical sites, b = all other terminal sites. High peak in (I) is due to bridge protons.

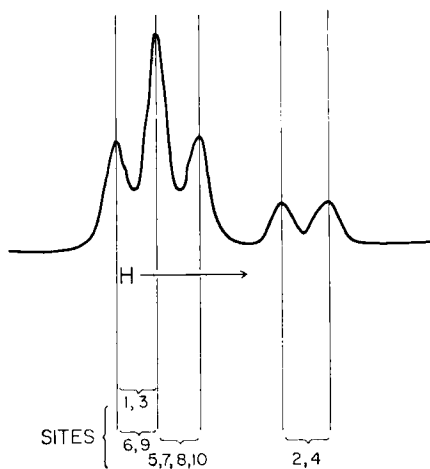


FIG. 5. B^{11} nuclear magnetic resonance spectrum of $B_{10}H_{14}$.

the resonances labeled (b) are comprised of all other terminal proton resonances. These assignments were made by Schaeffer *et al.* (73) on the basis of double resonance experiments with B^{11} excited. Due to the coincidental overlap of terminal protons in the H^1 spectrum many workers have found the B^{11} spectrum more informative.

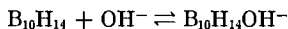
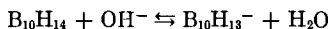
The B^{11} resonances presented in Fig. 5 are assigned as shown on the basis of the B^{11} spectrum of $B_{10}D_{14}$ first reported by Williams and Shapiro (83). The unusual feature found in the B^{11} spectrum is the coincidental near-identity of the resonances due to the 1,3 and the 6,9 boron atoms.

Phillips *et al.* (57) have shown that B^{11} NMR resonances are quite sensitive to the chemical environment of boron. They report chemical shifts for B^{11} over a range of 130 ppm. In comparison, fluorine chemical shifts extend over 300 ppm while hydrogen is observed over a 20 ppm range.

III. Proton Abstraction from Decaborane-14

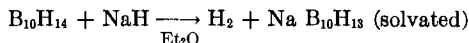
A. TITRIMETRIC EVIDENCE FOR $B_{10}H_{13}^-$

The acidic character of $B_{10}H_{14}$ was first recognized by Stock who observed that $B_{10}H_{14}$ dissolved in aqueous caustic. Much later, Guter and Schaeffer (23) successfully titrated $B_{10}H_{14}$ potentiometrically as a strong mono-protic acid in 75% ethanol-water. Decaborane-14 was recovered by acidification of the basic solution. Other solvent media have subsequently been employed in the titration of $B_{10}H_{14}$ (2, 20, 29) and amines have been employed as bases (29). A single report of the titration of $B_{10}H_{14}$ as a dibasic acid (2) was later shown to be in error (20). These results strongly suggested that the yellow (λ_{\max} 267 and 335 m μ ; ϵ , 2.5 and 1.7×10^3 , respectively) salt produced upon the neutralization of decaborane was the $B_{10}H_{13}^-$ ion and not the $B_{10}H_{14}OH^-$ ion.

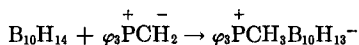


B. THE PREPARATION OF $B_{10}H_{13}^-$ SALTS

The reaction of $B_{10}H_{14}$ and sodium hydride in diethyl ether proceeded to form an ether soluble, yellow salt (36, 51) in accord with the following equation.



Attempts to isolate a crystalline sodium salt were unsuccessful due to formation of strong $B_{10}H_{13}^-$ -ether complexes. The first reported crystalline salt of the $B_{10}H_{13}^-$ ion was obtained by the reaction of triphenylmethylenephosphorane with decaborane in diethyl ether (25). The



product was characterized and found to display the ultraviolet absorption spectrum of the yellow salt produced by titration of decaborane with other

bases. Later work characterized the diethylammonium and the tetramethylammonium salts of the $B_{10}H_{13}^-$ ion (29). The former salt was obtained from the reaction of diethylamine with $B_{10}H_{14}$.

C. THE IDENTITY OF THE ACIDIC HYDROGEN ATOM

The demonstration that a proton could be readily removed from decaborane at once raised the question as to the identity of the acidic hydrogen atom. This problem was considered to be solved when infrared (28, 51) and nuclear magnetic resonance spectral studies (74) proved that the bridge hydrogen atoms of $B_{10}H_{14}$ were rapidly exchanged for deuterium atoms when $B_{10}H_{14}$ was equilibrated with D_2O -dioxane. Thus, $B_{10}H_{10}D_4$ (bridge $-d_4$) was made available. Later work (9) established that the same exchange reactions could be accomplished under more easily controlled conditions and with higher recovery by employing anhydrous DCl in dioxane solution as the deuterium source.

As a by-product of these base-catalyzed deuterium exchange studies it was established (28, 51, 74) that bridge deuterons would slowly equilibrate with the 5, 6, 7, 8, 9, and 10 protons of the $B_{10}H_{14}$ molecule in the presence of a basic solvent. Thus, it is a relatively simple process to prepare 5, 6, 7, 8, 9, 10 and bridge $-d_{10}$ decaborane by continued exchange with D_2O -dioxane (51, 74) or DCl-dioxane (9). The mechanism of the bridge hydrogen migration reaction is presently unknown but a mechanism has been proposed (74).

D. STRUCTURE OF THE $B_{10}H_{13}^-$ ION

The structure of the $B_{10}H_{13}^-$ ion has not been established experimentally. No single crystal X-ray diffraction studies or definitive nuclear magnetic resonance data have been reported.

Lipscomb (43) has proposed two possible structures which are related by hydrogen tautomerism. These two structures are represented topologically in Fig. 6. It is assumed that the $B_{10}H_{13}^-$ ion has the approximate geometry of $B_{10}H_{14}$. The tautomer which contains a BH_2 group is suggested by unpublished infrared data (71) which indicates the presence of a BH_2

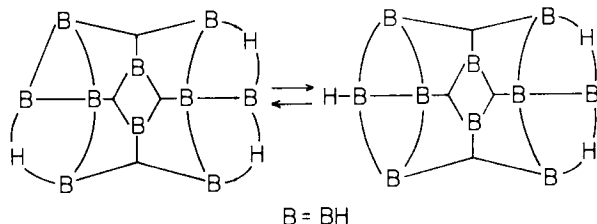
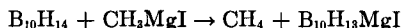


FIG. 6. Topological drawings of possible $B_{10}H_{13}^-$ tautomers.

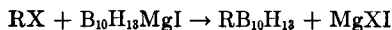
group. A BH_2 group was suggested by Lipscomb (43) as an efficient device for stabilizing negative charge.

E. DECABORAN(14)YL MAGNESIUM IODIDE

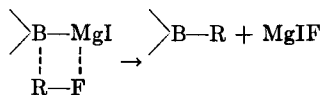
Siegel and co-workers (75), and later, Dunstan *et al.* (8) have described the preparation of a "decaboranyl Grignard reagent" from the reaction of decaborane-14 and methyl magnesium iodide.



Treatment of decaboran(14)yl magnesium iodide with benzyl chloride (75), alkyl fluorides (75), dialkyl sulfates (8) and trialkyloxonium ions (8, 75) produced a mono-alkylated decaborane.



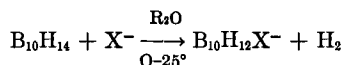
These are the first reported examples of alkylation with a derivative of the $\text{B}_{10}\text{H}_{13}^-$ ion. In these reactions the entering alkyl group is attached to the 6-position as shown by B^{11} NMR spectra (75). The question of the amount of covalent character between magnesium and boron in decaboran(14)yl magnesium iodide remains unanswered. If the degree of covalency is high, the magnesium derivative might best be considered as a substituted tautomer of $\text{B}_{10}\text{H}_{14}$. The fact that sulfate, fluoride and etheral oxygen are the most effective leaving groups suggests a four-center transition state for the displacement reactions.



Palchak, Norman, and Williams have reported that the reaction of $\text{NaB}_{10}\text{H}_{13}$ with benzyl bromide produces 6- or 1-benzyl decaborane-14 (56).

F. SUBSTITUTED $\text{B}_{10}\text{H}_{13}^-$ IONS

Aftandilian, Miller, and Muetterties (1) have prepared a series of $\text{B}_{10}\text{H}_{12}\text{Z}^-$ ions where Z is a monovalent anion. The cyanide, cyanate, thiocyanate, methoxide, and cyanofomate reactions were conducted in a variety of ethereal solvents and the products were characterized as their sodium or tetramethylammonium salts. The preparative reactions may be described by the following equation where X^- is the anionic reagent.



The structures of the products have not been determined although 6-(9-) substitution is preferred by the authors.

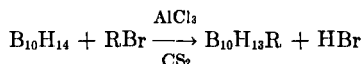
IV. Electrophilic Substitution of Hydrogen in Decaborane-14

A. HALOGENATION REACTIONS

Stock (76) first reported the preparation of halogen-substituted decaborane-14 derivatives from the uncatalyzed reaction of the halogens with $B_{10}H_{14}$. Stock succeeded in isolating a diiodo- and a dibromodecaborane-14. Single crystal X-ray diffraction studies by Schaeffer (70) proved the diiodo-compound (m.p. 261°) to be 2,4-diiododecaborane-14. A monoiodo derivative (m.p. 116°) was studied by Schaeffer *et al.* (72) by NMR techniques and shown to be 2-iododecaborane-14. Recently Hillman (33) has carried out a detailed study of the Stock iodination reaction. From these studies another $B_{10}H_{13}I$ (m.p. 100°) and another $B_{10}H_{12}I_2$ (m.p. 155°) were obtained. On the basis of deuterium tracer work and other chemical evidence, Hillman denoted these new derivatives as 5-iodo- and 2,5-diiododecaborane-14, respectively. The aluminum chloride-catalyzed-iodination of decaborane was later reported by Hillman (32) to produce the same products as the uncatalyzed iodination reaction.

B. ALKYLATION REACTIONS WITH INCIPIENT CARBONIUM IONS

R. L. Williams and co-workers (5, 82) have recently described a study of the ethylation and methylation of decaborane-14. These alkylation reactions were brought about through the use of an aluminum chloride catalyst and the corresponding alkyl bromide in carbon disulfide solution. The similarity of these reactions and the well known Friedel-Crafts reaction is obvious.



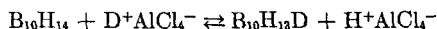
Depending upon the reaction conditions, mono-, di-, and higher alkylated products are obtained. Separation of these products by vapor-liquid chromatography followed by B^{11} nuclear magnetic resonance characterization proved that substitution occurred in the 1, 2, 3, and 4 positions of $B_{10}H_{14}$. The ratio of 2-methyldecaborane to 1-methyldecaborane was about 3:1. No evidence for substitution at the 5-position was obtained. This latter result contrasts strongly with the results of iodination described above (33).

C. ELECTROPHILIC PROTON EXCHANGE WITH DEUTERIUM CHLORIDE-ALUMINUM CHLORIDE

Under equilibrium conditions at room temperature, decaborane-14 was reported (11) to exchange six protons for deuterons when treated with a

large excess of deuterium chloride in the presence of aluminum chloride.

The six deuterons were erroneously assigned



to the 1, 2, 5, 7, 8, and 10 positions of $\text{B}_{10}\text{H}_{14}$ on the basis of B^{11} nuclear magnetic resonance spectra. More recently, this exchange reaction has been reexamined under kinetic conditions (9) and the original interpretation was modified. When $\text{B}_{10}\text{H}_{14}$ was treated with anhydrous deuterium chloride in carbon disulfide solution in a flow system and in the presence of a small quantity of aluminum chloride, rapid exchange of four protons was observed. These reactions were conducted at 26° . Kinetic analysis of the rate data proved that the exchange reactions were first-order in $\text{B}_{10}\text{H}_{14}$ at constant deuterium chloride and aluminum chloride activities. The four exchange positions were kinetically indistinguishable. Analysis of the reaction mixture by B^{11} nuclear magnetic resonance spectrum measurements as a function of time proved that the four exchanging protons were located at the 2,4- and either the 1,3- or the 6,9- positions. Since base-catalyzed exchange of the resultant $\text{B}_{10}\text{H}_{10}\text{D}_4$ with hydrogen chloride in dioxane did not occur it was concluded that the 1, 2, 3, and 4- positions were involved in electrophilic exchange. The kinetic characteristics of the reaction and the nature of the observed B^{11} nuclear magnetic resonance spectra proved that the 1,3-protons exchanged at the same rate as the 2,4-protons. This is quite different than the selectivity shown by the methylation reaction (82) which produces the 2-methyl three times faster than the 1-methyl compound.

D. MECHANISM OF ELECTROPHILIC SUBSTITUTION

The results described above indicate that $\text{B}_{10}\text{H}_{14}$ is labile to attack by electrophiles at the 1, 2, 3, and 4- positions. The deuterium exchange studies which were carried out under equilibrium conditions (11) are inconclusive since the long exchange times and tedious experimental technique employed may have allowed secondary reactions to enter the picture. No explanation of the 5-substitution observed in the case of iodination (33) may be offered at this time. However, the iodonium ion is an unusual electrophile due to its large steric requirement and its high polarizability. It appears likely that the process which leads to 5-iododecaborane-14 is not a typical electrophilic substitution reaction.

Previously, the orientation of substituents in electrophilic substitution reactions on decaborane-14 have been discussed in terms of the charge distribution in the unperturbed $\text{B}_{10}\text{H}_{14}$ molecule (70, 82). The 2 and 4-positions of $\text{B}_{10}\text{H}_{14}$ have been recognized as the points of highest electron density in $\text{B}_{10}\text{H}_{14}$ for some time (12). Indeed, the results of a detailed calcula-

tion of electron densities (Section I,C) confirms this conclusion and points out that the 5, 7, 8, and 10-positions are actually only slightly more positive ($+0.069e$) than the 1 and 3-positions. Consequently, the order with respect to increasing negative charge is $6,9 < 5,7,8,10 < 1,3 < 2,4$. These results are in agreement with experiment. The problem is quite similar to that encountered in predicting positions of electrophilic substitution in aromatic hydrocarbons. The fact that 1,3-substitution competes so favorably with 2,4-substitution in alkylation and deuterium exchange suggests that the transition state for 1,3-substitution is stabilized by a unique structural feature which compensates for a less favorable charge density in the reactant $B_{10}H_{14}$. An alternative explanation for the equality of 1,3- and 2,4-deuterium exchange rates has been advanced (9) and suggests that both 1,3- and 2,4-proton exchange proceed through a common intermediate which provides rapid distribution of the entering deuterium between the 1, 2, 3, and 4 positions.

V. Electron Transfer to Decaborane-14

A. DECABORANE-14 AS AN ELECTRON ACCEPTOR

Consideration of the valence bond structure of decaborane-14 led Lipscomb to predict (44) $B_{10}H_{14}^{2-}$ as a stable ion with a geometry resembling $B_{10}H_{14}$. The most probable topological structure of $B_{10}H_{14}^{2-}$ is shown in Fig. 7. It is to be noted that the negative charges are largely localized at

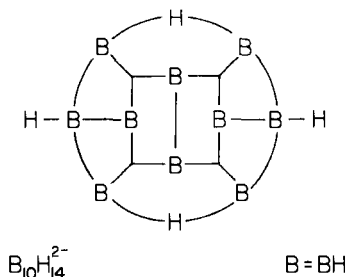


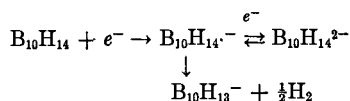
FIG. 7. Topological drawing of $B_{10}H_{14}^{2-}$.

the 6 and 9-positions which have been converted to BH_2 groups. Two bridge hydrogen atoms are placed in a plane of symmetry. As will be seen below, the $B_{10}H_{14}^{2-}$ ion and its substituted derivatives constitute an important series of decaborane derivatives.

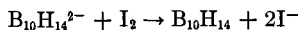
B. PREPARATION AND REACTIONS OF $B_{10}H_{14}^{2-}$

Toeniskoetter (77) and Toeniskoetter *et al.* (78) have described the reactions of decaborane-14 with sodium in liquid ammonia and ethereal

solvent systems. In the former case, $B_{10}H_{14}^{2-}$ is produced in high yield. Disodium tetradecahydrodecaborate is a white crystalline solid soluble in liquid ammonia and tetrahydrofuran. When the reaction of decaborane-14 with sodium is conducted in diethylether or tetrahydrofuran, a red intermediate is observed which either dimerizes (77) or reacts further with sodium to produce the colorless $B_{10}H_{14}^{2-}$ ion. On standing, the red intermediate decomposes to produce hydrogen and $NaB_{10}H_{13}$. On the basis of its color, stoichiometry of formation and low stability the red intermediate was formulated as a $B_{10}H_{14}^{\cdot -}$ ion-radical. Treatment of the $B_{10}H_{14}^{2-}$ ion with decaborane-14 generates the red species and illustrates the reversibility of the electron-transfer process. These interconversions are summarized in the following equations.



The reactions of the $B_{10}H_{14}^{2-}$ ion have not been fully investigated. Hydrogen chloride and $Na_2B_{10}H_{14}$ produce decaborane-14 along with some uncharacterized chlorination products (77). Iodine and $B_{10}H_{14}^{2-}$ react to produce decaborane-14 and iodide ion (66) in high yield.



C. THE $B_{10}H_{15}^-$ ION FROM $B_{10}H_{14}^{2-}$

Titration of $Na_2B_{10}H_{14}$ with hydrogen chloride in 50% ethanol results in the reversible uptake of one proton and the formation of the ion $B_{10}H_{15}^-$ (10). The addition of methyl triphenyl phosphonium, tetramethylammonium, or triethylammonium ions to acidified solution of the $B_{10}H_{14}^{2-}$ ion resulted in the formation of the corresponding $B_{10}H_{15}^-$ salts. The infrared spectrum of these salts contained terminal B—H stretching bands at 3.95, 4.20, and 4.30 μ . A weak absorption band was observed at 5.10 μ which

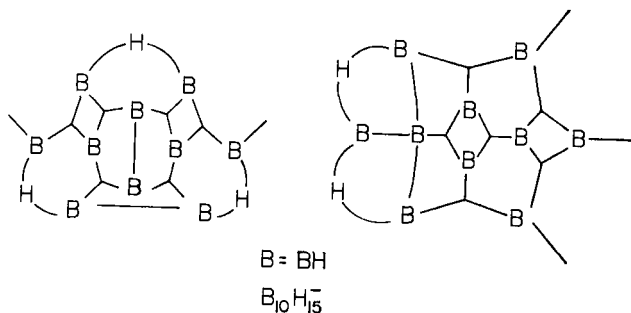


FIG. 8. Topological drawings of possible $B_{10}H_{15}^-$ structures.

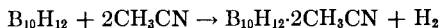
indicates the presence of B—H—B bridges. The B^{11} nuclear magnetic resonance spectrum of $B_{10}H_{15}^-$ salts revealed only three resonances at +27.6, 34.9, and 43.2 ppm relative to trimethyl borate. An interpretation of this spectrum has not been carried out.

It is interesting to note that Reddy and Lipscomb (64) predicted the possible existence of the $B_{10}H_{15}^-$ ion in 1959. Lipscomb has recently presented (45) two plausible topological formulations of this ion which are shown in Fig. 8.

VI. Substituted Tetradecahydrodecaborate Ions. $B_{10}H_{12}X_2$ Compounds

A. EARLY WORK WITH $B_{10}H_{12}X_2$ COMPOUNDS

In 1957 Riley Schaeffer reported (69) the preparation of a decaborane-14 derivative which presaged a new area of decaborane-14 chemistry. The reported reaction involved the treatment of decaborane-14 with excess acetonitrile at the reflux temperature. The compound $B_{10}H_{12} \cdot 2CH_3CN$ was formed in essentially quantitative yield along with one mole of hydrogen per mole of derivative.



Somewhat later, other derivatives of this general type were reported (30) in which diethylecyanamide or triphenylphosphine served as ligands. The observation was also made that the diethylecyanamide and triphenylphosphine derivatives could be prepared by displacement of acetonitrile from $B_{10}H_{12} \cdot 2CH_3CN$ with the desired ligand. Thus, the probable preparation a large series of $B_{10}H_{12}X_2$ derivatives became apparent.

B. STRUCTURE ELUCIDATION AND TOPOLOGY OF $B_{10}H_{12}X_2$ COMPOUNDS

Reddy and Lipscomb (64, 65) reported the results of their single crystal X-ray diffraction study of $B_{10}H_{12} \cdot 2CH_3CN$ in 1959. The structure of $B_{10}H_{12} \cdot 2CH_3CN$ obtained from this study was the topological equivalent of the 2632 structure of the $B_{10}H_{14}^{2-}$ ion. Reddy and Lipscomb (64) first recognized and established a most useful concept: The formal displacement of a hydride ion by a ligand carrying a nonbonded electron pair will produce a topologically equivalent structure. This rule is illustrated for the case at hand with the following equation.

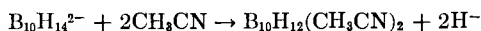
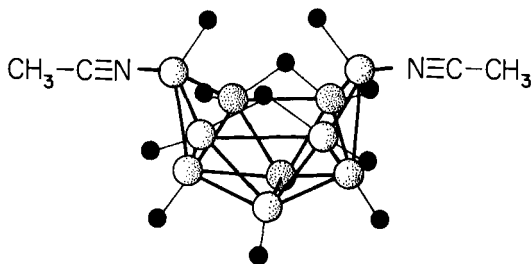


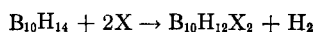
Figure 9 presents a schematic drawing which illustrates the $B_{10}H_{12} \cdot 2CH_3CN$ geometry and its topological representation. Later work by Sands and Zalkin (67) confirmed the assumption that $B_{10}H_{12} \cdot 2(CH_3)_2S$ (16) was isostructural with $B_{10}H_{12} \cdot 2CH_3CN$. Pace *et al.* (55) have obtained B^{11}

FIG. 9. Geometry of $B_{10}H_{12} \cdot 2CH_3CN$.

nuclear magnetic resonance spectra of $B_{10}H_{12} \cdot 2CH_3CN$ and $B_{10}H_{12} \cdot 2(CH_3)_2S$ which are in agreement with spectra predicted on the basis of the known structures of these compounds.

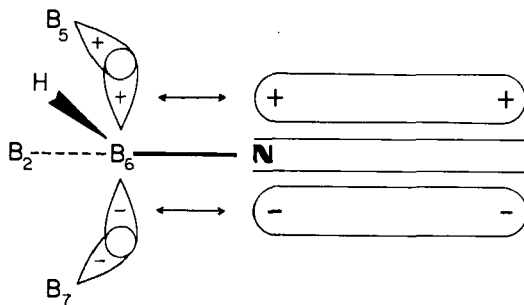
C. FURTHER EXAMPLES OF $B_{10}H_{12}X_2$ COMPOUNDS

Evidence accumulated over the past several years points out the generality of the reaction of decaborane-14 with two neutral ligand molecules. The types of



ligands which have been successfully employed include the following: nitriles (69), dialkylcyanamides (30), alkyl isonitriles (26), dialkylsulfides (16, 17), dialkylsulfoxides (41), phosphines (30), phosphite and phosphinite esters (63), phosphine oxides (41), amides (41), thioamides (41), tertiary amines (31), alkylated thioureas (4), heterocyclic amines (15) and tetrazoles (13). Other types of neutral ligand molecules will no doubt be found to be effective in this general reaction.

An unusual property of $B_{10}H_{12}X_2$ compounds which contain heterocyclic amines or tetrazoles as ligands is their highly colored nature. Thus $B_{10}H_{12}(\text{pyridine})_2$ is bright yellow. Other members of $B_{10}H_{12}X_2$ family are colorless or nearly so when pure. An explanation of this absorption in the

FIG. 10. Extended molecular orbitals in $B_{10}H_{12}Py_2$.

visible region has been proposed (15). In Fig. 7 it is seen that the topology of $B_{10}H_{12}X_2$ molecules suggests that the boron atoms which bear the ligand molecules are hybridized sp^2 . Each of these boron atoms contributes a $2p$ -orbital to an open three-center bond which in turn, must have the symmetry property of a p -orbital. When the attached ligand contains a π -electron system with a low-lying and empty antibonding orbital, back coordination of delocalized electrons in the $B_{10}H_{12}$ unit may occur upon excitation. Figure 10 depicts the geometrical arrangement involved. Figure 11 illustrates a successful correlation of excitation energies of absorption

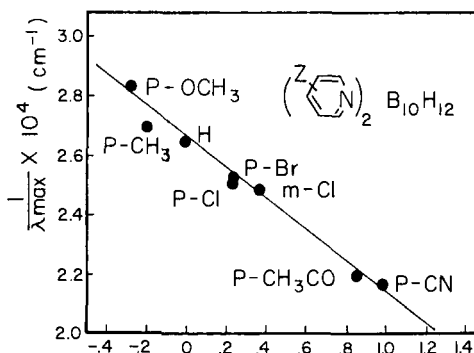
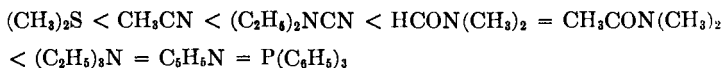


FIG. 11. Correlation of excitation energies with the Hammett sigma constants of substituents in $B_{10}H_{12}(Py-Z)_2$, Z = substituent.

bands in the visible with the Hammett sigma constants of substituents placed on the pyridine nucleus. This concept has been extended by Kaufman (39) in a more quantitative fashion.

