

Inorganic Syntheses

VOLUME V

Inorganic Syntheses

VOLUME V

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To
Raymond Eller Kirk
(1890–1957)
and
Arthur Alphonzo Blanchard
(1876–1956)

PREFACE

The enthusiastic reception accorded earlier volumes in this series and the continuing interest expressed in them have encouraged the Board of Editors of *INORGANIC SYNTHESSES* to continue the series in the present volume. The rapidly expanding interest in inorganic chemistry, as reflected by increased publication of the results of fundamental research, by greater emphasis upon instruction at the advanced level, and by development of new industrial processes, indicates clearly the necessity for making available exact and tested procedures for the preparation of inorganic substances. It is hoped that the material in these volumes will both aid in the solving of specific problems and stimulate additional interest in, and investigation of, other problems in the inorganic area.

The policy of having each synthesis carefully checked in at least one independent laboratory has been continued. This has provided a means of determining the exactness and correctness of each procedure and often a means of increasing the usefulness of the procedure through incorporation of the findings of the checker. Each synthesis has been edited after checking and approved in final form by both submitter and checker before publication. That many of the procedures either originated or were checked in industrial laboratories may be taken as indicative that the material here is of both technical and fundamental interest. The Board of Editors is particularly happy to point out that many of the procedures have come from abroad.

In accordance with the convention established in earlier

volumes, the syntheses in Volume V are arranged by chapters on the basis of the Mendeleev periodic classification. Further subdivision into A and B families has been effected also. A few brief survey articles have been included at pertinent places to broaden the scope of the treatment. The system of nomenclature is that followed in Volumes II to IV. The volume has been cross-referenced liberally, and the subject and formula indexes are cumulative for all five volumes.

Contributions are now being accepted for publication in Volume VI of the series. All manuscripts should be forwarded to Prof. Eugene G. Rochow, of Harvard University, who will serve as editor-in-chief of Volume VI. All such manuscripts should be submitted in triplicate and should follow, as nearly as possible, the style used in earlier volumes. Each manuscript should include in order a brief introduction summarizing reported methods of synthesis, a detailed procedure written in the present passive, a brief summation of important physical and chemical properties, and an accurate compilation of pertinent references listed with initials of the authors. Analytical methods which are distinctive should be included in a separate section after Procedure. Numerical data on yields and analytical results are essential in all possible cases.

The Board of Editors takes great pleasure in announcing the election to membership on the Editorial Board of Dr. Eugene O. Brimm, of Linde Air Products Company; Dr. Joseph J. Katz, of the Argonne National Laboratory; and Prof. Geoffrey Wilkinson, of the Imperial College, London.

The editors wish, again, to call attention to the fact that *INORGANIC SYNTHESSES* is a periodical publication and that a reference to an article appearing in any volume should include the names of the authors of that article and not the name of the editor-in-chief of the volume.

The editor-in-chief is most grateful to his associates on the Editorial and Advisory Boards for their assistance and advice in the preparation of Volume V. Miss Janet D.

Scott has been particularly helpful in handling all the problems of nomenclature and indexing. The editor wishes also to thank Mrs. Marie C. Hall for her aid in preparing the manuscript and Mr. Valentine D. Galasyn for his invaluable help in editing the manuscript and checking proof.

The editors will be most grateful to readers and users of this and other volumes of INORGANIC SYNTHESSES for information concerning any errors or omissions.

Therold Moeller

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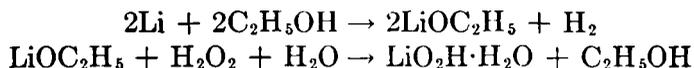
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CHAPTER IA

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1. LITHIUM HYDROPEROXIDE 1-HYDRATE, LITHIUM PEROXIDE, AND LITHIUM OXIDE

Hydrated lithium hydroperoxide was first obtained by de Forcrand¹ by treating an ethanolic solution of lithium hydroxide with hydrogen peroxide. The product was assigned the formula $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$. A modification of this procedure was reported to yield the substance $\text{Li}_2\text{O}_2 \cdot 0.79\text{H}_2\text{O}_2 \cdot 2.31\text{H}_2\text{O}$, which lost hydrogen peroxide on standing *in vacuo* over phosphorus(V) oxide to give a phase $\text{Li}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$.² Removal of water under similar conditions to yield lithium hydroperoxide has also been reported.³ However, it now appears that the initial compound is actually lithium hydroperoxide 1-hydrate and that desiccation over phosphorus(V) oxide gives lithium peroxide.⁴ The same decomposition to lithium peroxide is effected by adding a higher alcohol or amine to the initial reaction mixture, distilling to remove water, and separating the product from the residual organic liquid.⁵ Thermal decomposition of the peroxide gives lithium oxide. The procedures which follow involve preparation of the hydroperoxide under both ethanolic and aqueous conditions and subsequent conversions to the peroxide and oxide.