D. LIGAND DISPLACEMENT REACTIONS WITH $B_{10}H_{12}X_2$ COMPOUNDS

Treatment of $B_{10}H_{12} \cdot 2CH_3CN$ with triphenylphosphine or diethylcyanamide produced $B_{10}H_{12} \cdot 2P(C_6H_5)_3$ and $B_{10}H_{12} \cdot 2(C_2H_5)_2NCN$ which were identical to those obtained from decaborane-14 and these ligands (30). These reactions were found to be irreversible under ordinary conditions. Similarly, treatment of $B_{10}H_{12} \cdot 2(C_2H_5)_2NCN$ with triphenylphosphine produced $B_{10}H_{12} \cdot 2P(C_6H_5)_3$. The retroreaction could not be brought about. Later work by Pace *et al.* (55) included other examples of ligand displacement reactions which employed dimethylacetamide, triethylamine, and pyridine. With this additional data in hand it was possible to formulate a displacement reactivity series in which a ligand on the right would displace all ligands to its left.



Triphenylphosphine and pyridine are probably the most tightly bound ligands since triphenylphosphine will displace triethylamine (31). The possibility of back coordination of delocalized electrons in the $B_{10}H_{12}$ fragment with the unfilled π -orbitals of pyridine and an unfilled d -orbital of phosphorous in triphenylphosphine may account for this strong bonding.

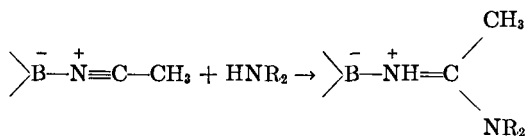
The mechanism of these displacement reactions has not been reported. It is interesting to note that these reactions are totally stereospecific.

It is important to note that dialkyl sulfides are the most readily replaced ligands known. This fact coupled with the ease of preparation of $B_{10}H_{12} \cdot 2SR_2$ derivatives (15, 16) makes these materials especially valuable intermediates for synthetic work.

E. NUCLEOPHILIC ADDITION REACTIONS WITH UNSATURATED LIGANDS AS SUBSTRATES

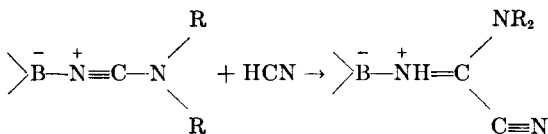
While the displacement of ligands from $B_{10}H_{12}X_2$ compounds by other ligands is a general reaction, an interesting side reaction often occurs when the ligand attached to boron is unsaturated and the attacking nucleophile is an extremely weak acid (31).

The compound $B_{10}H_{12} \cdot 2CH_3CN$ reacts with primary and secondary alkylamines to produce $B_{10}H_{12}X_2$ derivatives in which the attached ligand contains both the original ligand and the attacking nucleophile. The following equation presents this reaction in general terms.



Thus, nitrile ligands may be converted to substituted amidine ligands in high yield (31). The resulting $B_{10}H_{12} \cdot 2$ Amidine derivatives will not react with triphenylphosphine.

Liquid hydrogen cyanide and the compound $B_{10}H_{12} \cdot 2(C_2H_5)_2NCN$ react slowly at room temperature (30) and in the absence of solvent to produce a brilliant red derivative of composition $B_{10}H_{12} \cdot 2(C_2H_5)_2NCN \cdot 2HCN$. The product has an absorption maximum at $450 m\mu$ ($\epsilon = 9.5 \times 10^3$). The original formulation of the complex ligand in this derivative (30) is probably in error. In view of the now recognized spectral properties of $B_{10}H_{12}X_2$ compounds which contain conjugated, electron-withdrawing ligands (Section VI,C), it appears likely that the ligand is actually a C-cyanoformamidine. This view is strengthened by the observations of Pace *et al.* (55) that dialkylcyanamides are bonded to the $B_{10}H_{12}$ fragment through nitrile nitrogen. The over-all reaction may be written as follows:



These reactions are novel in that unusual organic reactions may be carried out while the unsaturated substrate is firmly bonded to the $\text{B}_{10}\text{H}_{12}$ fragment. The role of such reactions in synthetic organic chemistry has not, as yet, been exploited.

F. $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$ FROM $\text{B}_{10}\text{H}_{12}\cdot 2\text{S}(\text{CH}_3)_2$

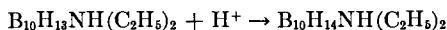
Knoth and Muetterties (41) have recently described the preparation of $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$ by the slow pyrolysis of $\text{B}_{10}\text{H}_{12}\cdot 2\text{S}(\text{CH}_3)_2$ in mesitylene solution. The product is a stable white solid which does not react with acetonitrile or dimethyl sulfide at room temperature. Treatment of $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$ with triphenylphosphine or dimethylsulfide at higher temperatures produces $\text{B}_{10}\text{H}_{12}\cdot 2\text{P}(\text{C}_6\text{H}_5)_3$ and $\text{B}_{10}\text{H}_{12}\cdot 2(\text{CH}_3)_2\text{S}$, respectively.

The ultraviolet spectrum of $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$ is similar to that of $\text{B}_{10}\text{H}_{13}^-$ ion and the B^{11} nuclear magnetic resonance spectrum of these two substances are identical in shape but not superimposable. Thus, $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$ was formulated as a substituted $\text{B}_{10}\text{H}_{13}^-$ ion (41). In this case an H^- of $\text{B}_{10}\text{H}_{13}^-$ is replaced by dimethylsulfide.

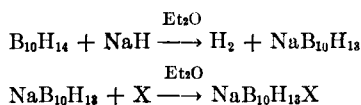
G. THE PREPARATION AND PROBABLE STRUCTURE OF $\text{B}_{10}\text{H}_{13}\text{X}^-$ IONS

The reaction of decaborane-14 with excess diethylamine in cyclohexane solution was reported (29) to give a product of composition $\text{B}_{10}\text{H}_{14}\cdot 2(\text{C}_2\text{H}_5)_2\text{NH}$. Later work (15, 18) proved this material to be a diethylammonium salt with the anion $\text{B}_{10}\text{H}_{13}\cdot (\text{C}_2\text{H}_5)_2\text{NH}^-$. The anion is undoubtedly produced by the coordination of the amine with the $\text{B}_{10}\text{H}_{13}^-$ ion.

Potentiometric titration of this salt with hydrogen chloride in non-aqueous media consumed one equivalent of acid and precipitated diethylammonium chloride. Hydrogen was not evolved. The neutralization of the anion undoubtedly produced $\text{B}_{10}\text{H}_{14}(\text{C}_2\text{H}_5)_2\text{NH}$, a monosubstituted $\text{B}_{10}\text{H}_{15}^-$ ion (18 and Section V,B).



An improved and general method for the preparation of $\text{B}_{10}\text{H}_{13}\text{X}^-$ ions was developed (18). This method made use of the following reaction sequence where X = ligand.

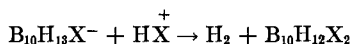


The resulting anions were isolated and characterized as their tetramethylammonium salts. Diethylamine, ethylamine, triethylamine, piperidine, pyridine, and triphenylphosphine were employed as ligands. Knoth and Muettterties (41) employed a similar method to prepare the anion $B_{10}H_{13}S(CH_3)_2^-$.

The structure of the $B_{10}H_{13}X^-$ anions is most likely identical to that of $B_{10}H_{12}X_2$ compounds (Fig. 9) in which one of the ligand molecules is replaced by a hydride ion (18, 41). This formulation is supported by the similarity of the B^{11} nuclear magnetic resonance spectra (41) of $B_{10}H_{12} \cdot 2(CH_3)_2S$ and $B_{10}H_{13}S(CH_3)_2^-$ and by chemical evidence cited below (18).

H. CONVERSION OF $B_{10}H_{13}X^-$ IONS TO $B_{10}H_{12}X_2$ DERIVATIVES

Since $B_{10}H_{13}X^-$ ions most likely contain a negatively charged BH_2 group at the 6-(9-) position it was reasonable to expect these ions to react with the conjugate acids of ligands in accord with the following equation where X = ligand.



This reaction proved to be general (18) and was employed in the preparation of a variety of $B_{10}H_{12}X_2$ derivatives. By employing the conjugate acid of a ligand which differed from the ligand present in $B_{10}H_{13}X^-$, it was possible to prepare unsymmetrical $B_{10}H_{12}XX'$ derivatives (18). Amine hydrochlorides were most commonly employed as HX^+ , however, $B_{10}H_{13}-(C_2H_5)_2NH^-$ and anhydrous hydrogen chloride reacted in acetonitrile or diethyl sulfide solvent to produce hydrogen and $B_{10}H_{12} \cdot CH_3CN \cdot (C_2H_5)_2NH$ and $B_{10}H_{12} \cdot (C_2H_5)_2S \cdot (C_2H_5)_2NH$, respectively. These reactions are to be contrasted with the titration of $B_{10}H_{13}(C_2H_5)_2NH^-$ with hydrogen chloride in dioxane (Section VI,G), a poorly nucleophilic solvent.

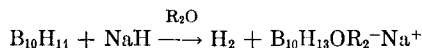
The mechanism of these protolysis reactions is presently obscure. However, it is likely that the attacking, protonated ligand enters into a three or four-center transition state with the BH_2 group of the anion to produce hydrogen and product (18). In the former case a discrete $B_{10}H_{12}X$ intermediate would be involved. In the latter case, the process would be concerted and lead directly to products.

I. OXIDATION OF A $B_{10}H_{13}X^-$ ION TO $B_{10}H_{13}X$. ALKOXYLATION OF DECABORANE-14

The attempted iodination of the $B_{10}H_{13}^-$ ion in diethyl ether led to the formation of an ethoxydecaborane-14, $B_{10}H_{13}OC_2H_5$. This reaction proved to be general and several alkoxy and aryloxy decaborane-14 derivatives were prepared (27). The position of substitution was not rigorously estab-

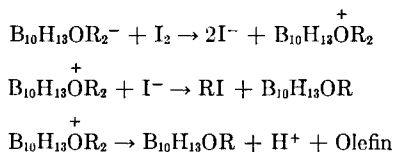
lished although 6-(9-) substitution is compatible with the B^{11} nuclear magnetic resonance spectra obtained.

In view of the ability of weakly nucleophilic ligands to coordinate with the $B_{10}H_{13}^-$ ion (Section VI,G) it appears likely that solutions of $B_{10}H_{13}^-$ prepared in ethereal solvents contain small quantities of the $B_{10}H_{13}X^-$ ion in which the ligand is identical to the solvent. The ether ligand would bear a positive



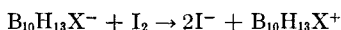
charge on oxygen. The reaction of $B_{10}H_{14}^{2-}$ with iodine produces $B_{10}H_{14}$ and iodide ion in high yield (Section V,B). Due to the topological identity of $B_{10}H_{14}^{2-}$ and $B_{10}H_{13}OR_2^-$ the oxidation of $B_{10}H_{13}OR_2^-$ to $B_{10}H_{13}OR_2^+$ might well occur upon the addition of iodine. Attack of the produced iodide

ion upon the $-OR_2^+$ group would produce alkyl iodide. The $-OR_2^+$ group might also eliminate a proton and an olefin molecule.



Palchak *et al.* (56) have reinvestigated the iodination of $B_{10}H_{13}^-$ in diethyl ether and have obtained evidence for the formation of ethyl iodide as well as ethoxy decaborane-14 and iodinated decaborane-14's.

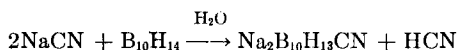
Further work with simple oxidation reactions might allow the preparation of $B_{10}H_{13}X^+$ cations which



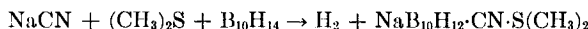
are substituted decaborane-14's.

J. $B_{10}H_{13}Z^{2-}$ IONS FROM $B_{10}H_{13}^-$ AND NUCLEOPHILIC ANIONS, Z^-

Knoth and Muetterties (41) have prepared the $B_{10}H_{13}CN^{2-}$ anion by the reaction of two equivalents of sodium cyanide with $B_{10}H_{14}$ in aqueous solution.



In the same publication these authors reported the preparation of the $B_{10}H_{12} \cdot CN \cdot S(CH_3)_2^-$ anion from the reaction of $B_{10}H_{14}$ with sodium cyanide in dimethyl sulfide solution.



Both the $B_{10}H_{13}CN^{2-}$ and the $B_{10}H_{12}\cdot CN\cdot S(CH_3)_2^-$ ions exhibited B^{11} nuclear magnetic resonance spectra which were similar in shape to that of the $B_{10}H_{13}S(CH_3)_2^-$ ion. The ultraviolet absorption spectra of these three ions were also similar. It therefore appears correct to assign the $B_{10}H_{13}CN^{2-}$ and the $B_{10}H_{12}\cdot CN\cdot S(CH_3)_2^-$ ions the structures of 6- and 9-substituted $B_{10}H_{14}^{2-}$ ions.

K. MECHANISM OF $B_{10}H_{12}X_2$ FORMATION

Only two studies which deal with the mechanism of $B_{10}H_{12}X_2$ formation have been reported in the literature. Beachell and Dietrich (3) have examined the kinetics of the reactions of a series of substituted anilines with decaborane-14 in benzene solution at 25.0°. In a later study Beachell and Hoffman (4) examined the kinetics of the reaction of *sym*-diethyl thiourea with decaborane-14 in benzene solution at 25.0°.

The reactions of substituted anilines with decaborane-14 were first-order in the aniline and first-order in a 1:1 aniline: $B_{10}H_{14}$ complex. All reactions were followed by measurement of evolved hydrogen. $d[H_2]/dt = k_2[B_{10}H_{14}\cdot Aniline][Aniline]$. Application of a Hammett treatment (24) to the data obtained indicated a ρ value of -2.75 . Small primary kinetic isotope effects were observed with partially deuterated reactants (B—D or N—D) and provided evidence for B—H bond-breaking in the rate-determining step. The product from N-deuterated *p*-toluidine contained B—D stretching bands in the infrared spectrum. Thus, equilibration of the protons attached to nitrogen with certain protons present in decaborane-14 readily occurs during the reaction. This exchange process most likely proceeds through the B—H—B bridge exchange described in Section III,C.

The kinetic study of the reaction of *sym*-diethyl thiourea with decaborane-14 was only briefly reported (4). The authors claim that the observed second-order reaction was consistent with the rate expression:

$$d[H_2]/dt = k_2 [thiourea \cdot B_{10}H_{14}] [thiourea]$$

An attempt to arrive at a generalized mechanism for $B_{10}H_{12}X_2$ formation is complicated by the relatively basic character of the anilines employed in the initial study and the known acid-base reactions of $B_{10}H_{14}$ with amines (Sections III,A and III,B). The study with *sym*-diethylthiourea as the nucleophile is perhaps more informative since the pK_B of this species is approximately 5 units greater than that of aniline. However, both studies point to a rate-determining transition state which has the composition of a ($B_{10}H_{14}\cdot nucleophile$) complex and a free nucleophile molecule. The data presently available are consistent with several possible ionic mechanisms. Before definite conclusions are drawn a great deal more experimental work must be carried out.

VII. Enneaborane-15 Derivatives from Substituted $B_{10}H_{14}^{2-}$ Ions

A. EARLY WORK ON ENNEABORANE-15 DERIVATIVES

In the first report of the preparation of a $B_{10}H_{12}X_2$ derivative, Schaeffer (69) referred to the solvolytic degradation of $B_{10}H_{12} \cdot 2CH_3CN$ with methanol at the reflux temperature. The product obtained from this reaction showed a C=N stretching band in its infrared spectrum. It was suggested by Schaeffer (68) that this product might be a B_9 derivative.

Fitch and Laubengayer (14) reported that the acidolysis of a product formed from $B_{10}H_{14}$ and dimethylamine produced a volatile solid derivative. It was suggested by these authors that the acidolysis product was a B_9 derivative. Later work, to be described below, proved that the compounds of Schaeffer and Fitch and Laubengayer were B_9H_{15} derivatives. These derivatives and many others constitute a series of substituted B_9H_{15} species which are analogous to the $B_{10}H_{12}X_2$ derivatives. Their general composition may be expressed as $B_9H_{13}X$ where X is a ligand molecule.

B. STRUCTURE AND TOPOLOGY OF $B_9H_{13}X$ COMPOUNDS

Wang *et al.* (79) first reported the results of a single crystal X-ray diffraction study of $B_9H_{13} \cdot CH_3CN$ (16) in 1961. A later publication by these authors (80) expanded their initial views and presented a review of the evolution of $B_9H_{13}X$ structural studies with respect to the present topological theory of boron hydrides and derivatives.

The determined geometry of $B_9H_{13} \cdot CH_3CN$ is shown in Fig. 12 along with the corresponding topological representation of this type of derivative. It is important to note that $B_9H_{13}X$ derivatives are topologically equivalent to the unknown $B_9H_{14}^-$ ion, which in turn, is related by proton transfer to the unknown B_9H_{15} with 6330 topology shown in Fig. 12. As previously pointed out (79, 80), this 6330 topology violates one of the original topological rules (6, 43). This rule states that it is impossible to bond two bridge hydrogen atoms to a boron atom which is connected to four other nearest boron atoms. Therefore, it was predicted that this particular B_9H_{15} would probably be unstable (80). The conceptual transformation of the hypothetical 6330 B_9H_{15} to $B_9H_{13}X$ derivatives involves a newly described tautomerization reaction which involves bridge hydrogen atoms and uniquely predicts the known $B_9H_{13}X$ structure without violation of any topological rule (80). The reader is referred to the original paper for details of this transformation.

The bonding of ligands to boron in $B_9H_{13}X$ derivatives is seen to be virtually identical to that found in $B_{10}H_{12}X_2$ derivatives (Section VI,B).

The hybridization of the boron atom which carries the ligand is seen in Fig. 12 to be sp^2 . It was interesting to find spectroscopic evidence (19) for this hybridization in the ultraviolet absorption spectra of a series of $B_9H_{13}Py$ derivatives where Py represents a substituted pyridine ligand. These compounds exhibited absorption maxima between 284 $m\mu$ (4-meth-

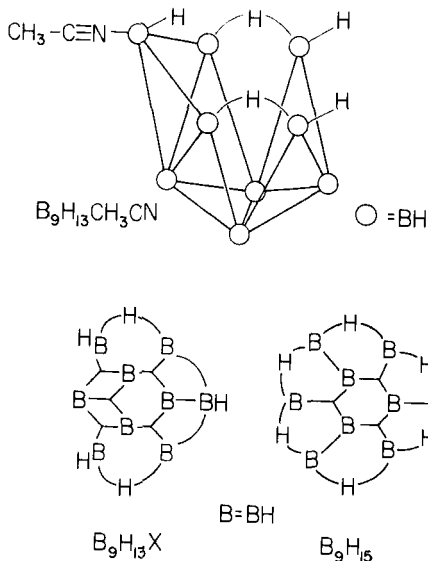
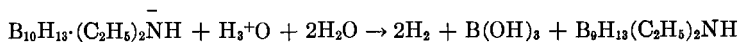


FIG. 12. Approximate geometry of $B_9H_{13}CH_3CN$; topological drawings of $B_9H_{13}X$, $B_9H_{14}^-$ ($X = H^-$), and B_9H_{15} .

oxypyridine) and 358 $m\mu$ (4-cyano-pyridine). The excitation energies of these maxima were successfully correlated with the Hammett sigma constant (24) of the various substituents. The rationale of these results is identical to that presented for the case of $B_{10}H_{12}Py_2$ derivatives (Section VI,C).

C. PREPARATION OF $B_9H_{13}X$ DERIVATIVES FROM $B_{10}H_{13}X^-$ IONS

The compound $(C_2H_5)_2NH_2^+B_{10}H_{13}^-(C_2H_5)_2NH$, described in Section VI,G, was found to react quantitatively with aqueous acids as shown in the following equation.



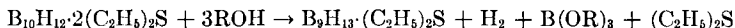
The composition of the hydride product was deduced (16, 19) from these quantitative results to be $B_9H_{13}^-(C_2H_5)_2NH$. Comparison of this reaction with that described by Fitch and Laubengayer (Section VII,A) leaves

no doubt that these authors obtained the compound $B_9H_{13} \cdot (CH_3)_2NH$. That a negatively charged 6-(9-) BH_2 group and its bonded hydrogen had been removed in this acidolysis reaction was deduced from this chemical evidence (16, 19) and further evidence presented below. On the basis of a preliminary B^{11} nuclear magnetic resonance spectrum Lipscomb predicted (46) the correct boron arrangement in $B_9H_{13}X$ derivatives.

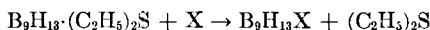
The acidolysis of $B_{10}H_{12}X^-$ ions to produce $B_9H_{13}X$ derivatives was extended to systems which contained other ligands and a general preparative method was developed (19). Thus, $B_9H_{13}X$ derivatives were prepared by this method which contained diethylamine, ethylamine, triethylamine, triphenylphosphine and pyridine as ligands.

D. PREPARATION OF $B_9H_{13}X$ DERIVATIVES BY ALCOHOLYSIS OF $B_{10}H_{12}X_2$ COMPOUNDS AND THEIR INTERCONVERSION

The early work of Schaeffer (Section VII,A) suggested that the alcoholysis of $B_{10}H_{12}X_2$ derivatives produced B_9 derivatives. Accordingly, the compound $B_{10}H_{12} \cdot 2(C_2H_5)_2S$ was solvolytically degraded in methanol at the reflux temperature (16, 19). The product of this reaction was obtained in 70% yield. Characterization by elemental analysis and its B^{11} nuclear magnetic resonance spectrum allowed this material to be formulated as $B_9H_{13} \cdot (C_2H_5)_2S$. Further characterization was afforded by the conversion of the diethyl sulfide derivative to the known $B_9H_{13} \cdot (C_2H_5)_2NH$ by a ligand displacement reaction (Section VI,D). Thus, the over-all degradation reaction may be written

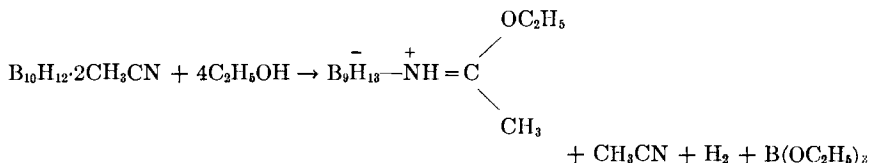


By employing ligand displacement reactions



it was possible to prepare derivatives (16, 19) which contained diethylamine, triphenylphosphine, acetonitrile, and a series of substituted pyridines. In every case in which comparison was possible, the products were identical to those produced by acidolysis of the $B_{10}H_{12}X^-$ ion (Section VII,C).

Reinvestigation (16, 19) of the alcoholysis of $B_{10}H_{12} \cdot 2CH_3CN$ (69) but with ethanol rather than methanol resulted in a product which was formulated as $B_9H_{13} \cdot NH = C(OC_2H_5)CH_3$.



The over-all transformation thus involved a solvolytic degradation reaction coupled with a ligand addition reaction (Section VI,E).

E. MECHANISM OF $B_9H_{13}X$ FORMATION

The fact that $B_{10}H_{12}X_2$ derivatives which contain a strongly bonded ligand (X = triphenylphosphine, triethylamine, etc.) are not solvolytically degraded to $B_9H_{13}X$ derivatives (19) suggests that these degradation reactions involve the initial displacement of a ligand molecule by solvent. In the case of acidolysis of $B_{10}H_{13}X^-$ ions this process may be accomplished by protonation of the "hydride ion ligand." Thus, the intermediate $B_{10}H_{12} \cdot X \cdot ROH$ is most likely involved in both types of reaction. Subsequent degradation of this intermediate could lead to the observed products by a variety of feasible paths. Further speculation is not worthwhile at the present time. It seems reasonable, however, to expect solvolytic degradation reactions to play a useful role in future synthetic work.