A. LITHIUM HYDROPEROXIDE 1-HYDRATE

SUBMITTED BY ALVIN J. COHEN*

CHECKED BY C. G. SCHULTZ† AND JOHN F. SUTTLE‡

Procedure

Caution. Mixtures of ethanol and concentrated hydrogen peroxide are potentially explosive. Hydrogen peroxide of concentration above 35% should not be used, and all filtrates should be kept cold and diluted immediately with water.

All of the following operations are carried out at room temperature in a dry box, preferably containing helium or other inert gas to exclude carbon dioxide. Two grams of pure lithium (ca. 0.3 mol), preferably as ribbon, is added to 250 ml. of absolute ethanol‡ in a 600-ml. beaker. The resulting suspension of lithium ethoxide is stirred vigorously and treated with 25 ml. of 30% hydrogen peroxide. The system is allowed to stand for 1 hour with occasional stirring and is then filtered in a sintered-glass filtering crucible using suction. The product is washed with two 25-ml. portions of cold absolute ethanol, dried by suction, and stored in a tightly closed bottle. Occasional checks for pressure build-up in the bottle due to decomposition must be made. The yield is 9.4 g. (56%, based on the lithium used).

Analysis

Lithium (reported as lithium oxide) is determined by adding water and a trace of platinum black, boiling until peroxide decomposition is complete, and titrating with standard acid. Peroxide oxygen is determined by direct

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† University of New Mexico, Albuquerque, N.Mex.

‡ If the solution is cooled during the reaction, 95% ethanol can be used.

titration with standard potassium permanganate solution.
Anal. Calcd. for $\text{LiO}_2\text{H}\cdot\text{H}_2\text{O}$: Li_2O , 25.8; peroxide O, 27.6.
Found: Li_2O , 25.4; peroxide O, 27.4.*

Properties

Lithium hydroperoxide 1-hydrate is a white, crystalline compound, which belongs to the orthorhombic system ($a = 7.92$ A., $b = 9.52$ A., $c = 3.20$ A.).⁴ The calculated density with four molecules to the unit cell is 1.60.⁴ The measured density is 1.69. Additional water may be trapped mechanically to give compositions slightly above the 1-hydrate.⁴ The compound reacts spontaneously with atmospheric carbon dioxide to form lithium carbonate and release oxygen. It decomposes gradually on standing in a closed system at room temperature to lithium hydroxide 1-hydrate.

B. LITHIUM PEROXIDE

Procedure A



SUBMITTED BY ALVIN J. COHEN†

CHECKED BY C. G. SCHULTZ‡ AND JOHN F. SUTTLE‡

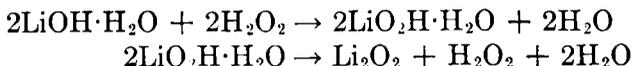
Lithium hydroperoxide 1-hydrate (part A) is placed in a vacuum desiccator over phosphorus(V) oxide, and the pressure is reduced to about 20 mm. After standing for 18 days at room temperature under these conditions, the material is converted quantitatively to 96% (or better) lithium peroxide. The anhydrous peroxide can be preserved indefinitely in a dark bottle under refrigeration.
Anal. Calcd. for Li_2O_2 : Li_2O , 65.0; peroxide O, 34.9.
Found: Li_2O , 64.5; peroxide O, 34.0.

* The checkers report partial decomposition to lithium peroxide as a result of prolonged drying by suction.

† U.S. Naval Ordnance Test Station, China Lake, Calif.

‡ University of New Mexico, Albuquerque, N.Mex.