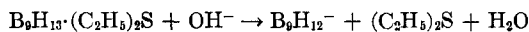
F. THE $B_9H_{12}X^-$ AND $B_9H_{12}^{2-}$ IONS

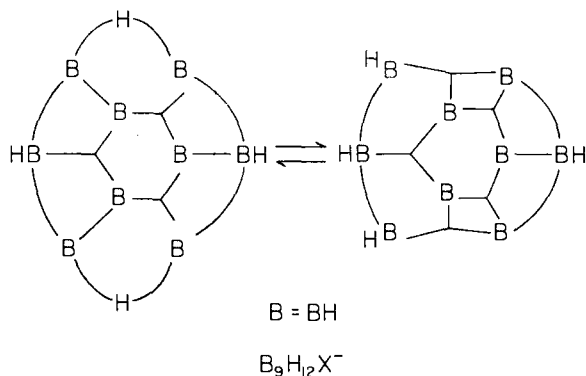
Treatment of $B_9H_{13} \cdot C_2H_5NH_2$ with one equivalent of ethylamine produced a salt $C_2H_5NH_3^+ B_9H_{12} \cdot C_2H_5NH_2$ in quantitative yield (16, 19). Similar reactions were attempted with other amine derivatives and were unsuccessful. Thus, anions of the general composition $B_9H_{12}X^-$ were shown to be capable of existence. Formally, such anions are topological equivalents of a $B_9H_{13}^{2-}$ ion.

The pyridine derivative, $B_9H_{13}Py$ was found to react with sodium hydride in tetrahydrofuran solution to produce an air-sensitive, blood-red anion and one mole of hydrogen. Neutralization of this anion with anhydrous hydrogen chloride regenerated the $B_9H_{13}Py$ (19). This represents the second reported preparation of a $B_9H_{12}X^-$ ion.

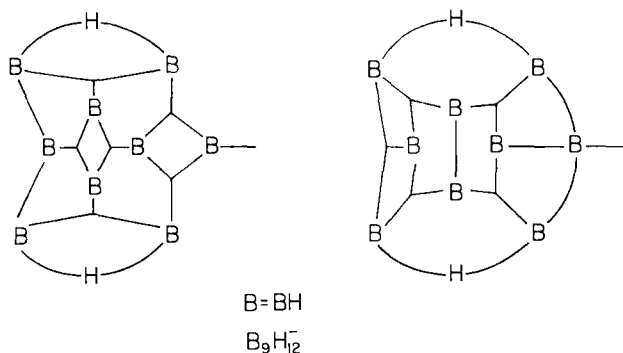
Wang *et al.* (79, 80) have formulated two possible structures for ions of this type. These structures are represented in topological form in Fig. 13. These authors have also proposed a novel tautomerization process for the interconversion of these isomers and suggest that $B_9H_{12}X^-$ ions are important candidates for structure determination.

In contrast to the results reported above, treatment of $B_9H_{13}(C_2H_5)_2S$ with very strong bases such as tetramethylammonium hydroxide or triphenylmethylene phosphorane results in the near quantitative formation of the ion $B_9H_{12}^-$ (16, 17, 19). This ion is probably similar in structure to the $B_9H_{13}X$ compounds since it may be converted to authentic $B_9H_{13}Py$ by treatment with pyridinium chloride in tetrahydrofuran (19).



FIG. 13. Topological drawing of possible $B_9H_{12}X^-$ structures.

Further reactions of the $B_9H_{12}^-$ ion have been observed. Methanolysis of the tetramethyl ammonium salt yields tetramethylammonium octahydrotriborate (17). This reaction is of preparative importance since the $B_3H_8^-$ ion is difficult to obtain by other means.

FIG. 14. Topological drawing of possible $B_9H_{12}^-$ structure.

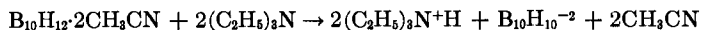
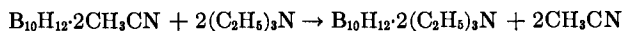
Recent studies by Lipscomb have led to two proposed structures for the $B_9H_{12}^-$ ion (47). These structures are shown in Fig. 14.

VIII. The $B_{10}H_{10}^{2-}$ Ion and Its Reactions

A. PREPARATION AND STRUCTURE OF $B_{10}H_{10}^{2-}$

During a study of the ligand displacement reactions of amines with the compound $B_{10}H_{12} \cdot 2CH_3CN$ (31), it was observed that triethylamine produced the expected $B_{10}H_{12} \cdot 2(C_2H_5)_3N$ and a second isomer which appeared to be ionic in nature. Conversion of this salt to a *bis*-tetramethylammonium

salt required that the accompanying anion be formulated as $B_{10}H_{10}^{2-}$ (31). Molecular weight determinations confirmed this formulation (59).



Later work proved that $B_{10}H_{10}^{2-}$ could be formed in essentially quantitative yield by simply treating $B_{10}H_{12} \cdot 2CH_3CN$ with excess triethylamine in benzene solution at the reflux temperature for several hours. The observation was also made (31) that covalent $B_{10}H_{12} \cdot 2(C_2H_5)_3N$ could be converted to the *bis*-triethylammonium salt of $B_{10}H_{10}^{2-}$ by heating with triethylamine in benzene. Thus, $B_{10}H_{12}X_2$ derivatives were tentatively identified as intermediates.

Examination of the reaction of $B_{10}H_{12} \cdot 2(C_2H_5)_2S$ with triethylamine, triphenylmethylene phosphorane and tetramethylammonium hydroxide led to the rapid formation of $B_{10}H_{10}^{2-}$ ion at low temperatures. The rate of conversion of $B_{10}H_{12}X_2$ derivatives to the $B_{10}H_{10}^{2-}$ ion therefore appears to involve the nature of ligand bonding in the $B_{10}H_{12}X_2$ derivative employed. The $B_{10}H_{12}X_2$ derivatives which contain the more weakly bound ligands react most rapidly with bases.

The B^{11} nuclear magnetic resonance spectrum of the $B_{10}H_{10}^{2-}$ ion is shown in Fig. 15. The striking simplicity of this spectrum suggested that the $B_{10}H_{10}^{2-}$ ion had a high order of symmetry. On the basis of this spectrum

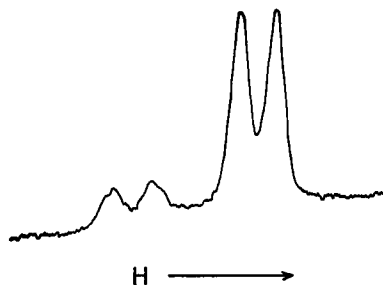


FIG. 15. B^{11} nuclear magnetic resonance spectrum of $B_{10}H_{10}^{2-}$.

it was proposed (49) that the $B_{10}H_{10}^{2-}$ ion was a polyhedron of D_{4d} symmetry. This geometry is presented in Fig. 16. A simplified molecular orbital treatment, based upon the accepted bonding modes in B_5H_9 and other simplifying assumptions, indicated that the D_{4d} structure was consistent with a $2-$ ionic charge (49). This structure was very recently confirmed by Dobrott and Lipscomb (?) by a single crystal X-ray diffraction study of $Cu_2B_{10}H_{10}$. This same study revealed evidence for a novel covalent inter-

action of Cu^{I} with the $\text{B}_{10}\text{H}_{10}^{2-}$ polyhedron; the first reported example of three-center interactions of metal ions with boron hydride derivatives.

The discovery and structure elucidation of the polyhedral $\text{B}_{10}\text{H}_{10}^{2-}$ ion has opened a new door along the corridor of chemistry. The icosahedral $\text{B}_{12}\text{H}_{12}^{2-}$ ion discussed in Section IX is a second example of a polyhedral ion. Lipscomb has presented attractive arguments for the possible existence of polyhedral $\text{B}_5\text{H}_5^{2-}(\text{D}_{3h})$, $\text{B}_6\text{H}_6^{2-}(\text{O}_h)$ and $\text{B}_7\text{H}_7^{2-}(\text{D}_{5h})$ ions (47).

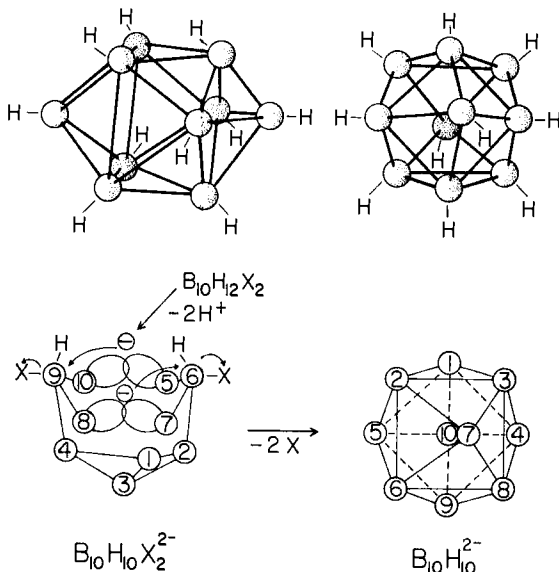


FIG. 16. Geometry of $\text{B}_{10}\text{H}_{10}^{2-}$ and probable mechanism of formation from $\text{B}_{10}\text{H}_{12}\text{X}_2$.

It is most important to emphasize the fact that polyhedral ions are stabilized by electron delocalization and they may be considered as the inorganic counterparts of aromatic organic compounds. For this reason the topological treatment is uninformative when applied to these polyhedral species. However, molecular orbital methods are most effective even in their most simplified form. The reader is referred to the recent work of Moore *et al.* (53) and Hoffmann and Lipscomb (35) for dramatic demonstrations of this procedure.

B. MECHANISM OF $\text{B}_{10}\text{H}_{10}^{2-}$ FORMATION

Evidence cited above strongly suggests that the $\text{B}_{10}\text{H}_{10}^{2-}$ ion is formed from $\text{B}_{10}\text{H}_{12}\text{X}_2$ derivatives (Section VI) in a base-promoted process. The geometrical arrangement of the



boron atoms in $B_{10}H_{12}X_2$ and $B_{10}H_{10}^{2-}$ are quite different and any proposed mechanism must take this factor into account. Consideration of this problem led to the conclusion that attachment of the 8-(10-) boron atom to the 6-position and similar attachment of 5-(7-) boron atom to the 9-position would uniquely produce the $B_{10}H_{10}^{2-}$ boron atom array (47, 58). The role of base has been attributed to the removal of the bridge hydrogens from the $B_{10}H_{12}X_2$ reactant. The resulting anionic species could collapse to form $B_{10}H_{10}^{2-}$ with the expulsion of the ligand molecules (58). The nature of the rate-determining step is not clear at the present time nor is it possible to state that the rearrangement process is concerted or involves discrete intermediates.

The suggested geometrical change has been confirmed (58) by determining the location of deuterium atoms in the $B_{10}H_{10}^{2-}$ produced from 1,2,3,4-tetradeuteriodecaborane-14 (9). In agreement with prediction, the resulting $B_{10}H_{10}^{2-}$ ion exhibited a "half-collapsed" high field doublet in its B^{11} nuclear magnetic resonance spectrum. This could only come about if the 1, 2, 3, and 4-boron atoms were converted to equatorial positions in the $B_{10}H_{10}^{2-}$ ion. Figure 16 illustrates this point and the proposed mechanism.

C. SUBSTITUTED $B_{10}H_{10}^{2-}$ IONS

Knoth *et al.* (40) recently reported the preparation of a series of substituted $B_{10}H_{10}^{2-}$ ions. These materials were, in essence, prepared by electrophilic substitution reactions. Details of this work are not available at the present time.

The $B_{10}H_{10}^{2-}$ ion was totally or partially halogenated by reaction with the halogens in aqueous or ethanolic solution. $B_{10}Cl_{10}^{2-}$, $B_{10}H_3Br_7^{2-}$, $B_{10}H_6I_4^{2-}$ and $B_{10}I_{10}^{2-}$ are examples of halogenated ions of this type (40). It was reported that $Cs_2B_{10}Cl_{10}$ was thermally stable to at least 400°C and inert to strong nucleophiles such as hydroxide and methoxide ions.

The hydronium ion salt of $B_{10}H_{10}^{2-}$, $(H_3O)_2B_{10}H_{10} \cdot XH_2O$, proved to be an important reagent in a wide variety of substitution reactions (40). As examples, $B_{10}H_9COC_6H_5^{2-}$ and $B_{10}H_9CH(CH_3)C_6H_5^{2-}$ were prepared from this reagent and benzoyl chloride and styrene, respectively. Chlorination of $B_{10}H_9COC_6H_5^{2-}$ produced $B_{10}Cl_9COC_6H_5^{2-}$. Oxidation of $B_{10}H_9COC_6H_5^{2-}$ with hydrogen peroxide produced $B_{10}H_9OCOC_6H_5^{2-}$. Amides, thioethers, ethers, alcohols, and other similar reagents react with the hydronium ion salt to produce substituted derivatives. Examples of these products are $B_{10}H_9N(CH_3)_2H^-$, $B_{10}H_9(CH_3)_2S^-$, $B_{10}H_8 \cdot 2(CH_3)_2S$ and $B_{10}H_9OCHO^{2-}$. Preliminary work (40) indicates that the $B_{10}H_{10}^{2-}$ ion is most sensitive to electrophilic attack at the apical positions since $B_{10}H_8 \cdot 2(CH_3)_2S$ is sub-

stituted in both apical positions. Similarly acid-catalyzed deuterium exchange initially occurs in the apical positions.

Hoffmann and Lipscomb (35) have carried out a series of molecular orbital calculations for the $B_{10}H_{10}^{2-}$ and substituted $B_{10}H_{10}^{2-}$ ions. From the results of these calculations these authors were able to predict the observed preference for electrophilic attack at the apical positions. By consideration of the resonance and inductive effects present in substituted $B_{10}H_{10}^{2-}$ ions the sequence of further electrophilic substitution was obtained. It is exceedingly clear that the first and second substituents which enter the $B_{10}H_{10}^{2-}$ ion must become attached to the two apical positions.

The preparation of $B_{10}H_9OH^{2-}$ by Kaczmarczyk *et al.* (37 and Section VIII,D) led to a product with the substituent initially located at an apical position. The large high field doublet, initially like that in $B_{10}H_{10}^{2-}$, of the B^{11} nuclear magnetic resonance spectrum became unsymmetrical after a few hours. This change suggested that the $-OH$ substituent had migrated to an equatorial position. A novel, and thus far substantiated, rearrangement was postulated (37). In this process the original $B-OH$ bond does not break, but rather, the polyhedron rearranges in such a fashion as to interconvert apical and equatorial positions with a surprisingly small movement of boron atoms. A further apparent example of this rearrangement is described in the following section (VIII,D). The generality of this type of rearrangement has not been fully examined, but it must be considered in treating the chemistry of all polyhedral ions and derivatives.

D. HYDROGEN-BRIDGE LINKED POLYHEDRAL IONS

In 1961 Lipscomb (47) presented arguments for the possible existence of ions which were derived from the known $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ (Section IX) ions by linking these simple polyhedra through hydrogen bridges. In the $B_{10}H_{10}^{2-}$ series these predicted species were $B_{20}H_{19}^{3-}$ and $B_{20}H_{18}^{2-}$. Figure 17 presents one possible structure for $B_{20}H_{19}^{3-}$ and two possible structures for $B_{20}H_{18}^{2-}$. Other isomers may be devised, but their existence is considered unlikely for steric reasons. The electronic structure within each B_{10} polyhedron is assumed to be the same as in the parent $B_{10}H_{10}^{2-}$ ion. The process of bridge-hydrogen linking may be looked upon as the replacement of two $B-H$ bonds, one from each $B_{10}H_{10}^{2-}$ ion, by a $B-H-B$ bridge. An infinite chain of doubly linked B_{10} polyhedra would approach the composition $(B_{10}H_8)_n^{2-}$. The resulting polymer would retain a net $2-$ charge, however (47).

Oxidation of the $B_{10}H_{10}^{2-}$ ion with aqueous acidified ferric ion (59) has been reported to produce one $B_{20}H_{18}^{2-}$ ion isomer. Similar oxidation reactions which employed ceric ion at low temperatures produced a second

$B_{20}H_{18}^{2-}$ ion isomer (62). The product of the ferric ion oxidation was tentatively assigned the asymmetrical structure and the ceric ion oxidation product was assigned the symmetrical structure (62). It was shown (62) that the presumed symmetrical isomer could be converted to the asymmetrical isomer by treatment with aqueous acids. It is likely that the symmetrical ion is a precursor to the asymmetrical ion. At the present time this novel acid-catalyzed rearrangement is looked upon as another example of B_{10} polyhedron inversion cited above (Section VIII,C) and presumably occurs without breaking bridge-hydrogen linkages.

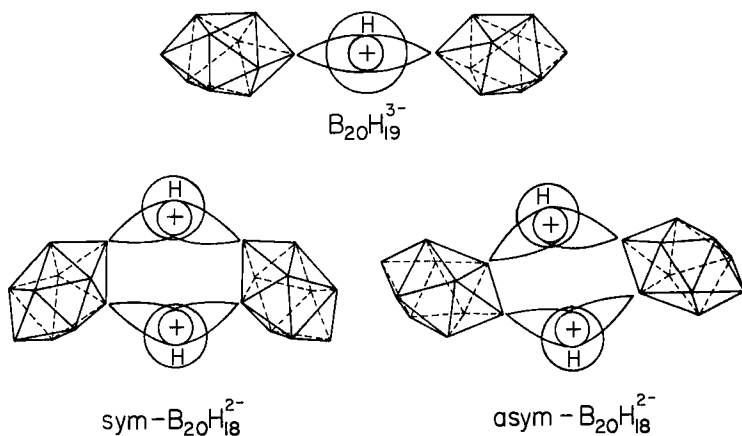


FIG. 17. Approximate geometries of $B_{20}H_{19}^{3-}$ and two $B_{20}H_{18}^{2-}$ isomers.

Treatment of the asymmetrical isomer of $B_{20}H_{18}^{2-}$ with aqueous hydroxide ion leads to the production of apically substituted $B_{10}H_9OH^{2-}$ in quantitative yield (37). On aging, the $-OH$ substituent appears, in part, in an equatorial position on the B_{10} polyhedron (Section VIII,C).

The heterogeneous reaction of $CuCl_2(s)$ with $K_2B_{20}H_{10}(s)$ in diethyl ether and other organic solvents produces a novel free radical which is soluble in diethyl ether and purple in color (37). The absorption band found at $550\text{ m}\mu$ is similar to that of known Cu^{II} complexes. Electron spin measurements yield a g value of 2.018 which is small for Cu^{II} but large for free radicals derived from first-row elements (excluding NO). The B^{11} nuclear magnetic resonance spectrum is smeared but resembles the characteristic $B_{10}H_{10}^{2-}$ spectrum (Fig. 15). It was suggested by the discoverers of this reaction that this unusual species is a Cu^{II} complex with a monomeric or polymeric H-bridged B_{10} polyhedron containing species in which the free electron resides most often, but not always, in the B_{10} framework.

Treatment of the presumed asymmetrical $B_{20}H_{18}^{2-}$ ion with an acid ion-exchange resin in ethanol solvent leads to the formation of the salt

$(C_2H_5OH)_2B_{20}H_{18}$ which was not isolated. Concentration of this acidic solution followed by the addition of water produced a new boron hydride in 70% yield (60). This hydride has been formulated as $B_{18}H_{22}$ and is of unknown structure. Titration of this B_{18} hydride with base proved it to be a strong monoprotic acid. The $B_{18}H_{21}^-$ ion is bright yellow in color with maxima at 216 and 352 $m\mu$.

The reaction of nitrogen dioxide alone or nitric oxide in the presence of ferric ion with the $B_{10}H_{10}^{2-}$ ion produces a variety of highly colored nitrogen containing products (81). One of these materials has been characterized (48) as a substituted $B_{20}H_{19}^{3-}$ ion, $B_{20}H_{18}NO^{3-}$. The substituted $B_{20}H_{18}^{2-}$ ions $B_{20}H_{14}(NO)_4^{2-}$ and $B_{20}H_{12}(NO)_6^{2-}$ are formed in significant amounts by the same method. The original report of these compounds (81) was incorrect in that molecular weight and precise analytical data were not available. The formulas above are based upon the deductions of Lipscomb (47, 48). Hydrogenation of these nitrososubstituted ions with a Raney nickel catalyst produced the corresponding amino derivatives (81).

IX. The Icosahedral $B_{12}H_{12}^{2-}$ Ion

A. PREPARATION AND STRUCTURE

The obscure reaction of 2-iododecaborane-14 with triethylamine at the reflux temperature in benzene solution produced the triethyl ammonium salts of the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ ions (61). The latter ion was isolated in little more than trace quantities and this method does not constitute a practical synthesis. Later work reported (40) by investigators at the du Pont Company suggests that a practical synthesis of $B_{12}H_{12}^{2-}$ must have been achieved. No other information has been made available on this point.

The $B_{12}H_{12}^{2-}$ ion exhibited a simple doublet in its B^{11} nuclear magnetic resonance spectrum (61) and the icosahedral geometry of this ion shown in Fig. 2 was observed by Wunderlich and Lipscomb (84) from single crystal X-ray diffraction studies with $K_2B_{12}H_{12}$. Longuet-Higgins (50) reported simplified molecular orbital calculations for this ion which were consistent with a 2- net charge. Later calculations by Moore *et al.* (53) employed another and more general technique and produced results for related B_{11} hydrides and ions, as well.

B. SUBSTITUTED $B_{12}H_{12}^{2-}$ IONS

Knoth *et al.* (40) have reported the preparation of a series of substituted $B_{12}H_{12}^{2-}$ ions. The experimental methods employed were identical to those reported for the preparation of substituted $B_{10}H_{10}^{2-}$ ions (Section VIII,C). Direct halogenation produced $B_{12}F_{12}^{2-}$, $B_{12}Br_{12}^{2-}$, $B_{12}Cl_{10}H_2^{2-}$, $B_{12}H_{11}I^{2-}$, $B_{12}I_{12}^{2-}$ and $B_{12}H_3Br_6Cl_3^{2-}$. Nitration with nitric acid produced the novel ion, $B_{12}H_{11}NO_2^{2-}$. Reaction of the hydronium ion salt $(H_3O)_2B_{12}H_{12} \cdot XH_2O$

with oxygen and sulfur containing donor molecules produced derivatives such as $B_{12}H_{11}OCH_3^{2-}$, $B_{12}H_{11}OH^{2-}$ and $B_{12}H_{11}OCOCH_3^{2-}$. Olefins produced alkylated ions such as $B_{12}H_{11}CH(CH_3)C_6H_5^{2-}$.

As in the case of the similar $B_{10}H_{10}^{2-}$ reactions, the mechanism of these reactions is obscure. The problem of sequential electrophilic substitution in the $B_{12}H_{12}^{2-}$ series has been attacked theoretically by Hoffmann and Lipscomb (35). Experimental evidence bearing on this point has not been presented.

Lipscomb (47) has presented arguments for the possible existence of hydrogen-bridge linked dimers and polymers derived from B_{12} icosahedra. Icosahedra linked by a single B—B bond was also suggested as a possible mode of polymerization. Although hydrogen-bridge linked molecules exist in the B_{10} polyhedra series, no compounds of this type have been reported with B_{12} derivatives.

X. Decaborane-16

A. PREPARATION AND STRUCTURE

A preparation and structure of a new "decaborane," decaborane-16, was recently reported by Grimes *et al.* (22). The new hydride was prepared by passing pentaborane-9 through a silent electrical discharge at low pressures and immediately trapping the effluent vapor with cold traps.

The determined structure of $B_{10}H_{16}$ (22) is that of two B_5H_9 molecules fused at the apices by a B—B bond with the loss of the apical hydrogen atoms originally present on the B_5H_9 molecules. Figure 18 indicates this

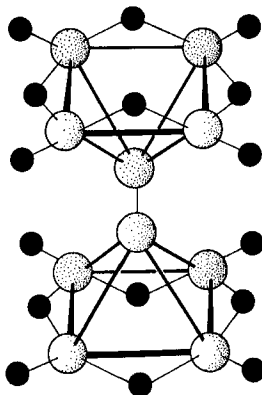
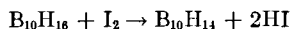


FIG. 18. Approximate geometry of $B_{10}H_{16}$.

geometry. The internal bonding in each B_5H_9 fragment was regarded as identical to that present in B_5H_9 (43).

B. REACTIONS OF $B_{10}H_{16}$

Grimes and Lipscomb (21) have examined a variety of reactions of $B_{10}H_{16}$. In every case, attempted reactions led to the formation of the known $B_{10}H_{14}$ or its derivatives. Thus, iodination of $B_{10}H_{16}$ at 150°C produced $B_{10}H_{14}$ and HI.



Aluminum chloride in carbon disulfide converts $B_{10}H_{16}$ to $B_{10}H_{14}$ without hydrogen or hydrogen chloride evolution.

Pyridine and $B_{10}H_{16}$ produced the same materials as were obtained from $B_{10}H_{14}$ and pyridine (Section VI).

The mechanism of these interconversion reactions has not been established. However, a plausible mechanism has been proposed (21) which is based upon topological arguments and the known rearrangement (54) of apical substituted alkylpentaborane-9 to the basal substituted isomer. The suggestion has also been made that the pyrolytic reaction of B_2H_6 to produce $B_{10}H_{14}$ proceeds via $B_{10}H_{16}$ (21, Section II,A).

Hydrogen iodide at room temperature cleaves the apex-apex bond with the formation of pentaborane-9 and iodopentaborane-9. At 100° this reaction produces a quantitative yield of pentaborane-9 while the iodopentaborane-9 is converted to polymeric products. Similar reactions were observed with hydrogen bromide at elevated temperatures.

Decaborane-16 is inert toward iodine and bromine in an anhydrous medium.

XI. Conclusion

As indicated by this brief review, the chemistry of the higher hydrides of boron has barely been touched. It is hoped that research workers and teachers will find this review useful. Its timeliness cannot be guaranteed.

Notes Added in Proof

1. A DERIVATIVE OF AN OCTABORANE

The compound referred to in Section VII,F(16, 19) as a $B_9H_{12}X^-$ anion ($X = C_2H_5NH_2$) has recently been shown [R. Lewin, P. G. Simpson, and W. N. Lipscomb, *J. Am. Chem. Soc.* (in press)] to actually be an octaborane derivative. Treatment of $B_9H_{13}X$ ($X = C_2H_5NH_2$) with ethylamine does not result in proton abstraction but rather produces a cleavage reaction with loss of a BH_3 group. The structure of the resulting compound, $C_2H_5NH_2B_8H_{11}NHC_2H_5$, is novel in that it contains a nitrogen atom in a bridge position. The determined structure shows this new octaborane derivative to be a icosahedral fragment and Figure 19 presents its structure in

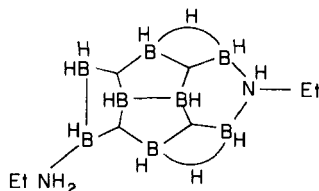


FIG. 19. Topological drawing of $\text{C}_2\text{H}_5\text{NH}_2\text{B}_9\text{H}_{11}\text{NHC}_2\text{H}_5$.

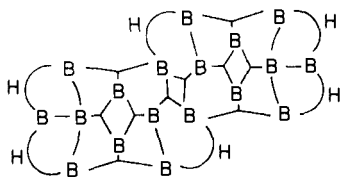


FIG. 20. Topological drawing of $\text{B}_{18}\text{H}_{22}$.

topological form. This new result does not exclude the probable existence of a $\text{B}_9\text{H}_{12}\text{X}^-$ anion with pyridine as the ligand, X.

2. THE STRUCTURE OF $\text{B}_{18}\text{H}_{22}$

The new boron hydride $\text{B}_{18}\text{H}_{22}$ described in Section VII,D(60) has been shown by single crystal X-ray studies [P. G. Simpson and W. N. Lipscomb, *Proc. Nat'l. Acad. Sci. U.S.* (in press)] to be closely related to $\text{B}_{10}\text{H}_{14}$. The determined structure of $\text{B}_{18}\text{H}_{22}$ is that of two decaborane molecules sharing boron atoms 6 and 9 in common. The topological structure of $\text{B}_{18}\text{H}_{22}$ is shown in Fig. 20. The unusual boron atoms which are shared in common by the two icosahedral fragments are each co-ordinated to six other boron atoms. In addition, a hydrogen bridge serves to connect each shared boron atom to one of its 6 neighboring boron atoms.

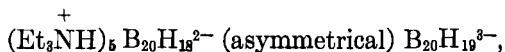
3. THE PREPARATION OF ICOSAHEDRAL 11,12-DICARBADODECABORANE

Very recently workers at the Olin Mathieson Chemical Corporation, [H. Schroeder, T. L. Heying, J. R. Reiner, *J. Inorg. Chem.* (in press)] have described the preparation of a carborane isoelectronic with the $\text{B}_{12}\text{H}_{12}^{2-}$ ion. This carborane, $\text{B}_{10}\text{C}_2\text{H}_{12}$, was readily formed from acetylene, decaborane and diethylsulfide in *n*-propyl ether at elevated temperatures. [C. C. Clark, U.S. Patent 3,062,756 (November 6, 1962).]

Chlorination of this new carborane results in successive replacements of hydrogen by chlorine at boron. In this manner $\text{B}_{10}\text{Cl}_{10}\text{C}_2\text{H}_2$ and $\text{B}_{10}\text{Cl}_{10}\text{C}_2\text{HCl}$ were prepared. Examination of the B^{11} nuclear magnetic resonance spectra of $\text{B}_{10}\text{C}_2\text{H}_{12}$ and its chlorinated derivatives indicates that the two carbon atoms were nearest neighbors in the icosahedral framework.

4. CORRECTION REGARDING $\text{B}_{20}\text{H}_{18}^{2-}$ ISOMERS

The oxidation of triethylammonium $\text{B}_{10}\text{H}_{10}^{2-}$ with ceric ion does not produce the second (symmetrical) isomer of $\text{B}_{20}\text{H}_{18}^{2-}$ (62) (M. F. Hawthorne and R. L. Pilling, unpublished results) as discussed in Section VIII,D. The product obtained is a double salt,



which has been separated into its component ions.

The hydroxide ion cleavage of asymmetrical $B_{20}H_{18}^{2-}$ yields $B_{20}H_{17}OH^{4-}$ rather than the previously reported apically substituted $B_{10}H_9OH^{2-}$ (37). These and other related results will be reported elsewhere in the near future.

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THE STRUCTURE AND REACTIVITY OF ORGANO-PHOSPHORUS COMPOUNDS

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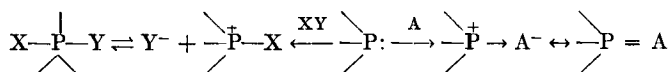
I. Introduction

Structural and mechanistic investigations of organo-phosphorus compounds have received considerable stimulus in recent years because of the importance of nucleic acids, coenzymes, and allylic pyrophosphates in living systems (170). Thus an organic phosphorus chemistry analogous to organic carbon chemistry has rapidly developed. The reactions of such compounds are usually classified under organic chemistry since the same experimental techniques are used, and some of the reactions are common to both elements. From an electronic point of view however, reactions at a phosphorus atom should undoubtedly be classified as inorganic, and the relationship between the structure and reactivity of organophosphorus compounds is therefore of interest in theoretical and mechanistic studies of inorganic chemistry.

In the present review we shall be concerned primarily with the structural description of 4- and 5-coordinated compounds in an attempt to provide a general basis for the interpretation of their reactivity. Before doing so the general basis of phosphorus chemistry will be discussed briefly.

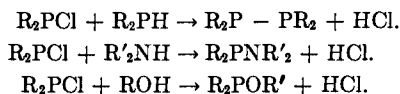
The electronic structure of elementary phosphorus, $1s^2 2s^2, 2p^6 3s^2 3p^3$ shows that three $3p$ orbitals are available for σ -bonding, thus giving rise to the trivalent compounds PX_3 . The valency angles* in phosphine (93°) show less sp^3 hybridization than in ammonia (106 – 107°), but the bond angles in the halides PX_3 (100 – 102°) are close to those in NF_3 (102.5°), which are probably determined by nonbonded repulsions.

The reactivity of such compounds, and most of phosphorus chemistry are determined by the behavior of the $3s$ electrons, and the main reactions may be represented briefly as follows,

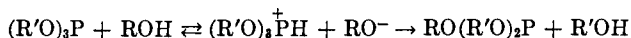


Tervalent phosphorus compounds are very reactive, passing readily into the sp^3 hybridized state by protonation, alkylation, the addition to Lewis acids (18, 174) and by complexing with transition metal ions (27). Many of these reactions have been reviewed recently, and the participation of ultimate d -orbitals in complex formation has been discussed (2).

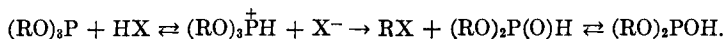
Further the trivalent phosphorus atom is highly electrophilic, and in this way resembles bivalent sulfur. Thus displacement reactions with nucleophilic reagents proceed rapidly, e.g.,



Trans-esterification (91, 92) of trialkyl phosphites is a rapid process, but it is not known whether the reaction proceeds via a quasi-phosphonium derivative,



although in acid solution this intermediate is rapidly de-alkylated (67).



Systematic investigations of nucleophilic displacement at the trivalent phosphorus atom of the kind recently made with sulfur compounds are necessary before the reactivity can be discussed further.

The substitution of alkyl groups in phosphine (87a) produces large increases in basicity (e.g., $PH_3 \rightarrow Me_3P$; $\Delta pK \simeq 22.5$) in contrast to the

* Unless stated otherwise, bond lengths and bond angles are taken from "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.* 11, 1958.

small changes for amines (e.g., $\text{NH}_3 \rightarrow \text{Me}_3\text{N}$; $\Delta pK < 1$), which may be attributed to strong inductive effects, probably produced partly by hybridization changes, steric effects being relatively unimportant. (See however the nucleophilic order (87b) $\text{Me}_2\text{PEt} > \text{MeEt}_2\text{P} > \text{Me}_3\text{P} > \text{Et}_3\text{P}$.)

Aromatic groups reduce the basicity (43) but the effect is smaller than for the corresponding amines. Thus for methylamine and aniline, $\Delta pK_a = 6.2$, whereas for methyl phosphine and phenyl phosphine, a value of $\Delta pK_a \simeq 2$ may be estimated. This large difference may be attributed to weaker p_π - p_π bonding for the second row element on interaction of the lone pair electrons with the benzene ring, as predicted by the ultraviolet spectrum of triphenyl phosphine (106).

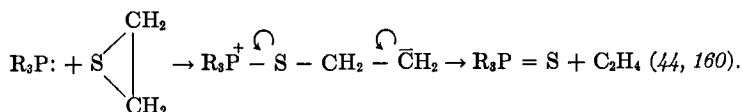
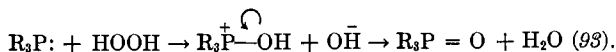
The short lived molecules P_2 , PO , and PN are probably stabilized by $3p_\pi$ bonds in view of the short bond lengths and relatively high dissociation energies. These are compared with the corresponding values for the nitrogen compounds in Table I.

TABLE I
A COMPARISON OF BOND LENGTHS AND BOND ENERGIES OF DIATOMIC
COMPOUNDS OF PHOSPHORUS AND NITROGEN

Bond	DAB	r_{AB}	Molecule	DAB	r_{AB}
P—P	50	2.18	P_2	116	1.894
P—N	67	1.80	PN	164	1.491
P—O	84	1.76	PO	143	1.448
P—S	55	2.14	PS	—	1.92
P—C	62	—	PC	159	1.562
N—N	12	1.40	N_2	225	1.095
N—O	48	1.36	NO	162	1.15

Apart from the existence of these unstable diatomic molecules, and the molecule HCP (68) there is little evidence of multiple bonding in trivalent phosphorus compounds, although several workers (152, 179) have reported the dimer $(\text{PhP})_2$. The structure of this and the alkyl analogues is in doubt as most workers believe them to be in the form of tetramers (114, 136) or higher cyclic polymers, and the structure $(\text{CF}_3)_5\text{P}_5$ has been investigated by X-ray analysis (165). These compounds are very reactive and in contrast to the corresponding azo compounds, the P-P bond is invariably broken (89, 90, 103).

The typical reactions of phosphines acting as nucleophiles lead to either phosphonium derivatives, or by oxidation to the quinquevalent state giving phosphoryl or thiophosphoryl derivatives. Thus oxygen and sulfur are rapidly removed from many compounds in reactions which may be regarded formally as nucleophilic displacements on oxygen and sulfur, e.g.,

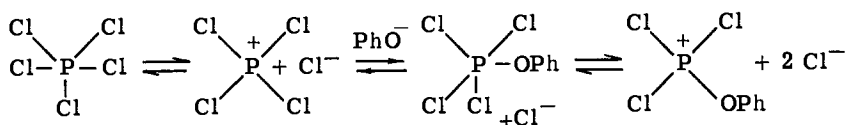


In many cases however, as for example in auto-oxidation (22) these are radical reactions.

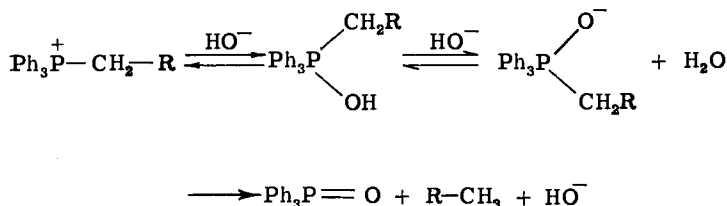
The basic structure of a phosphoryl compound is an sp^3 hybridized σ -bonded system, although the XPX angles are significantly less than 109° . This is usually attributed (138) to the influence of π bonding in the $P=O$ group, although the use of $3d_\pi$ orbitals for this purpose is highly controversial (see below). The bond angle decrease may alternatively be due to nonbonded repulsions.

Owing to the highly polar $P=O$ bond, the phosphorus atom is highly electrophilic. Displacement reactions at this center are therefore rapid, and phosphorylations, which will be discussed in more detail in a subsequent section have been widely investigated.

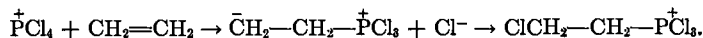
The bonding in phosphonium salts and pseudo-phosphonium salts is assumed to be sp^3 , although the bond angles have not been measured. Electronegative atoms interact strongly at the phosphonium center to produce 5-coordinated intermediates and rapid interchange of the groups, e.g., (154, 155).



The highly electrophilic nature of the phosphorus atom is shown by the displacement of carbanions by hydroxide (63) and alkoxide (71, 88) ions, e.g.,



and by the reaction of phosphorus pentachloride with olefins (13) which are very weak nucleophiles.

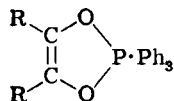


These and similar displacements involving phosphoryl and thiophosphoryl compounds may be regarded as passing through five coordinated transition states, sometimes producing stable intermediates. Before chemical reactivity is discussed in more detail therefore, the bonding and stereochemistry of these five coordinated compounds will be discussed further.

II. The Electronic Structure of PX_5

In the solid state PCl_5 and PBr_5 exist in ionic forms as $P^+Cl_4PCl_6^-$ and $P^+Br_4Br^-$ (29, 146), respectively, but in the gaseous phase both adopt the trigonal bipyramidal configuration like PF_5 and PCl_3F_2 .* In the case of PCl_5 (54, 131, 153) the axial and radial bonds are not equivalent (2.04 ± 0.06 and 2.19 ± 0.02), but in PF_5 they were assumed to be equivalent in the structural determination.

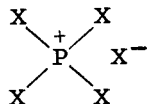
More recently, pentavalent molecules with less electronegative ligands, e.g., Ph_5P (185) and



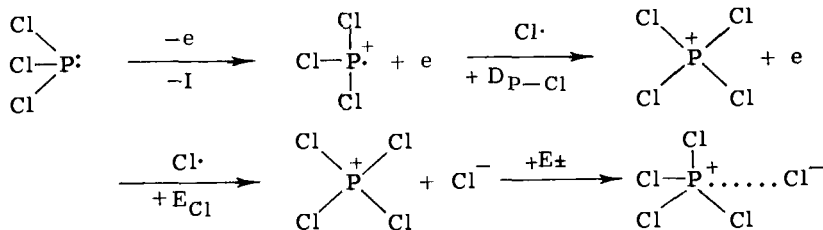
have been prepared, but the detailed structures of these are unknown.†

The 6-covalent ions, PF_6^- and PCl_6^- (only found in solid PCl_5), show octahedral symmetry (29) as anticipated.

In view of the high energy of $3d$ orbitals, and the influence of electronegative groups on the stability of 5-covalent molecules, Pauling (137) concluded that d -orbitals are not used and suggested resonance between the structures



That such a structure is energetically possible is readily shown by the following simple argument. Consider the sequence of processes



* See "Interatomic Distance," *Chem. Soc. Spec. Publ.* **11**, pp. M.54 and M.55, 1958.

† Note added in proof. Wheatley (182a) has shown that Ph_5Sb , Ph_5As and Ph_5P have square-pyramidal structures.

The total bond energy is given by

$$D_{P-Cl} + E_{Cl} + E \pm - I.$$

This gives a value of 47 kcal/mole ($I_{PCl_3} = 12.3$ ev) and 87 kcal/mole if allowance is made for the initial P-Cl partial ionic character in PCl_3 , compared with the experimental value of 78 kcal/mole (169).

According to Pauling the 5 atoms are held by the 3s and 3p orbitals, together with electrostatic attraction with the unit negative charge distributed over the 5 chlorine atoms. Although this explanation is energetically reasonable, the stereochemistry is not predicted, although the five "4/5 electron pair" bonds will take up a position of minimum electronic repulsion.

For this reason the use of *d* orbitals is usually invoked in spite of the high promotion energy. This is not known accurately, but an approximate value has been estimated (69) from the following excitation energies.

$$(1) \quad 3s^2 3p^3 \rightarrow 3s 3p^4 \sim 8 \text{ ev}$$

$$(2) \quad 3s^2 3p^3 \rightarrow 3s^2 3p^2 3d \sim 9 \text{ ev}$$

The combined value of 17 ev is overestimated by several electron volts by the repulsion of two *p* electrons in the same orbital in transition (1), but the actual valency state will be 2-3 ev higher than the lowest energy state given by (1) + (2). Thus the approximate value, 17 ev may be compared with the corresponding value 23 ev for nitrogen. Since the transition (1) gives the difference in energy of an electron in the 3p and 3s levels, the sum of this energy and the ionization potential of phosphorus (which refers to a 3p electron) gives an approximate value of 19 ev for the ionization potential of an *s* electron in the free atom.

The ionization potential (~ 10 ev for PH_3) and consequently the energy of the 3d level are reduced considerably by molecule formation, due to the presence of the additional electrons in the 3p orbitals, but the 3d promotional energy remains considerably greater than the energy of bond formation in PCl_5 (~ 3 ev). This is the main objection to the use of 3d orbitals in second row elements.

In an orbital description of the 5-coordinated system, the angular functions are such that hybridization of the *s*, and *p* orbitals with a *d* orbital leads to a bipyramidal arrangement (111). For effective hybridization the exponents characterizing the radial functions must be of similar size. Detailed calculations of Slater radial functions for ultimate 3d orbitals have been used to calculate the overlap integrals between the *s*, *p*, and *d* orbitals of the same atom and between these orbitals and a *p_σ* orbital of a chlorine atom (34, 104). Maximum overlap and hence maximum binding energy is given by a small contribution from the *d*-orbital, hence the bond-

ing is determined mainly by the sp^3 orbitals. Moreover the axial and radial bonds give maximum overlap for slightly different lengths, the former being slightly the longer.

Calculations of the $(3d_\sigma - 3p_\sigma)$ overlap integrals for the P-Cl bond show that the d -orbitals are too diffuse for effective bonding when the nuclear charges Z calculated by Slater rules, are equal. The overlap integral is very sensitive to the effective charges on the atoms (see Fig. 1), and becomes comparable to the corresponding values for s and p orbitals when*

$$\frac{\alpha_P - \alpha_{Cl}}{\alpha_P + \alpha_{Cl}} \sim 0.2$$

This and similar calculations (35) have led to the idea that d -orbitals are contracted by perturbation by the ligands. It has been suggested that the electrons in the $3d$ -orbital of the phosphorus atom are partially ionized and located on the chlorine atoms (34). This creates a positive charge on the phosphorus atom, which by causing preferential contraction of the more polarizable d -orbitals makes these compatible with the $3p$ -orbitals. In valency bond terms the resulting structure could be regarded as a resonance hybrid of the ionic $(PX_4^+X^-)$ and covalent, PX_5 , forms.

In a modified treatment, Craig and Magnusson (35) have shown that orbital contraction may be produced by the electrostatic field of the ligands, each regarded as a point charge Z_s , without ionization of the electron from the $3d$ orbital, due to the high polarity of the sp^3d hybridized bonds.

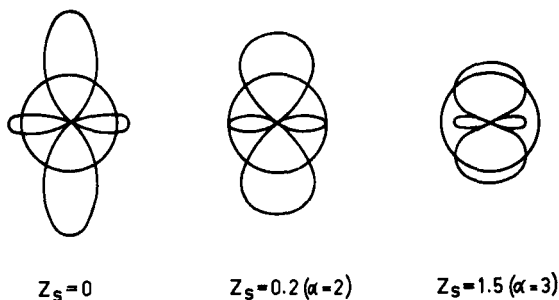


FIG. 1. The contraction of a d_z^2 orbital in the presence of perturbing ligands (35) with effective charges Z_s .

However, the increase in the central charge caused by the perturbing ligands *increases* the $3d$ promotional energy considerably, as an inner orbital is stabilized relative to a projecting orbital. For example, the energy of an electron in a $3d$ -orbital is increased by 8 ev by 6 unit charges at a distance

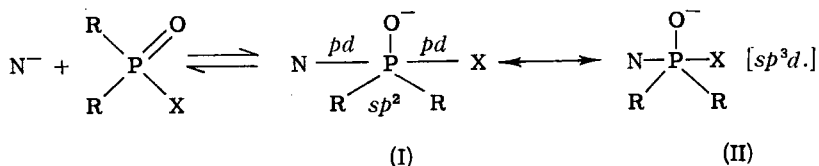
* $\alpha = Z/n$, where n is the effective principal quantum number.

of 4 a.u. assuming a spherical field, although this value is somewhat less for an octahedral field.

It follows therefore that the increase in the promotional energy is greater than the gain in energy by d -orbital hybridization and the importance of d_σ -orbitals in phosphorus chemistry is probably very small.

III. Configuration of the Transition State

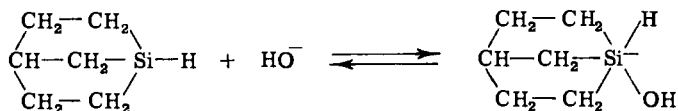
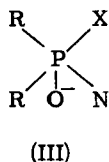
Although the contribution of d_σ -orbitals to the ground states of 5-coordinated phosphorus compounds may be small, the importance will increase in excited states and pd hybridization may well stabilize the transition state of a displacement at 4 coordinated phosphorus. According to Gillespie (69) three of the 4 original sp^3 bonds rehybridize to give sp^2 bonds leaving a more diffuse p -orbital which hybridizes with the d_{z^2} -orbital to give pd hybrids (I). These bonds will be relatively polar, and the structure is very similar to an S_N2 transition state, viz.,

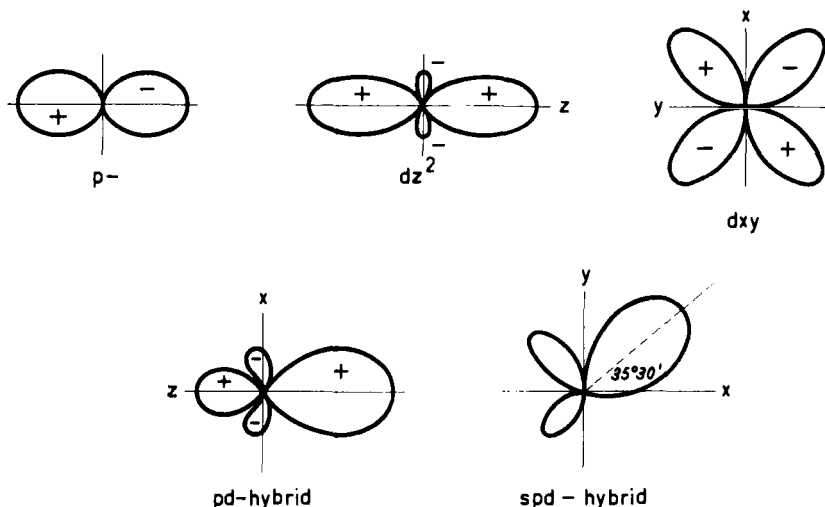


This description of the transition state is supported by the absence of O^{18} exchange of the phosphoryl oxygen atom in the hydrolysis of chlorides (53) fluorides (84) and esters (80), suggesting that the two P-O bonds of a possible intermediate diol are not equivalent, as would be the case in (II).

Alternative forms of hybridization are possible, and Gillespie (69) has shown that an sp^3 -orbital may hybridize with a suitably orientated d -orbital (d_{xy}) to give two equal spd bonds, mutually inclined at 71° .

In this structure, (III), 3 bonds remain in the sp^3 hybridized state. Although there is so far no evidence for this structure in phosphorus reactions, the high reactivity of the bridgehead silicon compounds (164) may be due to this transition state.

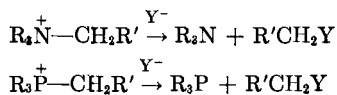


FIG. 2. *pd* and *spd* hybrid orbitals (69).

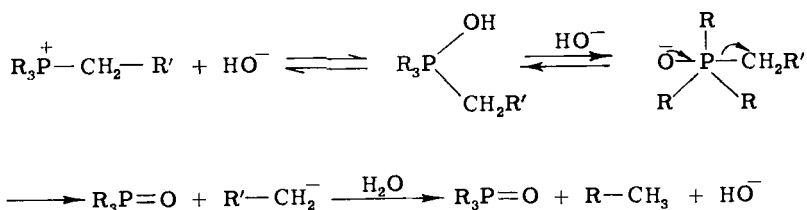
Evidence on the nature of the transition state for phosphorus may be obtained from optical activity studies, since structure (I) would lead to inversion, structure (II) to inversion and retention, and structure (III) to retention of configuration, and considerable advances in this direction have been made in the past 2-3 years.

IV. Reactions of Phosphonium Compounds

Differences in the reactions of quaternary phosphonium and ammonium salts also suggest that *d*-orbitals may be used in the former cases. Thus although halide ions and other reagents which are highly reactive towards the saturated carbon atom give de-alkylation (62), viz.,

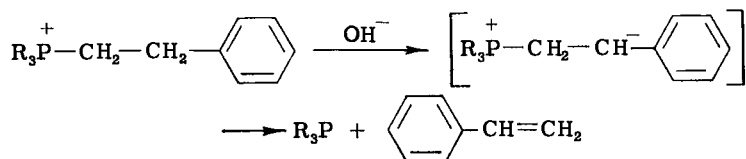


hydroxide (88) and alkoxide (71) ions, which produce β -elimination with quaternary ammonium compounds (102), give the corresponding paraffins with phosphonium salts. Kinetic studies (189) have shown these reactions to be second order with respect to base, suggesting the following mechanism,

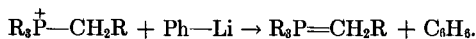


Recent work with optically active phosphonium salts has shown that this reaction is stereospecific (116) giving the phosphinoyl which was originally characterized by Meisenheimer (125, 126). This reaction probably involves inversion of configuration in view of the comparison with the Wittig reaction given below.*

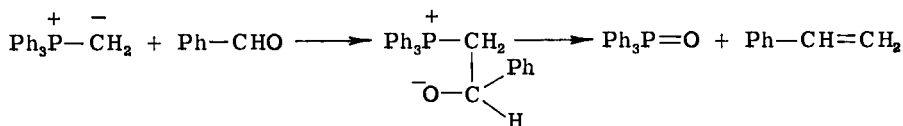
In view of the strongly electrophilic nature of the phosphorus atom, β -elimination from phosphonium compounds is only observed (63) when the incipient carbanion is stabilized by conjugation, e.g.,



Alternatively strong bases can remove an α -proton (166, 184) to give the phosphomethylene (or ylid), the stability of which is usually attributed to $d_\pi - p_\pi$ bonding (see p. 362)

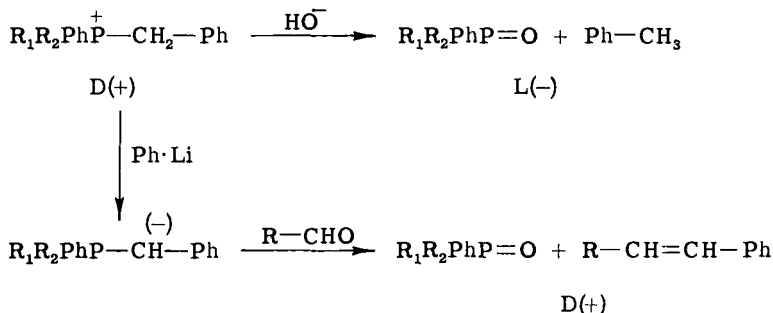


Phosphine methylenes are very reactive towards electrophilic reagents in particular towards the carbonyl group (186) giving the celebrated Wittig reaction (158). The intermediate has been isolated in the reaction of benzaldehyde (186) so the reaction presumably occurs by way of a four-membered ring with entering and leaving groups on the same side of the phosphorus atom.

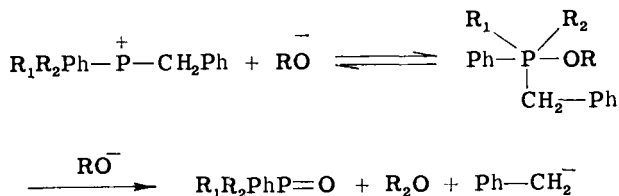


By carrying out this reaction with the optically active methyl ethyl phenyl benzyl phosphonium salt an optically pure phosphinoyl was obtained with opposite rotation to that obtained by the displacement reaction with hydroxide ions. By assuming that, of these two processes, the Wittig reaction is the more likely to proceed with retention of configuration, it follows that the displacement proceeds with complete inversion (15)

* The work of Horner *et al.* (93a) supports this view.

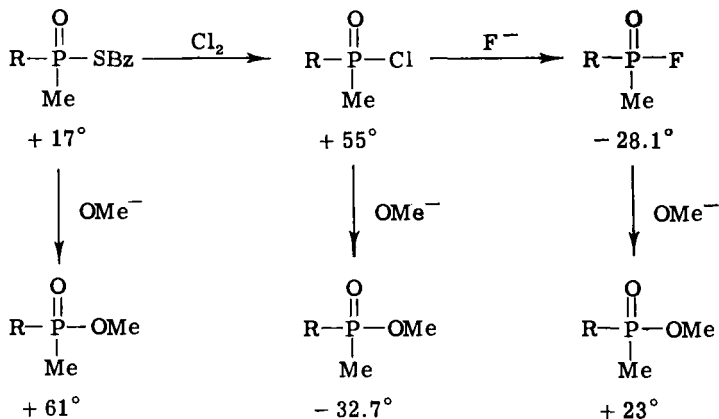


It is significant that in the corresponding displacement by alkoxide ions, the phosphinoyl is racemic (135), thus indicating that a 5-coordinated intermediate is formed, the decomposition of which is slow compared with the reversion to the original ions, viz.,



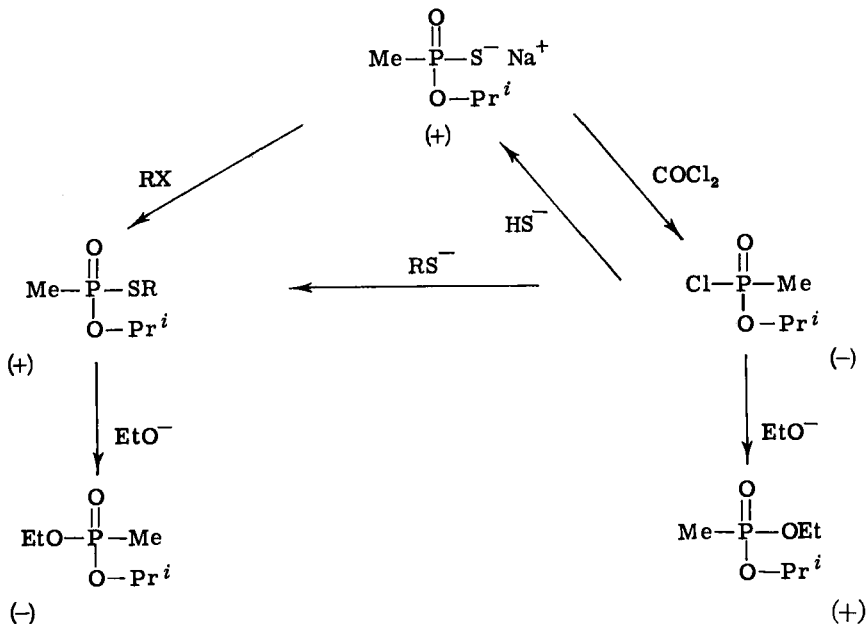
V. Stereochemical Change on Phosphorylation

Optical activity studies of phosphorylation are particularly difficult owing to the frequently rapid racemization (probably due to traces of anions present) of the compounds. Several workers have carried out cycles which show that inversion of configuration occurs predominantly in some reactions. Thus Green and Hudson (74) have carried out the following series of reactions.



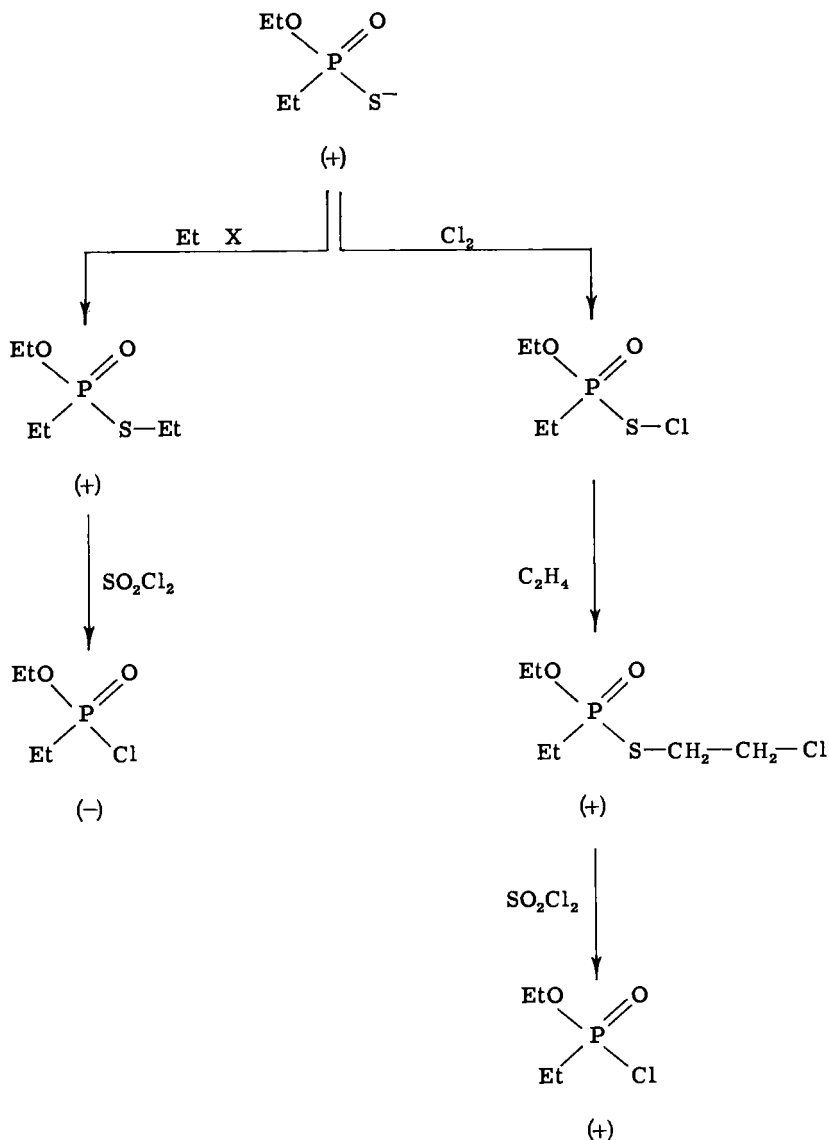
In these experiments the products were not isolated, as the reactions were known to proceed to completion, and distillation reduces the activities considerably. All activity measurements were made in benzene solution. Traces of fluoride ions were shown to racemize the phosphinic fluoride very rapidly.

A similar scheme has been established by Aaron and co-workers (1), who based the investigations on the chloridate as follows.

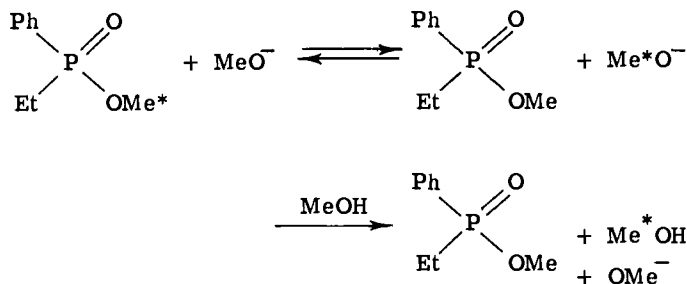


The chloridates were found to racemize very rapidly owing to traces of chloride ions or hydrochloric acid, and consequently products of low optical purity were obtained in these displacements and in the similar reactions carried out by Michalski and Ratajczak (127).

By assuming that the two displacements involving ethoxide ions involve similar stereochemical changes, Aaron *et al.* (1) concluded that the compounds $\text{Pr}^i\text{O}(\text{RS})\text{P}(\text{O})\text{Me}$ and $\text{Pr}^i\text{O}(\text{Me})\text{POCl}$ of different sign have different configurations. However this assumption must be applied with caution in view of the various observations with silicon compounds (163) that products of different sign are obtained by making relatively small changes in the reaction conditions. Moreover Michalski and Ratajczak obtained the same chloridate with different rotations, by chlorination of two different thiolates with the same sign of rotation,

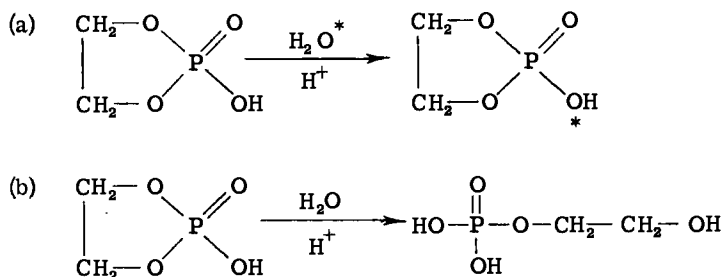


Very recently, the displacement of the methoxide group of methyl ethylphenylphosphinate by methoxide ions has been shown to be completely stereospecific proceeding with inversion of configuration (75). Thus the rate of racemization of the ester was found to be exactly twice the rate of displacement of the methoxide group labelled with C^{14} ,

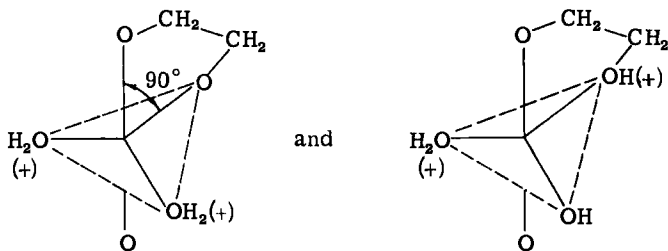


It appears therefore that, as in the case of silicon (163) inversion is the preferred configurational change in homogeneous solution.

By considering the reactions of strained cyclic esters (115), Haake and Westheimer (80) have shown recently that both O^{18} exchange (a) and hydrolysis (b) of ethylene hydrogen phosphate, proceed at similar rates in acid solution.

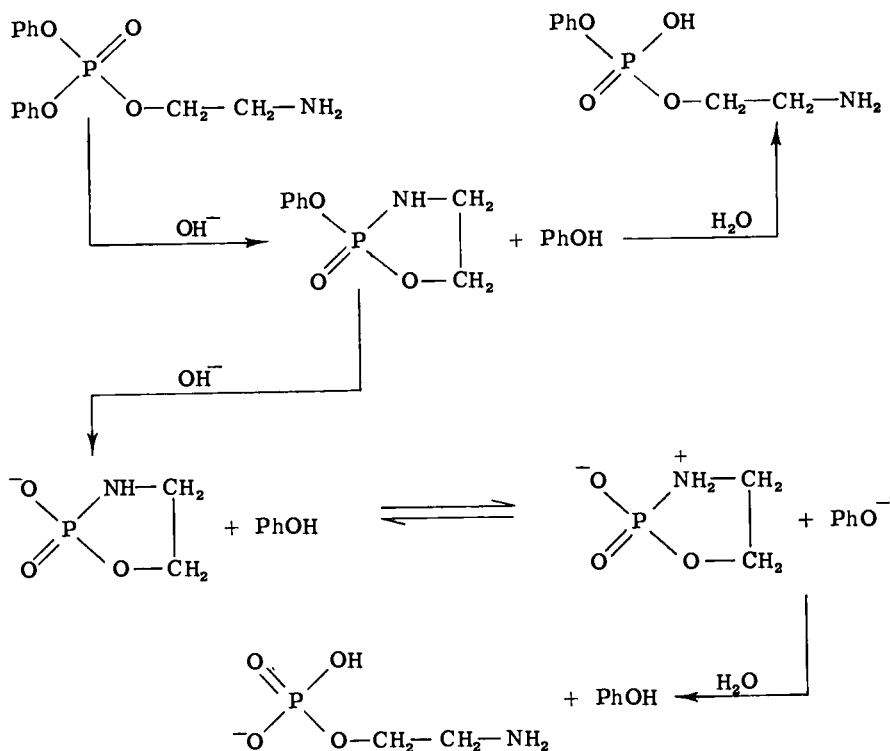


Since the rate of hydrolysis is about 10^7 times greater than the corresponding rate for diethyl phosphate, due to the release from steric strain on formation of the transition state (181), the O-P-O angle in the ring is considered to be the same in the transition states of (a) and (b). After considering various possibilities, transition states with O-P-O angles of 90° were considered to be the most likely, corresponding to a trigonal bipyramid or a square pyramid. In view of the less favorable electronic distribution in the latter case (111) these observations suggest that the transition state adopts the sp^3d hybridized form as follows:

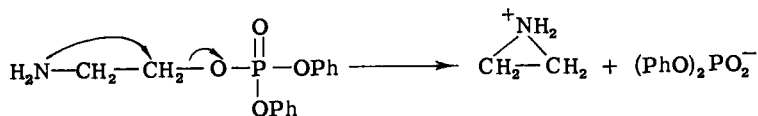


This configuration requires the sp^3d bonds in the basal plane to be weaker than the axial bonds, leading to inversion of configuration. This is an interesting suggestion, which requires further investigation with suitable conformations at the phosphorus atom.

The comparable rates of (a) and (b) suggest that displacement of the noncyclic group attached to a phosphorus atom which is also part of a 5-membered ring is extremely rapid. This may explain the rapid alkaline hydrolysis of 2-aminoethyl diphenyl phosphate with the liberation of two moles of phenol (55) since the monophenyl 2-aminoethyl ester is unreactive in alkaline solution, according to the scheme.



In dilute alkaline media, the reaction proceeds by the usual ionization reaction giving ethylene imine and its cyclic dimer (20)



Although studies of the configurational changes accompanying displacement are in a very early stage, the following tentative conclusions may be drawn:

(a) Displacements usually proceed through an S_N2 bimolecular transition state with the pd bonds weaker than the radial sp^3 bonds.

(b) In view of possible sp^3d and spd hybridization however, reaction may proceed by retention of configuration in suitable cases with velocities comparable to those observed in the more usual mechanism.

VI. The Symmetry of d_π - p_π Bonds

In carbon chemistry, changes in π -bonding affect the reactivity to such an extent that in many reactions conjugation changes outweigh σ -bond effects. It is very important therefore to ascertain whether conjugation is possible in phosphorus compounds.

Considering initially an isolated $P=O$ double bond, π -bonding can be formed as follows (34).

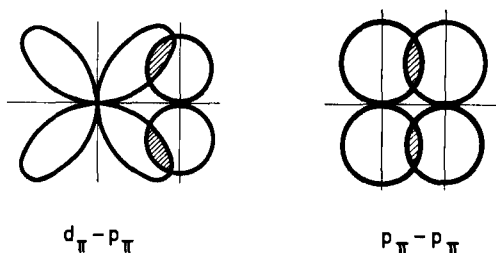


Fig. 3. A comparison of p_π - p_π and d_π - p_π overlap.

As with σ -bonds, d -orbitals are found to be too diffuse (if $Z_a = 0$) for significant overlap, but the overlap integral increases with positive charge on the phosphorus atom, thus conferring conditional stability to the d -orbitals (34), (Fig. 4). This is quite different from p_π - p_π overlap which is maximum when the two p_π -exponents are equal. Here overlap occurs in the region between the nuclei giving strong bonding, whereas d_π - p_π overlap occurs in the region of the oxygen atom, so that a d_π - p_π bond is necessarily polar. The bond is therefore weaker than a corresponding p_π - p_π bond, since overlap occurs in a region away from the phosphorus nucleus (34).

The symmetry and overlap will be affected considerably by the nature of the groups σ -bonded to the phosphorus atom. Thus the overlap will be most efficient if the O-P bond lies not only in the common nodal plane of the two orbitals but also in the plane defined by the vectors of maximum density of the d -orbitals. This situation is found in the C_{3v} symmetry of the system POX_3 , which could give two strong π -bonds between the phosphorus and oxygen atoms, using the d_{xz} and d_{yz} orbitals.

The orbitals in the xy -plane can overlap with the p_π -orbitals of the three X groups to give symmetrical overlap with the degenerate d_{xy} and $d_{x^2-y^2}$ orbitals (Fig. 5). The overlap is less than in the case of the P=O bond,

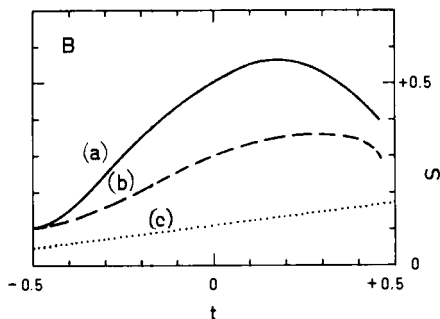


FIG. 4. Overlap integrals (S) for $3p_\pi-3d_\pi$ as functions of $t (= (\alpha_A + \alpha_B)/(\alpha_A + \alpha_B))$ with several values of $p (= \frac{1}{2}(\alpha_A + \alpha_B)r)$ where $\alpha_A = Z_A/n_A$ (Z_A is the effective atomic number of A and n_A the effective principal quantum number of atom A) and r is the internuclear distance in Bohr units.

since the p_π -orbitals lie out of the xy plane. The X groups can therefore conjugate weakly between themselves but not with the P=O group, thus giving a type of conjugation also possible for other symmetries, which is not found in $p_\pi-p_\pi$ conjugation.

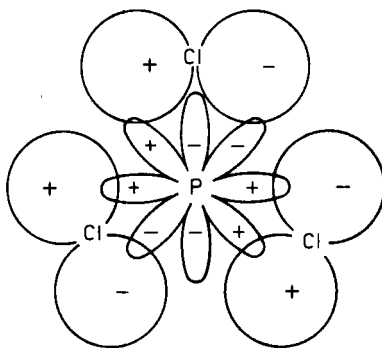


FIG. 5. Overlap ($d_\pi-p_\pi$) of the X_3 group of POX_3 (C_{3v}) (123).

If it is assumed that the P=O triple bond is considerably stronger than the π bonds formed by the other groups (123), this orientation provides a convenient basis for discussing d_π conjugation in the completely unsymmetrical case ABCP=O. In discussing the effect of substituents (the p_π exponents of which are usually less than those of the O atom) on the reactivity of phosphorylating agents (Section X), this symmetry will be used.

When strongly conjugating groups are present however, (in particular

in the case of oxyanions) other symmetries have to be considered (105), the most important of which, PO_4^{3-} and R_2PO_2^- , will be described briefly below.

In the absence of electrostatic fields, the five $3d$ -orbitals are degenerate. However the electron pairs of σ -bonds and the lone pair electrons of the ligands split the energy levels in a way which has been discussed in great detail in the case of penultimate d -orbitals (78). Since ultimate d -orbitals are not screened so well from the ligands, a similar splitting must occur here.

Tetrahedral symmetry (T_d) is such that the coordinates x , y , and z bisect the edges of the tetrahedron. Figure 2 shows that the d_{xy} , d_{xz} , and d_{yz} -orbitals have considerable amplitudes along the valency bonds, whereas the d_{x^2} and $d_{x^2-y^2}$ tend to avoid them. Thus the orbitals are split into two groups, a doubly degenerate group of lower energy ($d\nu$) and a triply degenerate group of higher energy ($d\epsilon$).

Reference to Fig. 6 shows that the $d\nu$ -orbitals have the correct symmetry to form π -bonds with p_π -electrons of the four groups to give two systems of molecular π -orbitals (40, 188). The overlap integral for this symmetry is given in Table II.

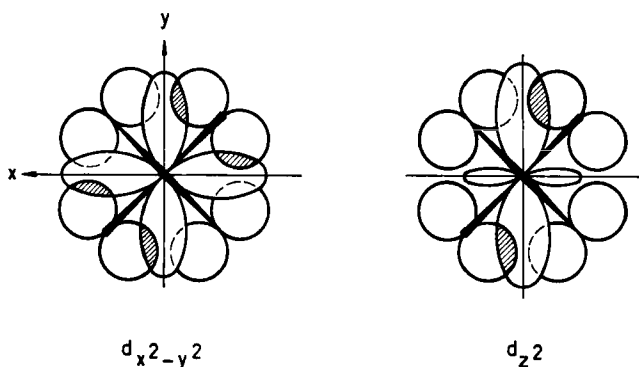


FIG. 6. Overlap (d_π — p_π) for the PX_4 system (T_d).

In the more general case, the following factors have to be considered (105): (a) maximum d_π — p_π overlap for the C_{3v} system is not in general observed for other 4-coordinated systems; (b) the orientation depends on the number and nature of the σ -bonded groups, e.g., the magnitude of the p_π -exponents.

In view of the strongly polar character of the $\overset{+}{\text{P}} \rightarrow \overset{-}{\text{O}}$ bond this will tend to take up the position of maximum d_π — p_π -bonding (123). An increase in the p_π -exponents of the groups A, B, and C will result in a decrease in $\text{P} = \text{O}$ π -bond energy (see Table VI).

In view of this competition for the d_π -orbitals and the relatively strong

$P=O$ π -bonds, other groups may use alternative d -orbitals in spite of the increased ligand field energy. Such π -bonding, which would not affect the $P=O$ bond except through polarity changes, is sometimes referred to as back coordination.

Of particular interest is the R_2XO_2 system (where $X = S$ or P) of symmetry C_{2v} for which the appropriate MO's have been considered in detail by Moffitt (129).

Here the formation of two molecular orbitals may be represented as follows (Fig. 7).

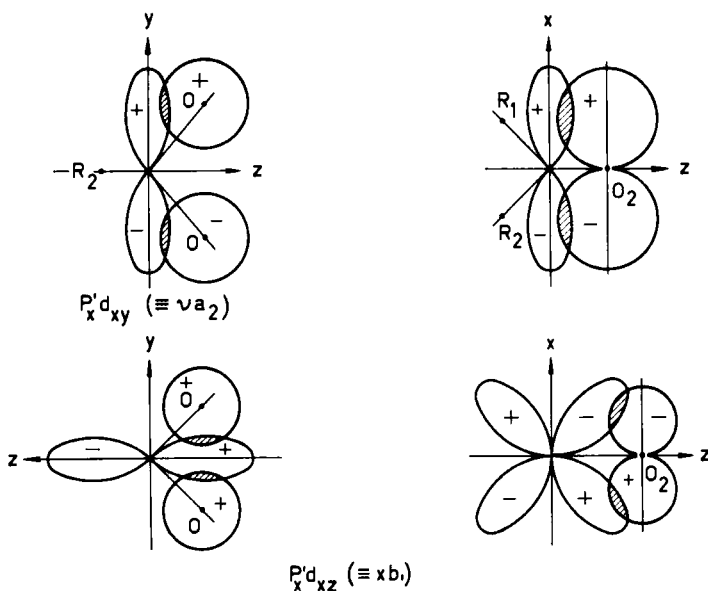
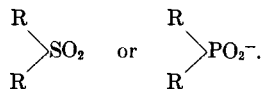


FIG. 7. Orbital overlap for the C_{2v} system showing (112) the formation of two different kinds of molecular orbitals (νa_2 and $x b_1$) for the groups



These orbitals can conjugate in two essentially different ways (112): (a) by using the νa_2 -orbital, strong conjugation is possible with p_r -orbitals on the groups R , to give a molecular orbital, the plane of which is rotated through 90° on passing through the phosphorus atom; this is equivalent to the conjugation described for the T_d system (Fig. 6); (b) this is a donor type of orbital which cannot conjugate with the $x b_1$ molecular orbital of the XO_2 group, as shown in Fig. 8.

This kind of conjugation like that described for the POX_3 system should not therefore affect the properties of the $\text{P}=\text{O}$ group.

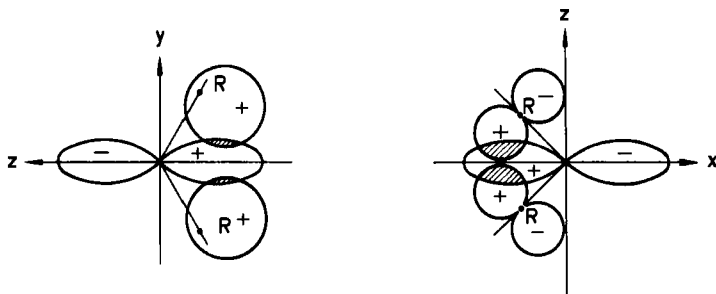


FIG. 8. Conjugation of the groups R in R_2SO_2 and R_2PO_2^- with the xb_1 orbital (112).

Jaffé (105) has pointed out that the p -orbital of the oxygen atoms in the xy -plane can conjugate strongly to give an orbital (wa_1) of the kind given in Fig. 9. This allows no conjugation with the R_2 groups, and hence is an alternative strong bonding orbital for the SO_2 or PO_2^- group.

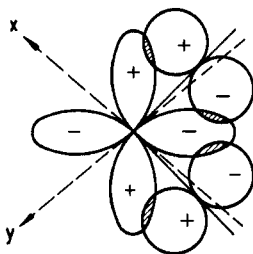


FIG. 9. An alternative strong bonding molecular orbital (wa_2) for the XO_2 system, incapable of conjugating with the R groups (105).

The relative group overlap integrals of the orbitals considered are given in Table II in terms of the overlap integral S , for an isolated $\text{P}=\text{O}$ bond.

The symmetry group C_{2v} also characterizes the stereochemistry of the very interesting phosphonitrilic compounds (134). Since p_π -orbitals of nitrogen are strongly conjugating, phosphorus and nitrogen should form relatively strong π -bonds. In these compounds, owing to the cyclic system, the p_π -orbital of the nitrogen atom can be orientated in one direction only (Fig. 10). Here the d_{yz} -orbital interacts with the p_π -orbital of the nitrogen atom to give p_π - p_π type of symmetry.

Owing to field splitting, this orbital is probably of higher energy than the d_{xz} -orbital which has symmetry of the kind shown in Fig. 11.

Construction of the appropriate molecular orbitals (33) leads to a doubly degenerate set of d_π - p_π orbitals, the special feature of which is that they do

TABLE II
OVERLAP INTEGRALS FOR VARIOUS CONFIGURATIONS IN TERMS OF
THE VALUE FOR THE ISOLATED P=O BOND

Compound	Configuration	Orbitals	Overlap integral
MA ₂ R ₂	Tetrahedral C _{2v}	xb_1	$(2/3)^{1/2}S$
		νa_2	$(4/3)^{1/2}S$
		wa_1	$4/3S$
	Square C _{2v}		$2^{1/2}S$
MA ₄	Tetrahedral, T_d		$2(2/3)^{1/2}S$
	E , or T_2		
	Square D_{4h} or octahedral O_h		$2S$

not conform to the Huckel $8-n$ rule. On the contrary, conjugation in the tetramer (Fig. 11b) is greater than in the trimer (Fig. 11a) as indicated by the symmetry considerations represented in a simple way in Fig. 11.

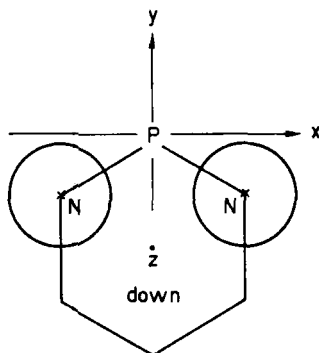


FIG. 10. Orientation of the nitrogen p_π -orbitals in the phosphonitrilic chloride system, (C_{2v}) (47).

Experimental data does not support a conventional aromatic structure for these compounds, e.g., the uv spectra is quite different from that of benzene and the broad maximum at $200\text{ m}\mu$ is independent of the number of atoms in the ring (161). The chlorides are not particularly inert, being readily replaced by nucleophilic reagents, e.g., fluoride ions, alkoxide ions and amines (134).

For these reasons an alternative structural interpretation has been proposed (47), involving hybridization of the d_{xz} and d_{xy} orbitals to give two degenerate orbitals with the plane lying close to the P-N bonds (Fig. 12). In this structure the N-P-N bonds may conjugate whereas the P-N-P

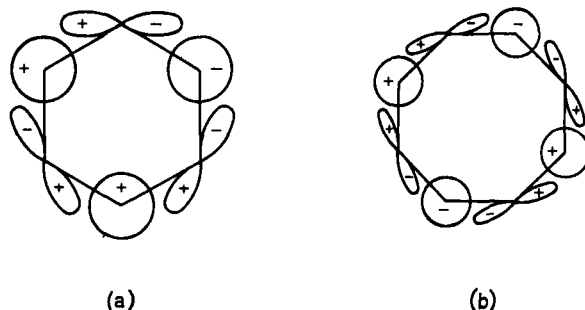


FIG. 11. Representation of conjugation in the phosphonitrilic trimer and tetramer.

bonds may not, giving rise to separate units similar to the allylic system. This interpretation retains the idea of π -bonding, and explains the equivalence of the P-N bonds, but predicts a nonaromatic structure. Further experimental evidence is required before the aromatic nature of these compounds can be ascertained.

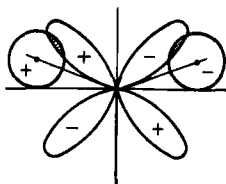


FIG. 12. Alternative conjugation of the "allylic" type in the phosphonitrilic chloride system (47).

VII. Experimental Evidence for d_{π} - p_{π} Bonding

A. BOND LENGTHS AND BOND ENERGIES

Although the orientation is highly favorable, the importance of d_{π} - p_{π} -bonding using ultimate d -orbitals is still a subject of controversy in view of the large difference in the energies of $3p$ and $3d$ levels.* Thus by constructing nonlocalized molecular orbitals for structures of T_d symmetry (Fig. 6), Wolfsberg and Helmholtz (188) have calculated the energies of excitation from the ground state non-bonding p_{π} -orbital (t_1) to the lowest excited state, that is an antibonding $3d_{\pi}$ - $3p_{\pi}$ hybrid ($3t_2$). The high energies for the perchlorate ion corresponding to absorption in the far ultraviolet suggests that the d -orbital exponent is too small for effective hybridization.

* See "Atomic Energy Levels," National Bureau of Standards Circular No. 467, Vol. I, p. 163, 1949.

Similarly PO_4^{3-} and SO_4^{2-} ions do not absorb* below 7–8 eV (21) suggesting that in these cases also the energies of the d -orbitals are too high for significant mixing with the corresponding s - and p -orbitals.

Conjugation in these systems must therefore be regarded as very weak compared with p_π - p_π -bonding involving first row elements.

With the advent of the Lewis theory the $\text{P}=\text{O}$ bond was assumed to be a coordinate bond (120), but the bond shortening of the oxy ions of phosphorus and sulfur was subsequently explained (140) in terms of d_π - p_π bond-

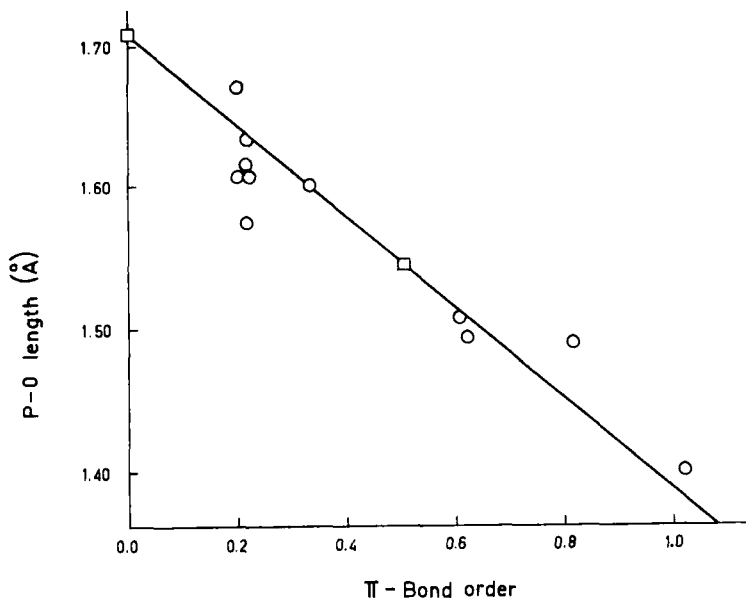


Fig. 13. The relationship between π -bond order and bond length for phosphoric acid derivatives (40).

ing. The correlation between bond order and bond lengths has recently been discussed in detail by Cruickshank (40). Assuming that each of the two equivalent d_π - p_π -orbitals (Fig. 6) is capable of π -bonding to four oxygen atoms, each P-O bond has a bond order of 0.5, in valence-bond terminology. For other structures the bond order is given by the number of π electrons available, e.g. for ROPO_3^{2-} , the RO-P π -bond order is 0.25, the P-O bond order is 0.583. In this way a linear relation between bond order and bond length is obtained (Fig. 13).

* The author wishes to acknowledge interesting discussions on this subject with Dr. Chr. Klixbüll Jørgensen of the Cyanamid European Research Institute, Geneva.

The significance of the bond shortenings has also been discussed by Phillips *et al.* (142), who drew attention to the high bond energies (Table III).

TABLE III
P=O DISSOCIATION ENERGIES

$D_{P=O}$ (kcal/mole)	Basis of determination	Reference
115	ΔH_f of P_4O_6 and P_4O_{10}	(113)
127.5	ΔH_f of PCl_3 and $POCl_3$	(132)
129.8	ΔH of oxidation of PF_3	(56)
121.8	ΔH_f of PCl_3 and $POCl_3$	(26)
119.3	ΔH_f of PBr_3 and $POBr_3$	(26)
131.0	ΔH of oxidation of $EtPCl_2$	(133)
134.1	ΔH of oxidation of $(Pr^iO)_3P$	(133)
138.3 ± 4	ΔH of oxidation of Pr^i_3P	(28)
~ 137	ΔH of oxidation of Bu_3^nP	(28)

The values are seen to vary considerably with the other groups attached to the phosphorus atom. By assuming the minimum value of 115.3 kcal for the P=O bond energy (113), Neale and Williams (133) obtained values for the energies of several single bonds including values of about 95 kcal/mole for the P-OP bond and about 104 kcal/mole for the P-OH bond. These values are compared with the values for trivalent phosphorus compounds in Table IV.

TABLE IV
SINGLE BOND ENERGIES FOR THE POX_3 AND PX_3 SYSTEMS (133)

Bond	D_{P-X} in POX_3	D_{PX} in PX_3
P—Cl	80	78
P—Br	65	63
P—OH	104	84
P—F	120	117
P—OP	96	$\sim 80(?)$
P—H	78	77

With the exception of the values for the P-O bonds, the agreement between the two series is surprisingly close in view of the hybridization differences. Smaller values would be obtained for the tetrahedral σ -bonds if higher values were taken for the P=O energy.

Although the estimated P=O bond energies (Table III) are significantly greater than the P—O bond energies, and approach the value for PO (Table I), no allowance has been made for changes in hybridization and

for increased ionic attraction of the four bonds. Thus the P-Cl bonds in PCl_4 are stronger than the bonds in PCl_3 (which is taken as the reference in thermochemical work) as shown by the shorter bond lengths (Table V).

TABLE V
BOND LENGTHS IN PHOSPHORUS HALIDES

Bond	PX_3	$^+\text{PX}_4$	PX_5	PX_6^-
P—Cl	2.04	1.98	2.04 ^a 2.19 ^a	2.07
P—Br	2.23	2.13	—	—
P—F	1.535 (1.52) ^b	—	1.54 (1.57) ^b	1.73

^a Axial and radial bonds.

^b Alternative values.

This may be attributed alternatively to π -bonding involving the chlorine atoms (see Table VI). By using a relationship between bond length, modified for polarity differences, and π -bond character, proposed by Pauling (139), Van Wazer (175) has estimated the degree of π -bonding per atom (Table VI) for the phosphoryl halides. It is seen that the π -bond order of

TABLE VI
 π -BOND CHARACTER IN PHOSPHORUS OXYHALIDES (175)

Molecule	POF_3	POCl_3	POBr_3
π -bonds/ σ -bond ^a	0.4	1.0	1.1
in P—O bond ^b	0.3	0.9	1.0
π -bonds/ σ -bond ^a	0.3	0.0	0.3
in P—X bond ^b	0.2	0.1	—
π -bonds in molecule ^a	1.3	1.0	2.0
π -bonds in molecule ^b	0.9	1.2	1.9

^a Based on σ -bond distance calculated according to Schomaker and Stevenson (159).

^b Based on σ -bond distance calculated according to Huggins (101).

$\text{P}=\text{O}$ decreases in the order $\text{Br} > \text{Cl} > \text{F}$, i.e., the order of increasing competition for the available d -orbitals (p. 364). No simple relation is found however between π -bonding of the halogen atoms, i.e., $F = \text{Br} > \text{Cl}$, and their electronic structure.

By comparison with amine oxides and boron-ether adducts, in which cases coordinate bonds are formed, Phillips *et al.* (142) estimated that the $\text{P} \rightarrow \text{O}$ coordinate bond has an energy of 40–70 kcal/mole compared with the values of 115–150 actually observed (Table III). Moreover the bond moment of the phosphorus oxygen bond in $(\text{CH}_3)_3\text{P}=\text{O}$ leads to an esti-

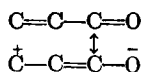
mate of ca 47% partial ionic character (27% in the sulfide) compared to 70% for $(\text{CH}_3)_3\text{NO}$ (121). Since nitrogen is more electronegative than phosphorus, the partial ionic character of $\text{P} \rightarrow \text{O}$ should be greater than that of $\text{N} \rightarrow \text{O}$ if both were coordinate.

This comparison of bonds formed with second row and first row elements has been criticized by Wells (180) who also pointed out that a comparison of the lengths of P-OP and P=O bonds is not valid owing to the different coordination numbers of oxygen. The decrease in polarity of the coordinate bond in $\text{Me}_3\text{N} \rightarrow \text{O}$ compared with the estimated value for $\text{N}^+ \rightarrow \text{O}^-$ must be due to polarization. In view of the greater polarizability of the phosphorus atom, the bond shortenings may well be electrostatic in origin as suggested by Pitzer (144).

He also pointed out that the inner shell repulsions are quite different for first and second row elements. Thus for N_2 the valency shell repulsion is important in determining the internuclear distance, whereas for P_2 repulsion between an inner shell of one atom and a valency shell of the other is more important. In a combination of oxygen and phosphorus therefore the equilibrium distance will be shorter than given by the Schomacher-Stevenson rule (159).

B. SPECTRA

In organic compounds, the strongest evidence for conjugation comes from spectra. Thus in an isolated C=O bond, the uv-absorption can be represented satisfactorily as an $n \rightarrow \pi$ transition, and conjugation, in the classical sense, e.g., in



leads to optical exaltation, and a decrease in the carbonyl stretching frequency.

The spectroscopic behavior of the corresponding phosphorus compounds in general is quite different. The infrared (9, 10) and Raman spectra (3) of a large number of phosphorus compounds have been examined, and the P=O vibration frequency shown to increase regularly with the electronegativity of the substituent (Fig. 14) (9). This generalization together with the regular decreases in the frequency increments with successive substitution is characteristic of an inductive effect.

Hydrogen bonding of the phosphoryl oxygen atom (3, 4), which is known to be nucleophilic (76), suggests that the P=O bond is conjugated. Since in $d_\pi-p_\pi$ -bonding, the overlap is a sensitive function of the charge on the phosphorus atom, and most conjugating groups are electronegative, conjugative electronic release to the P=O group would be difficult to detect.

Some evidence for conjugation is given by the phosphoroamidates. In some cases, R_2N groups give two bands for the $P=O$ group, one of greater and one of lower frequency (11) than the alkyl compound. Thus Me_2NPOCl_2 and $Me_2N(EtO)POCl$ show bands at 9.94 and 10.11, and 13.70 and 14.20, respectively. A single band is observed if the Me_2N group is replaced by an NH_2 group. The two bands might be due to rotational isomers, the higher frequency being produced by induction, the lower by conjugation promoted by steric control.

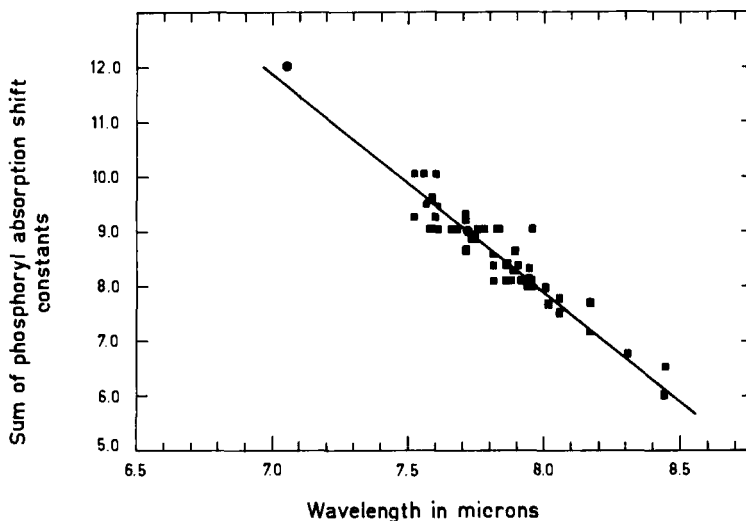
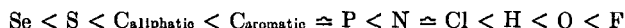


FIG. 14. The relationship between the wavelength of the $P=O$ stretching mode and shift constants related to the electronegativities of the substituents (9).

The ultraviolet spectra of a number of aryl phosphonic and diaryl phosphinic acids have been studied (8, 64, 106, 107, 145), and in no case is a large change in the benzene spectrum observed, and in particular the fine structure remains unaltered. The intensity is however increased by a factor of 1.5–5.0, and a bathochromic shift of about 10 $m\mu$ is observed (106). These small changes could be explained by weak conjugation between the benzene ring and the phosphorus atom. If this is so, substitution of a stronger conjugating group should lead to an exalted spectrum (162), and recently the spectra of tri α pyrrole phosphin oxide and the corresponding methiodide have been found (77) to be similar to the spectra of the corresponding ketones with similar extinction coefficients ($\sim 10^4$). The wavelength shift is however appreciably less than for the carbonyl derivatives, indicating weaker π -bonding.

The NMR spectra of phosphorus compounds, compiled by van Wazer

(176) also suggest different bonding for P^{III} and P^{IV} compounds. Thus trivalent phosphorus compounds show large changes in nuclear shielding, and large chemical shifts (~ 500 ppm), being attributed to changes in hybridization as shown by changes in bond angles. For 4-coordinated compounds the shifts are very small (50–100 ppm) probably due to the variation in the distribution of π bonds between the four groups. Electron shielding of the central nucleus by substituting atoms at the phosphoryl, or thiophosphoryl, group increases in the following order.



i.e., with the exception of H and P the order of electronegativity. This is opposite to the predictions of a simple polar theory, since the more electronegative elements are the most shielding. These results are rationalized if the second substituent withdraws electrons from a previously formed π bond of the $P=O$ or $P=S$ linkage in agreement with the bond length deduction (Table VI).

Finally, recent quadruple Cl^{35} coupling spectra measurements (123) are also in agreement with weak $d_{\pi}-p_{\pi}$ -bonding, and the shifts in the coupling frequencies for the phosphoryl compounds (123) although smaller, are related fairly closely to the corresponding values for carbonyl compounds. Thus, as discussed above, the strong $P=O$ bond and weaker conjugating groups X of the C_{3v} system probably use different $3d_{\pi}$ -orbitals, and consequently π -bonding of the groups X in general affects the $P=O$ stretching frequency, $\nu_{P=O}$, by the inductive effect only.

Thus a plot of the N.Q.R. coupling frequency against $\nu_{P=O}$, gives two approximately parallel lines, one for conjugating and the other for non-conjugating substituents.

C. ACID-DISSOCIATION CONSTANTS

The transmission of electrical effects across a phosphorus atom as influenced by π -bonding, should also be reflected in acid dissociation constants. Thus Jaffé *et al.* (108) have shown that p -substituted benzene phosphonic acids (8) obey the Hammett relation.

TABLE VII
VALUES OF THE REACTION CONSTANTS OF THE HAMMETT EQUATION FOR THE
DISSOCIATION OF ACIDS AND THE REFRACTIVITY OF THE
CORRESPONDING CENTRAL ION (108)

	ρ	Ion	Ion refractivity
$ArCO_2H$	1.00	C^{4+}	88
$ArAsO_3H_2$	0.95	As^{3+}	76
$ArPO_3H_2$	0.76	P^{3+}	67

The reaction constants ρ for phosphonic, arsonic, and benzoic acids are similar, and vary with the ionic refractivity of the central atom (Table VII).

This correlation suggests that the differences in ρ are determined by the transfer of electronic effects from the substituent to the OH group. Pressman and Brown (147) have however argued against the influence of a charged central arsenic atom in the dissociation of the arsonic acids.

D. CHEMICAL EVIDENCE FOR $3d_\pi$ BONDING

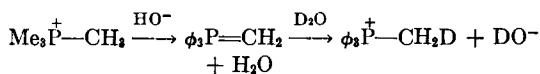
The stability of phosphinemethylenes relative to the corresponding nitrogen derivatives (186) is normally attributed to p_π - d_π bonding as mentioned in a previous section.

The reactivity of the α -proton in several cations has been investigated quantitatively by Doering and Hoffmann (49) who showed that tetramethyl phosphonium and trimethyl sulfonium ions undergo base catalyzed deuterium exchange much more rapidly than the tetramethyl ammonium ion (Table VIII). The orders $P > As > Sb$ and $S > Se > Te$ suggest

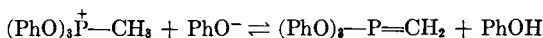
TABLE VIII
RATE OF DEUTERATION OF TETRAMETHYL CATIONS OF NITROGEN, PHOSPHORUS,
ARSENIC, AND ANTIMONY AND OF THE TRIMETHYL CATIONS OF
SULFUR, SELENIUM AND TELLURIUM (49)

Ion (central atom)	N ⁺	P ⁺	As ⁺	Sb ⁺	S ⁺	Se ⁺	Te ⁺
Exchange rate, log k	-9.75	-3.37	-4.61	-5.62	-2.44	-4.09	-4.63

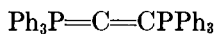
that the rate is not determined simply by electronegativity differences and that the high reactivities of the P^+ and S^+ ions are due to conjugation, viz.,



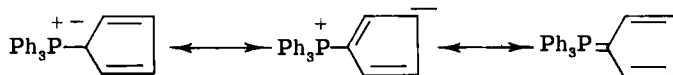
Phosphine methylenes can be formed more readily than originally anticipated, e.g., by the weakly basic phenoxide ion as in the following case (187)



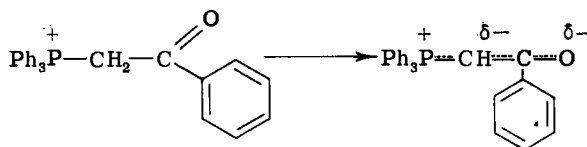
and by the formation of an allenic di-methylene (149)



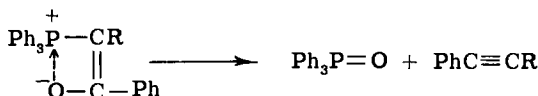
Phosphinemethylenes stabilized by conjugation may be readily prepared in the free state.* Thus the 9-fluorenyl trimethyl phosphonium ion, but not the corresponding ammonium ion gives an isolable fluorenylidide (143). Similarly a stable phosphonium cyclopentadienyliide has been isolated and the structure investigated by Ramirez (151). The u-v spectrum indicates strong conjugation with the ring, and the dipole moment corresponds to approximately equal contributions from the covalent and ionic forms.



The structure is also stabilized by α -carbonyl groups as in the phosphobetaines (150), the carbonyl frequency in which is low owing to the following conjugation



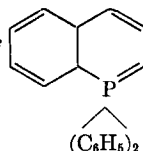
On prolonged heating, these reagents undergo an internal Wittig reaction (173), viz.,

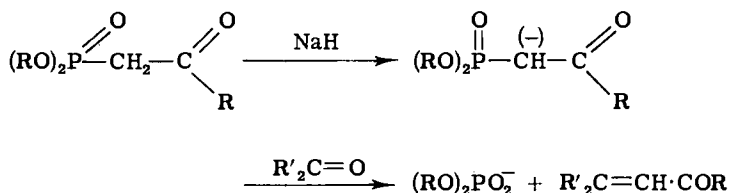


The strong conjugation in these betaines also explains the rapid racemization of optically active ethyl α -trimethyl phosphonium propionate under conditions where the corresponding ammonium salt is unaffected (14).

Similar reagents have been prepared from phosphate esters containing conjugating groups in the α -position (177), which undergo the following reaction.

* Märkl (123a) has recently reported the preparation of

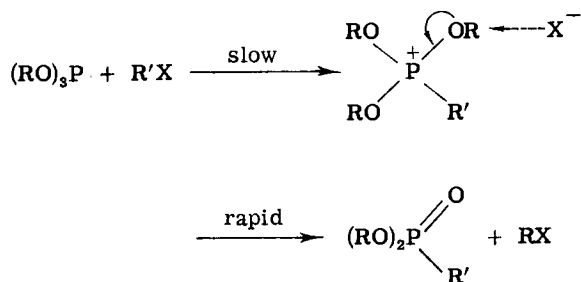




Similarly active reagents may be made from the phosphoramidates (178),



The main driving force in the Wittig type of rearrangement is the strong P=O bond formed, which is indicative of double bond formation. This affinity is characteristic of many reactions of phosphorus compounds, e.g., in the Arbusov rearrangement (5)

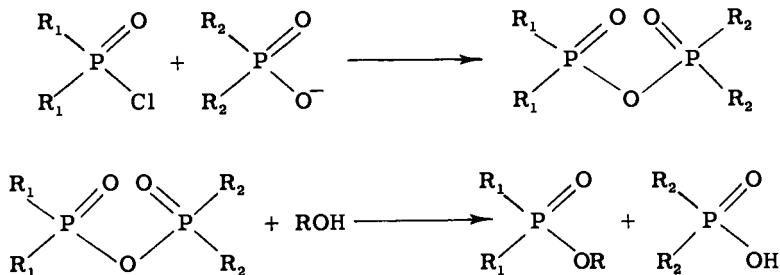


The intermediate has been isolated recently in the form of the borofluoride and perchlorate salts (48).

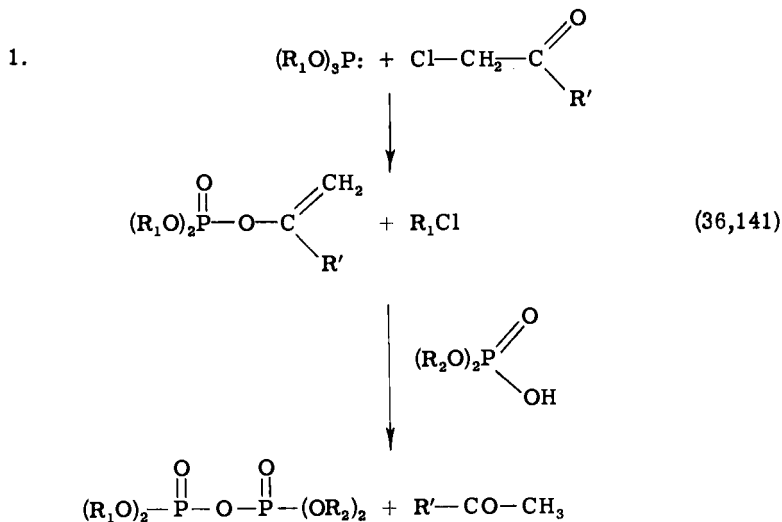
VIII. Phosphorylation

Quantitative investigations of the reactivity of phosphorus compounds have been limited to phosphorylation and related reactions at the phosphoryl group (51, 70, 86, 97, 118). Such studies which have been made only recently, have been stimulated by the great increase in preparative organo-phosphorus chemistry within recent years, and by the biological importance of phosphorylation.

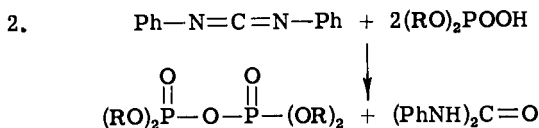
From a mechanistic point of view, phosphorylation reactions may be subdivided in the following way: (a) nucleophilic displacement of an acidic group by a nucleophilic reagent, as for example in classical phosphorylation reactions of the following type, which are analogous to acylation.



These may be regarded as simple bimolecular displacements, the lability of the groups increasing with their acidity in the case of unsymmetrical pyrophosphates (171); (b) the conversion of a nonphosphorylating agent into a phosphorylating agent, followed by reaction of an acid (in the Brønsted sense), e.g.,

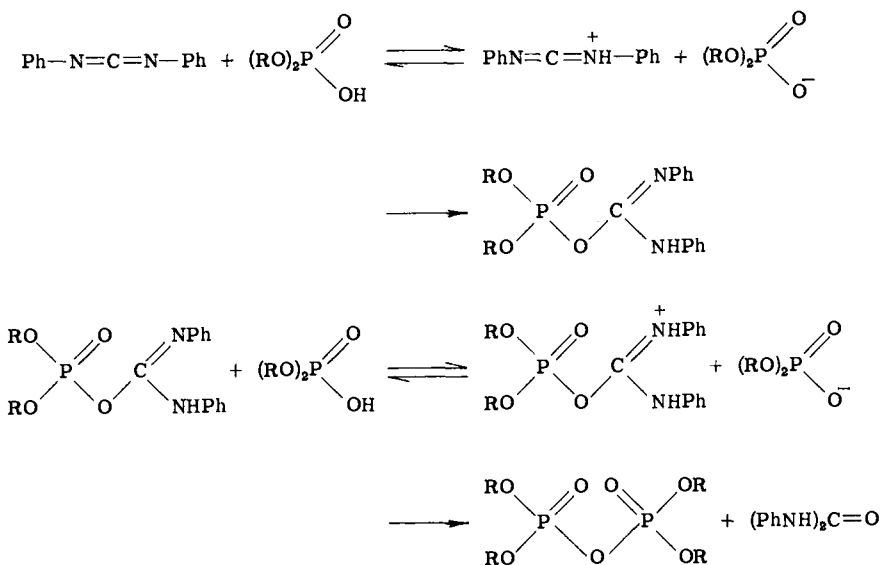


and

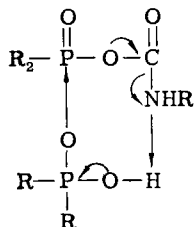


Since the first use of carbodimides (110), other similar reagents, e.g., isocyanates (38, 122) and trichloro acetonitrile (37) have been used. These

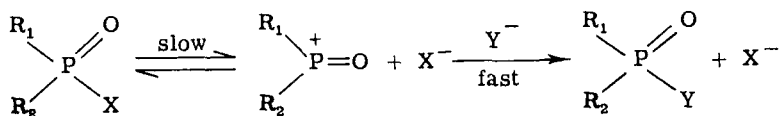
reactions may be regarded as proceeding through the protonated form, followed by a nucleophilic displacement of the kind given in (a), e.g.,



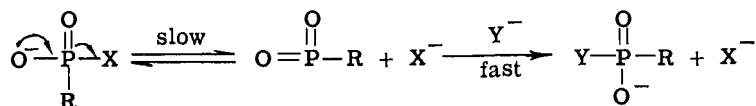
The phosphorylation stage essentially involves the attack of an anion on the phosphorus atom containing a positively charged leaving group, although this process may involve a cyclic transition state in some cases, e.g.,



(c) the possibility of pre-ionization (83), as in the formation of carbonium and acylium ions, followed by rapid phosphorylation,



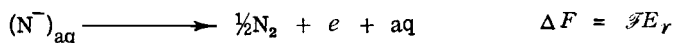
or alternatively the unimolecular release of a group from a phosphorus anion, e.g.,



From a theoretical point of view these reactions can be classified into two groups (a) bimolecular displacement on the phosphorus atom and (b) unimolecular ionization followed by rapid phosphorylation. The influence of the nucleophilic reagent, the reaction conditions and the structure of the phosphorus compound will be reviewed in the following sections.

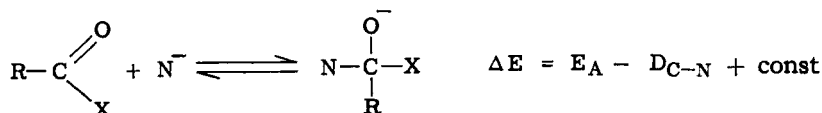
IX. The Influence of the Nucleophile on Phosphorylation

The similarity between phosphoryl and carbonyl compounds is further shown by the relative reactivity of various nucleophiles (94). It is well known (167) that highly polarizable ions and molecules, e.g., Br^- , I^- , CNS^- , $\text{S}_2\text{O}_3^{2-}$, and $(\text{NH}_2)\text{C}=\text{S}$ are particularly reactive towards the saturated carbon atom. The reactivity tends to follow the oxidation reduction potential (57), suggesting that the variations in the energy required to remove an electron from the nucleophile are more important (because of the influence of electronic repulsion) than the corresponding bond energy changes,



The rate is therefore controlled mainly by the apparent electron affinity (which includes solvation energy), E_A .

On the other hand, reactivity towards a more electrophilic (positively charged) center is more sensitive to bond energy changes (58). Thus the transition state structure for acylation may be close to that of the addition intermediate (12),



Since changes in the bond energy $D_{\text{C-N}}$ are usually greater than the changes in E_A , the nucleophilic reactivity tends to follow the bond forming energy, and hence the pK_a of the conjugate acid of the nucleophile (58).

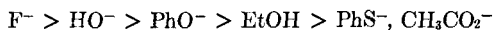
Nucleophilic reactivity may therefore be represented in general by an equation of the kind

$$\log (k/k_0) = \alpha pK_a + \beta E_r$$

first proposed by Edwards (57), where the relative magnitude of α and β gives a measure of the influence of bonding in the transition state.

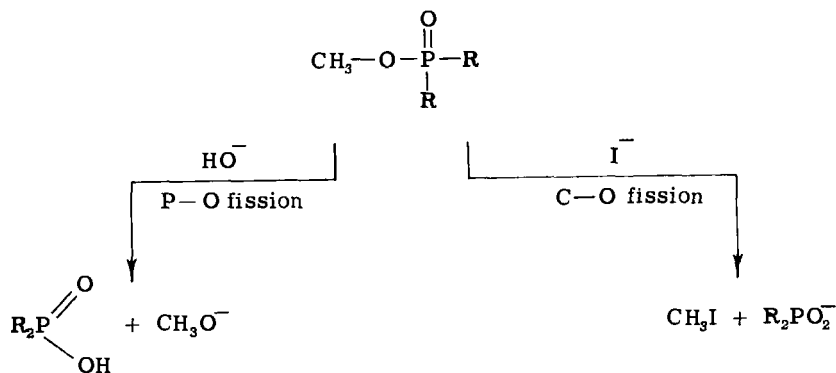
It follows therefore that strongly basic ions are readily acylated whereas the more polarizable ions, e.g., I^- , RS^- , are less reactive.

A similar reactivity order has been observed for phosphorochloridates (50), viz.,

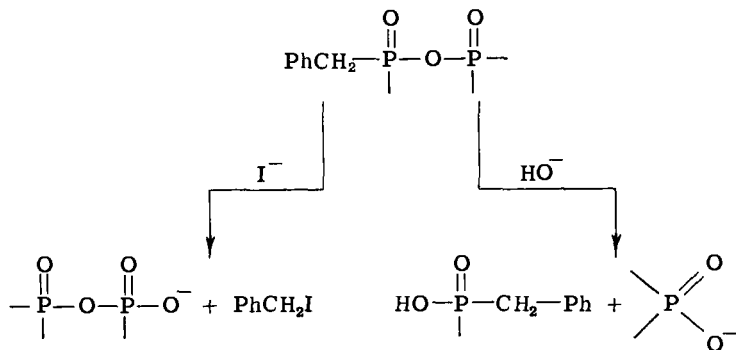


and recent data by Miller (128) have shown that the reactivities of oxyanions (RO^-) and the corresponding sulphur anions (RS^-) follow the corresponding pK_a 's closely. The high reactivity of the fluoride ion does not follow the Edwards equation, but is probably due to the high P-F bond energy (cf. the high Si-F bond energy).

The completely different nucleophilic order towards the saturated carbon atom and the phosphoryl phosphorus atom has been used to predict the position of bond fission in the hydrolysis of esters of quinquivalent phosphorus (85).




and is the basis of anionic de-benzylation of pyrophosphates introduced by Clark and Todd (32),



The nucleophilic order towards the phosphoryl group thus suggests (58, 94) that the bond forming energy is high in the transition state, which probably resembles the addition intermediate (see p. 354).

The degree of bond formation in the transition state is also indicated by the coefficient α of the Brønsted equation (99), $\log k = \alpha pK_a + \text{constant}$, which relates reactivity and acid dissociation constant for a series of similar nucleophiles.

TABLE IX
A COMPARISON OF THE BRØNSTED COEFFICIENT α FOR REACTIONS OF
NUCLEOPHILES WITH ALKYLATING, ACYLATING, AND
PHOSPHORYLATING AGENTS (99)

Compound	Nucleophiles	α	Reference
MeOSO_3^-	$\text{R}\cdot\text{C}_6\text{H}_4\text{O}^-$	0.16	^a
$\text{Cl}\cdot\text{CH}_2\cdot\text{COO}^-$	$\text{R}\cdot\text{COO}^-$	0.20	^b
$\text{Br}\cdot(\text{CH}_2)_3\cdot\text{OH}$	$\text{R}\cdot\text{C}_6\text{H}_4\text{O}^-$	0.22	^c
	$\text{R}\cdot\text{C}_6\text{H}_4\text{O}^-$	0.32	^d
$\text{EtO}\cdot\text{COCl}$	$\text{R}\cdot\text{C}_6\text{H}_4\text{O}^-$	0.78	^e
$p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{COCH}_3$	$\text{R}\cdot\text{C}_6\text{H}_4\text{O}^-$; $\text{R}\cdot\text{C}_6\text{H}_4\text{N}$	0.80	^e
$(\text{CH}_3\text{CO})_2\cdot\text{O}$	$\text{R}\cdot\text{C}_6\text{H}_4\text{N}$	0.92	^f
$\text{Et}_2\text{N}(\text{OEt})\text{P}(\text{O})\text{CN}$	R_2CNO^-	0.50	^g
$(\text{EtO})_2\text{P}(\text{O})\text{OP}(\text{O})(\text{OEt})_2$	R_2CNO^-	0.70	^g
$\text{Pr}^i\text{O}\cdot(\text{Me})\cdot\text{POF}$	$\text{R}\cdot\text{CONHO}^-$	0.82	^g
$\text{Pr}^i\text{O}\cdot(\text{Me})\cdot\text{POF}$	$\text{R}\cdot\text{C}_6\text{H}_5(\text{OH})\text{O}^-$	0.90	^h

^a Green and Kenyon, *J. Chem. Soc.* p. 1595 (1950).

^b Smith, *J. Chem. Soc.* p. 521 (1943).

^c Hudson and Loveday, *J. Chem. Soc.* p. 1068 (1962).

^d Goldsworthy, *J. Chem. Soc.* p. 1254 (1926).

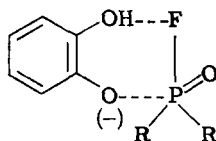
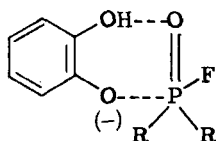
^e Bruce and Lapinski, *J. Am. Chem. Soc.* **80**, 2265 (1958).

^f Gold and Jefferson, *J. Chem. Soc.* p. 1409 (1953).

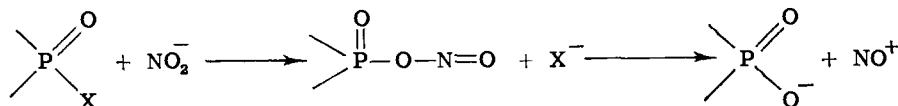
^g Green, Saville, Sainsbury, and Stansfield, *J. Chem. Soc.* p. 1583 (1958).

^h Epstein *et al.*, *J. Am. Chem. Soc.* **78**, 341 (1956).

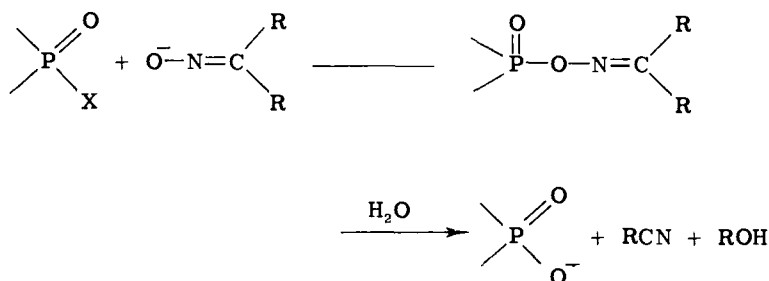
The value of α is observed to increase with the electronegativity of the substituents (72) which produce a decrease in the electron density at the reaction center, thus increasing the charge transfer and bond forming energy in the transition state. The value of α is further increased when the charge transfer is assisted by hydrogen bonding as in the reaction with substituted catechols (60).



Basic oxyanions, e.g., oxime anions (73, 81), ClO^- (59), HO_2^- (124) are considerably more reactive towards both phosphoryl and carbonyl centers (Table X), than predicted from the reactivity of the hydroxide ion and the Brønsted relation. The nitrite ion, which is also very reactive gives rise to an incipient nitroso cation (119) as shown by the formation of a dye with phenylene diamine (130).



and oxime anions give similar rearrangements and fragmentation (73)



Various interpretations have been advanced for the high reactivities of these anions, including bifunctional catalysis (59), the influence of the electron pair on the atom adjacent to the oxygen atom (58), and the influence of solvation and conjugation (94), but a completely satisfactory explanation is still lacking. It should be noted that the high reactivity is quite general and is therefore characteristic of the anion and not of the nature of the bonding (e.g., the use of *d*-orbitals) at the electrophilic center.

TABLE X
THE REACTIVITY OF NUCLEOPHILES TOWARDS ISOPROPYL METHYL-
PHOSPHONOFUORIDATE (B) AND TETRAETHYL PYROPHOSPHATE (A) (72)

Nucleophile	$k_{(A)}$	$k_{(B)}$	pK_a	k_A/k_B
H_2O	0.0017	0.0001	0	17
NH_2OH	26	2.6	6	10
ClO^-	267	600	7.4	0.45
$\text{Ac}_2\text{C:NO}^-$	35	73	7.4	0.48
AcCH:NO^-	59	240	8.3	0.24
$\text{BzCO}_2\text{NHO}^-$	160	1020	8.8	0.16
AcCMe:NO^-	16	380	9.3	0.043
HO_2^-	2180	94,000	11.8	0.023
HO^-	21	2000	14	0.011

From the above discussion it may be inferred that bond formation is advanced in the transition state (94), and hence the reactivity is probably increased by electron withdrawal from the phosphorus atom. This influence is considered further in the following discussion of the effect of structural changes on the reactivity of the phosphorus compound.

X. Substituent Effects in Bimolecular Phosphorylation*

Since most phosphorylations are bimolecular reactions, the rates are affected by steric and electronic factors. Owing to the greater coordination number of phosphorus, steric hindrance is more important than in acylation, and this must be carefully considered before an electronic interpretation of a change in reactivity is assumed. Most of the published reactivity data is unfortunately difficult to analyze for this reason.

The importance of steric hindrance was shown (52) by the reactivity order, primary > secondary > tertiary in the reactions of amines with di-isopropyl phosphorochloridate. The rate differences are somewhat less when isopropyl methyl-phosphonochloridate is used (109). Similarly the rate of reaction of the latter with alcohols is decreased by substitution of alkyl groups in the alcohol, although the activation energy decreases owing to the increased basicity (98).

The substitution of alkyl groups in the groups R_1 and R_2 of derivatives of phosphonic acids decreases the reactivity, as shown for example by the data of Table XI for the alkaline hydrolysis of phosphonates (96). Similar

TABLE XI
THE ALKALINE HYDROLYSIS OF DIALKYL METHYLPHOSPHONATES $(R'O)_2P(R)O$ (96)

$R'(R=Me)$		Me	Et	Pr ⁱ	neo-Pentyl	
Relative rate		600	40	1	0.33	
E* (kcal/mole)		13.5	14.0	14.9	13.6	
10^{-4} PZ		1900	360	27	1.5	
$R(R'=Pr^{\beta})$		Me	Et	Pr ⁿ	Bu ⁿ	Bu ^t
Relative rate		1	0.16	0.062	0.039	0.002
E* (kcal/mole)		14.9	16.2	15.9	16.2	—
10^{-3} PZ		2.7	2.8	0.75	0.69	—

observations have been made for the chloridates (97), fluoridates (86), anhydrides (172), and *p*-nitrophenyl esters (70, 118).

As in the case of reactions at a saturated carbon atom (61), steric and

* In view of the excellent summary given by Heath (86), individual papers containing rate data prior to 1956 are not normally cited, particularly as few attempts have been made to differentiate between steric and electronic influences.

inductive effects cannot be separated. However di-neopentyl methyl phosphonate is considerably less reactive than the diethyl ester (98), although the activation energies are the same (Table XI). Both reactions involve displacement at the phosphorus atom, and the large difference in the PZ factors is attributed to the steric influence of the bulky neopentyl groups. Similarly diethyl t-butylphosphonate (96) is considerably less reactive than the corresponding methylphosphonate, and triphenylmethyl phosphonyl chloride ($\text{Ph}_3\text{C}\cdot\text{POCl}_2$) is reported to be unreactive towards water (6).

The very low reactivity of $(\text{Me}_3\text{N})_3\text{P}=\text{O}$ towards alkali (86) is almost certainly mainly steric in origin (cf. the relatively low reactivity of Pr_3SiCl), although this has been attributed to conjugation (86), and the low reactivity of derivatives of tetra-alkyl phosphoroamidic acids (42, 86) may be explained similarly (see below). Considerable care must therefore be exercised in discussing the reactivity of phosphorus compounds in electronic terms.

A. ELECTRONIC EFFECTS

In view of the large steric effects which may be exerted, our attention will be limited to rate increases which are observed in spite of steric hindrance increases, and to comparisons where the steric effects are approximately constant (homomorphs).

Following the usual practice in organic chemistry, the effect of changes in σ -bond and π -bond energies will be discussed separately.

There is at present little data on the influence of the inductive effect on σ bonds. In general phenyl groups and halogen atoms in either groups R_1 or R_2 increase the rate of solvolysis and alkaline hydrolysis as shown by the data in Tables XII, XIII and XIV.

TABLE XII
THE INDUCTIVE EFFECT PRODUCED BY SUBSTITUTION IN THE OR GROUP OF
DERIVATIVES OF PHOSPHORIC AND PHOSPHONIC ACIDS

Compound	k^d	E (kcal/mole)	Compound	k^d
$(\text{C}_2\text{H}_5\text{O})_2\text{POCl}^a$	11	13.4	$\text{EtO}(\text{Me})\text{POCl}^b$	181
$(\text{PhCH}_2\text{O})_2\text{POCl}^a$	8.5	14.6	$\text{PhO}(\text{Me})\text{POCl}^b$	87.6
$(\text{PhO})_2\text{POCl}^a$	5.1	11.9	$\text{EtO}(\text{Me})\text{POF}^c$	60.7
			$\text{Br}(\text{CH}_2)_2\text{O}(\text{Me})\text{POF}^c$	162

^a Reaction in ethanol at 40° (51).

^b Reaction in 5% aqueous acetone at 0° (117).

^c Alkaline hydrolysis (66).

^d Relative values.

Although these effects are small, it is seen that electron attracting substituents usually increase the reactivity particularly in alkaline hydrolysis.

TABLE XIII
THE RATE OF ALKALINE HYDROLYSIS (25°, pH 8.3) OF O-ETHYL O-*p* NITROPHENYL
ALKYLPHOSPHONATES—EtO(R)P(O)O·C₆H₄·NO₂ (66)

<i>R</i>	10 ⁴ <i>k</i> , min ⁻¹	<i>R</i>	10 ⁴ <i>k</i> , min ⁻¹
CH ₃ ·CH ₂ ·CH ₂	4.17	Ph·CH ₂	7.05
Cl·CH ₂ ·CH ₂ ·CH ₂	7.5	Ph	26.4

This is to be expected in view of the increased electrostatic interaction between a negative ion and the electrophilic center. In solvolysis the bond forming and bond breaking energies are similar and hence the rate differences are small. This is shown clearly by the data (130) in Table XIV.

TABLE XIV
THE INFLUENCE OF α -CHLORINE ATOMS IN THE METHYL GROUP OF
PHOSPHONCHLORIDATES AND PHOSPHONATES ON THEIR REACTIVITY (130)

	Me	Et	Cl·CH ₂
<i>Solvolysis of EtO(R)POCl in 5° aqueous acetone at 0°</i>			
10 ³ <i>k</i> min ⁻¹ (0°)	87.6	29.7	107 (1.3°)
<i>E</i> _A kcal/mole	8.5	8.9	10.9
log ₁₀ PZ	4.0	3.9	5.9
<i>Alkaline hydrolysis of RP(O)(OEt)₂</i>			
<i>k</i> ₂ l mole ⁻¹ hr ⁻¹ (60°)	9.36	4.41	111
<i>E</i> _A , kcal/mole	14.0	14.2	12.0
log ₁₀ PZ	6.5	6.3	6.8

The rate increases are considerably less than observed with the corresponding carbonyl compounds [e.g., the relative rate of alcoholysis of Cl·CH₂·COCl and CH₃COCl (17) is about 20], which may be attributed to the weaker bonding in the 5 coordinated transition state (see p. 354).

B. CONJUGATING GROUPS

When the atom of group *R* attached to the phosphorus atom contains lone pair (*p*_π) electrons, the rate may be also modified by *d*_π-*p*_π conjugation which may stabilize the ground state as described on p. 362. Substitution of a chlorine atom usually increases the reactivity by a small factor (2-3) as shown by the following comparisons (130) (EtO)POCl₂ and EtO(Me)-POCl; MePOCl₂ and POCl₃, suggesting that the inductive effect is slightly more important than conjugation.

Replacement of an alkyl group by an alkoxy group (51, 70, 86, 97, 118)

TABLE XV
THE EFFECT OF ALKOXY AND ALKYLAMINO GROUPS ON THE REACTIVITY OF SOME PHOSPHONYL COMPOUNDS

Reference	Compound	Conditions	Temperature	<i>k</i>
(97)	Et ₂ POCl	95% acetone—5% water (v/v)	0	$1.500 \times 10^{-3} \text{ sec}^{-1}$
(97)	MeOP·EtOCl	95% acetone—5% water		$98 \times 10^{-3} \text{ sec}^{-1}$
(97)	(MeO) ₂ POCl	95% acetone—5% water		$1.75 \times 10^{-3} \text{ sec}^{-1}$
(72)	Et ₂ POF	OH ⁻ in water	25	$50.000 \text{ l. mole}^{-1} \text{ hr}^{-1}$
(72)	EtOPEtF	OH ⁻ in water	25	$1.200/\text{mole}^{-1} \text{ hr}^{-1}$
(72)	(EtO) ₂ POF	OH ⁻ in water	25	$110 \text{ mole}^{-1} \text{ hr}^{-1}$
(70)	EtO·P·Pr ⁿ (O)O·C ₆ H ₄ ·NO ₂ -p	OH ⁻ in water	37.5	$4.17 \times 10^{-4} \text{ min}^{-1a}$
(70)	(EtO) ₂ P(O)·OC ₆ H ₄ ·NO ₂ -p	OH ⁻ in water	37.5	$6.14 \times 10^{-4} \text{ min}^{-1a}$
(85)	Et ₂ P·(O)·OMe	OH ⁻ in water	80	5.9^b
(85)	(MeO) ₂ P·(Et)·O	OH ⁻ in water	80	4.2^b
(85)	(MeO) ₂ PO	OH ⁻ in water	80	1.0^b
(86)	(Pr ⁱ O) ₂ POF	water	25	$1.2 \times 10^{-4} \text{ sec}^{-1}$
(86)	(Pr ⁱ NH) ₂ POF	water	25	$2.3 \times 10^{-5} \text{ sec}^{-1}$

^a Pseudounimolecular constants.

^b Relative reactivity per OMe group.

however invariably decreases the rate (Table XV) which has been attributed to π -bonding in the ground state (51, 86, 97).

These rate decreases may alternatively be attributed (97) to increased σ -bond energies, (as shown by the increased infrared frequencies (9) if $d_{\pi}-p_{\pi}$ bonding is discounted). This explanation is however unlikely for the following reasons (97): (a) electron-withdrawing groups usually increase the reactivity; (b) alkyl amino-groups decrease the reactivity further (Table XV), which is the reverse of the inductive effect predicted by the electronegativities. The reduced reactivity produced by an amino group (42, 86) is explained by increased π -bonding with the phosphorus atom. This effect, if indeed present, is considerably less than for the corresponding carbon compounds as shown by comparing the values given in Table XV with the value of ca 10^4 for the relative reactivity of a chloroformate and acid chloride (97).

Moreover phenyl groups which produce large rate decreases in carbonyl compounds owing to the conjugation $\text{Ph}-\overset{\curvearrowright}{\text{C}}=\text{O}$, increase the rate of solvolysis of phosphorochloridates (51, 98) and the rate of alkaline hydrolysis of the corresponding phosphonates (96).

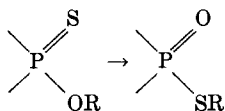
Although few rate studies have been made with derivatives of thioic acids, the effect of an RS group is considerably less than that of the corresponding alkoxy group (86).

In general therefore, the following rate order is observed (in particular for solvolysis)



which is the order of increasing $p_{\pi}-p_{\pi}$ conjugation in organic compounds. Since this gives a measure of the exponent of the p_{π} electrons of the group, $d_{\pi}-p_{\pi}$ bonding should increase in the same order (although this may be modified to some extent by conditional stability). This rate order and the magnitude of the effects observed support the contention of weak $d_{\pi}-p_{\pi}$ bonding in phosphoryl compounds and cannot be explained on inductive effects alone.

The substitution of sulfur for oxygen in the phosphoryl group (86) reduces the solvolysis rate of phosphorochloridates and phosphonochloridates by about 10^2 ($\Delta E \sim 2.5$ kcal/mole), and similar rate reductions are found in the hydrolysis of aromatic esters (86). Since the π -bond energy for the $\text{P}=\text{S}$ group is probably less than for the $\text{P}=\text{O}$ group, as indicated by the thiono-thiolo rearrangement (65)



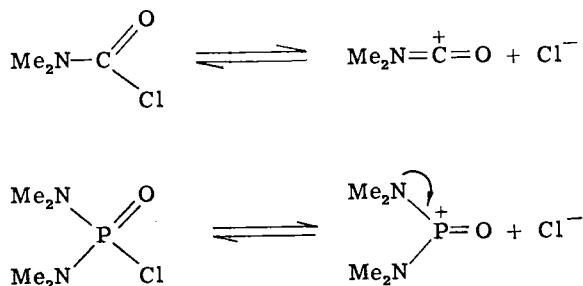
thionates would be more reactive than the oxygen analogs if conjugation were dominant. The rate factor suggests that electrostatic factors are more important in this case. It should be noted that thiocarbonyl compounds are less reactive than the corresponding carbonyl derivatives (16) indicating that even here π -bond energy changes are less significant than the polarity and solvation energy changes.

XI. Ionization Reactions

The reactivity data discussed in the previous section can be interpreted satisfactorily on the hypothesis that $d_{\pi}-p_{\pi}$ conjugation in the ground state, which is weak compared with $p_{\pi}-p_{\pi}$ bonding, opposes the (electron withdrawing) inductive effect which normally increases the reactivity. If this interpretation is correct, it should be possible for reactions to proceed through ionization intermediates to give ions of the kind postulated in the POCl_3 solvo system (79)



when the π -bonding energy is greater than the P-X bond energy.* A mechanism of this kind has been suggested for the solvolysis of phosphoroamidic chlorides (83), to account for the lack of reaction with hydroxide ions, and the rate sequence. $(\text{R}_2\text{N})_2\text{POCl} > \text{R}_2\text{N}(\text{OEt})\text{POCl}$, since carbamyl chlorides are known to react by an ionization mechanism (82)



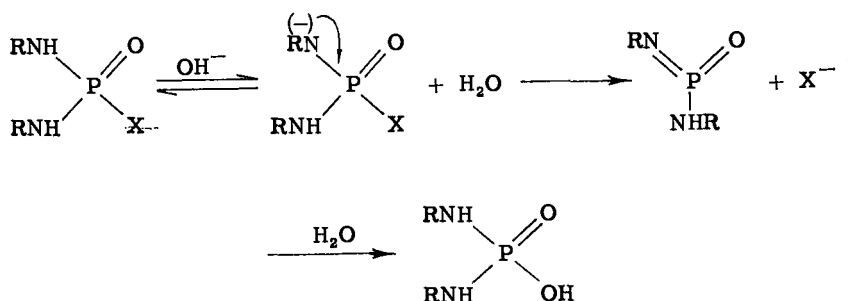
It is known that hydroxide ions increase the rate of hydrolysis of the corresponding fluorides (86) and anhydrides (86), although the rate increases are relatively small.

Further kinetic investigations (41, 157) have suggested that the hydrolyses of tetra-alkyl phosphoroamidic chlorides are bimolecular, although bond breaking is more important in the transition state than in other cases considered (41). In particular nitrite (41) and azide (157) ions increase the rate of reaction, in the latter case giving stable azides (157).

The corresponding derivatives of primary amines are very sensitive to

* These ions would be stabilized by $p_{\pi}-p_{\pi}$ bonding, probably involving $(pd)_{\pi}$ hybrids.

alkali (Table XVI), and Westheimer (182) suggested a mechanism involving preliminary ionization of the α -proton:



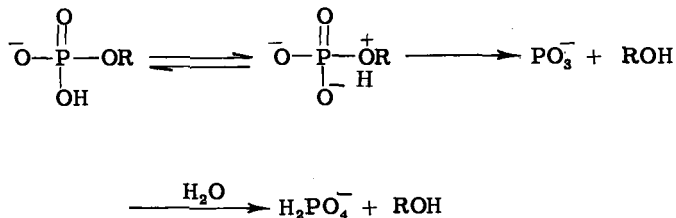
X = Cl, F, (RNH)₂PO₂

Support for this suggestion was provided by the observation that 2:6 lutidine increases the rate of solvolysis of phosphoroamidic chlorides but has no effect on the homomorphous phosphorochloridates (41).

TABLE XVI
ALKALINE HYDROLYSIS OF PHOSPHORODIAMIDIC FLUORIDES RR'POF AT 25° (86)

R	R'	$k(\text{OH}^-) \text{ min}^{-1}$	E (kcal/mole)
Pr ⁿ NH	Pr ⁿ NH	48.9	11.2
MeNH	Me ₂ N	17.6	11.2
EtNH	Me ₂ N	12.3	11.4
Bu ⁿ NH	Me ₂ N	11.1	11.4
Pr ⁱ NH	Me ₂ N	8.43	11.9
Me ₂ N	Me ₂ N	4.7×10^{-3}	16.6
Et ₂ N	Me ₂ N	2.88×10^{-4}	16.6
Et ₂ N	Et ₂ N	2.5×10^{-5}	17.1

Similar mechanisms have been postulated for other reactions involving phosphoryl compounds in the ionized form. Thus the very high reactivity of mono-alkyl phosphates (7, 45) in the pH range where the mono-ionized form is present in maximum concentration (Fig. 15), has been interpreted by the following mechanism (23), or a modification thereof (24).



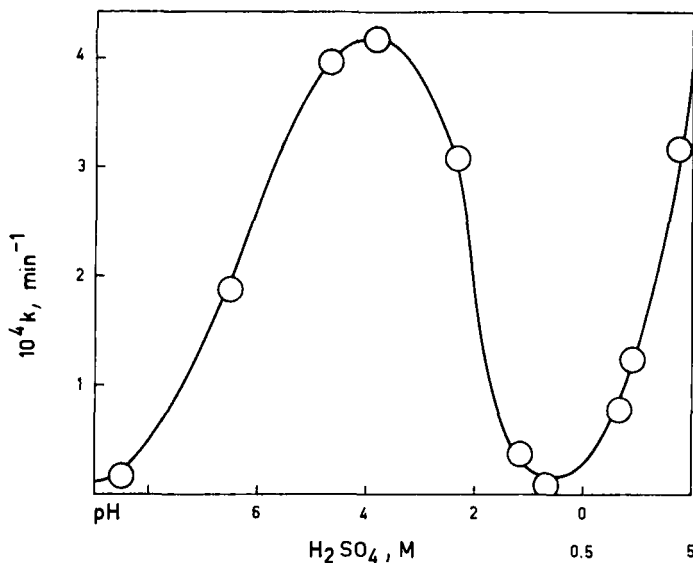
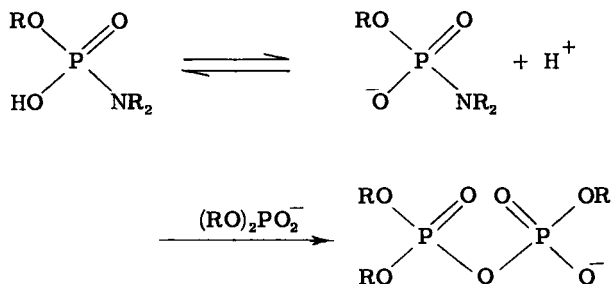


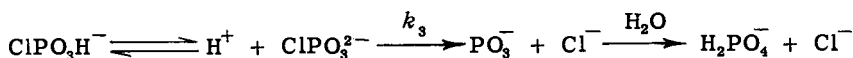
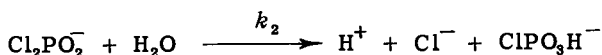
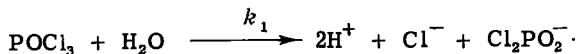
Fig. 15. The change in the rate of hydrolysis of 1-methoxy propyl 2-phosphate with pH of the solution (24).

By comparison, dialkyl phosphates are very inert, suggesting that this mechanism requires conjugation of two P-O groups. Similarly the corresponding amidates probably react by the bimolecular mechanism as in the pyrophosphate synthesis (25, 30).



Recent investigations of the mechanism of hydrolysis of phosphoryl chloride (100) have shown that the first rapid stage, giving dichlorophosphoric acid, is followed by a slow reaction involving the dichlorophosphate anion which gives two equivalents of chloride ion simultaneously in acid and in alkaline solution.

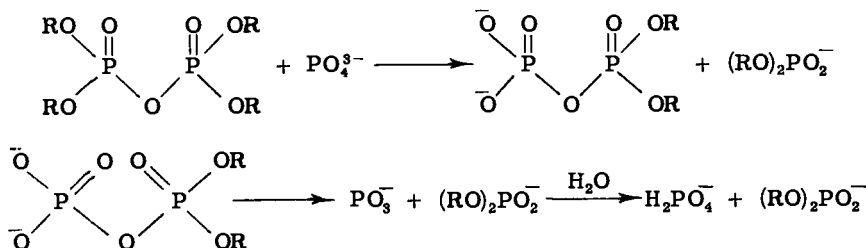
Since amines strongly catalyse the second stage, this reaction probably proceeds by a bimolecular displacement involving a water molecule. The



where $k_1 \gg k_2 \ll k_3$

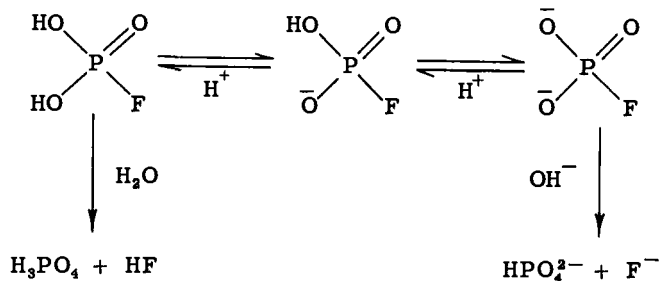
rate order $k_3 \gg k_2$ suggests that the third stage proceeds by the unimolecular mechanism, as shown in the above scheme.

This rate sequence is also observed with the corresponding pyro-esters. Thus the catalysis of the hydrolysis of tetra-alkyl pyrophosphates by phosphate ions has been explained by the following mechanism (19, 156),



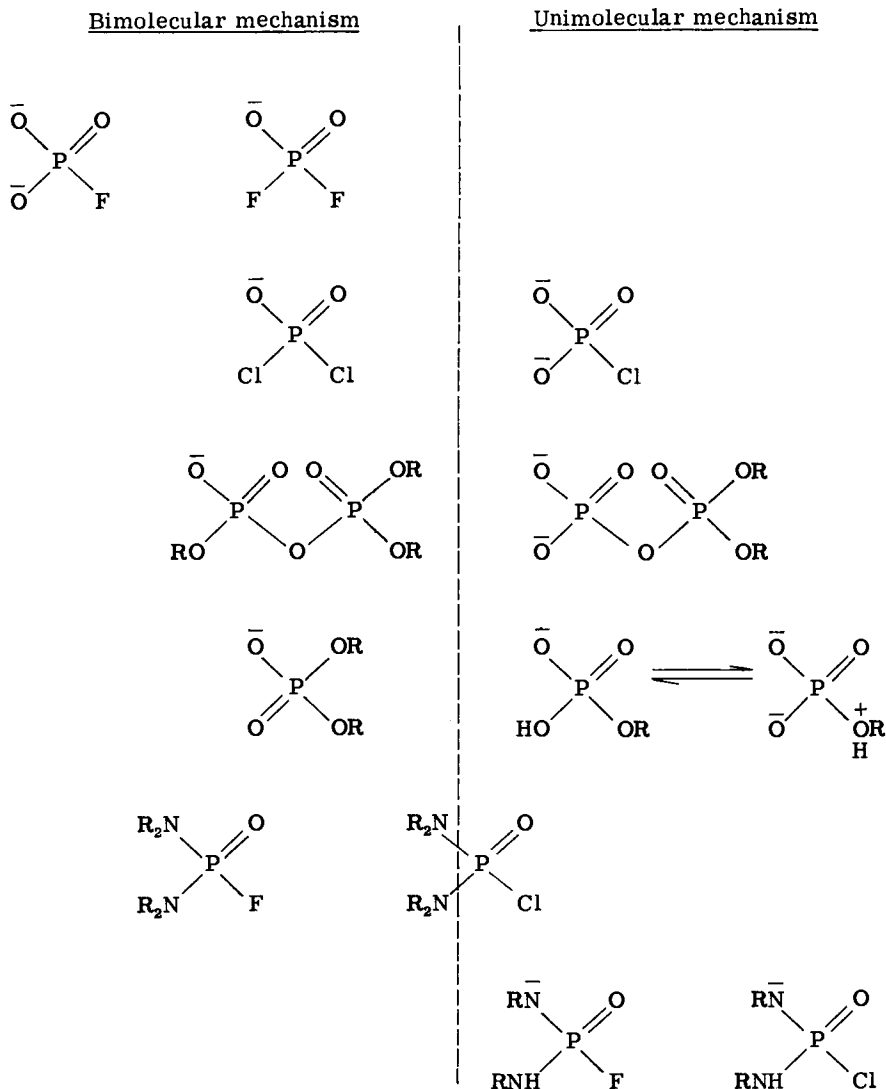
The corresponding triesters are relatively stable, and can be readily isolated (39).

The rate order $k_3 \gg k_2$ is the inverse of that expected for bimolecular reactions as shown by the reactions of the corresponding fluorides (46). The hydrolysis of mono-fluorophosphoric acid is catalyzed by alkali and acid (46) according to the scheme.

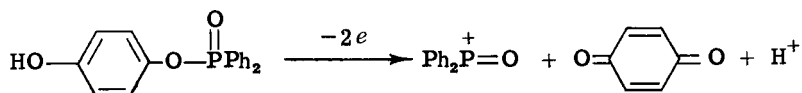


The unimolecular mechanism also explains the rapid rate of decomposition of β -chloroethylphosphonic acid (168) formed by the action of the olefin on phosphorus pentachloride (p. 350).

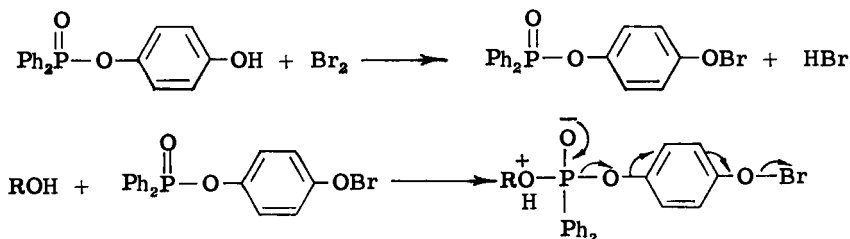
The rate data discussed in this section defines fairly clearly the conditions leading to an ionization mechanism, in terms of conjugation energy in the intermediate, and the P-X bond energy. These conclusions can be summarized diagrammatically in the following way (95),



The concept of an intermediate phosphoryl ion as a strong phosphorylating agent, has led to the discovery of oxidative phosphorylation (31, 183), which may be represented in a general form as follows,



Although the mechanism of this interesting reaction has not been established, it probably proceeds by bimolecular phosphorylation involving a reactive intermediate. When halogens are used as the oxidizing agent, a scheme of the following kind can be proposed,



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