Procedure B



SUBMITTED BY STEPHEN E. STEPHANOU* AND JACOB KLEINBERG*
 CHECKED BY E. S. SHANLEY† AND BY JOHN F. SUTTLE‡ AND F. H. KRUSE‡

The apparatus consists of a 500-ml. round-bottomed flask *A* (Fig. 1) equipped with a single side arm bearing a 250-ml. separatory funnel *B* and with an inverted sintered-glass filter funnel *C*. The latter is held in place by a gum-rubber Gooch crucible holder *D* and is inserted into an

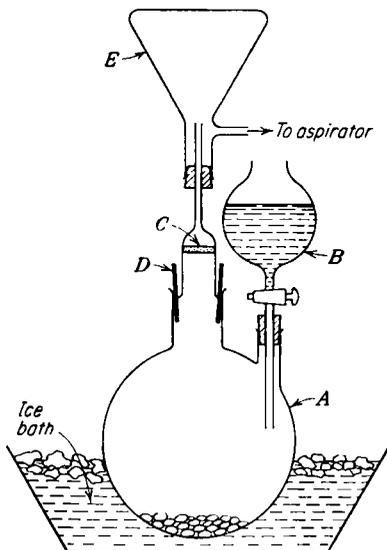


FIG. 1. Apparatus for the preparation of lithium peroxide.

inverted 500-ml. filter flask *E*. Flask *A* is cooled in an ice bath, and 60 g. of lithium hydroxide 1-hydrate (1.43 mols) is added. The system is closed, and a slight vacuum is established by manipulating the aspirator.§ The apparatus is shaken vigorously,|| while flask *A* remains in the ice bath, and 250 g. of 30% hydrogen peroxide is added dropwise from the separatory funnel. When the addition of the peroxide is complete, the stopcock of the separatory funnel

is nearly closed, a drying tube containing soda lime is attached to the separatory funnel, the entire apparatus

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‡ University of New Mexico, Albuquerque, N.Mex.

§ A slight vacuum is maintained during the entire reaction to prevent the building up of pressure by released oxygen.

|| Caking in the reaction flask and subsequent difficulties in handling the product are avoided by vigorous agitation.

is inverted and supported on a ring stand, and the solid product is separated from the mother liquor by suction filtration through the sintered-glass funnel. The product is dried as completely as possible by aspiration and then transferred rapidly to a vacuum desiccator containing phosphorus(V) oxide. The desiccator is allowed to stand at room temperature with daily evacuation with an aspirator for 1 to 2 months. The yield is about 26 g. (about 80%, based on the lithium hydroxide 1-hydrate used) of 96% lithium peroxide.*

Properties

Anhydrous lithium peroxide is a white, extremely light powder consisting of tiny crystals, which have been reported as both tetragonal ($a = 5.44$ A., $c = 7.74$ A., $c/a = 1.42$)^{3,4,6} and hexagonal ($a = 6.305$ A., $c = 7.710$ A.).⁷ There are eight molecules to the unit cell.^{4,7} The calculated density is 2.66,⁴ and the measured density is 2.26.⁴ The compound absorbs carbon dioxide on standing and decomposes to lithium oxide when heated.

C. LITHIUM OXIDE



SUBMITTED BY ALVIN J. COHEN†

CHECKED BY C. G. SCHULTZ‡ AND JOHN F. SUTTLE‡

Procedure

Anhydrous lithium peroxide (part B) is placed in an aluminum boat in a combustion tube and heated at 450° in an atmosphere of helium in a tube furnace for 6 hours. The product is cooled in helium, transferred to a dry box containing no carbon dioxide, and bottled. The yield is quantitative.

* Major impurities are ca. 2.0% lithium carbonate and ca. 1.8% hydrogen peroxide.

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‡ University of New Mexico, Albuquerque, N.Mex.

Properties

Lithium oxide is obtained as a white, finely divided powder. It readily absorbs both water and carbon dioxide from the atmosphere. At elevated temperatures it attacks glass, silica, and many metals. The high-temperature heat content and entropy have been evaluated.⁸

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2. SODIUM DISPERSIONS

SUBMITTED BY T. P. WHALEY*

CHECKED BY C. C. CHAPPELOW, JR.†

At temperatures above 97.5°, a mixture of sodium metal and a saturated hydrocarbon constitutes a binary system of mutually insoluble liquids that can be emulsified in much the same manner as oil and water. When this sodium-in-oil emulsion is permitted to cool below this temperature, the sodium solidifies as microscopic spheres suspended in the hydrocarbon. Addition of certain surface-active agents¹ such as oleic acid, prior to cooling, assists in keeping the sodium in suspension. Such a formulation is known as a sodium dispersion.

Procedure

Caution. All work with sodium and sodium dispersions should be planned and conducted carefully. Face shield, rubber apron, and rubber gloves should be worn in order

* Ethyl Corporation, Baton Rouge, La.

† Midwest Research Institute, Kansas City, Mo.

to avoid damage to clothing or skin by splashing dispersion. Contact with water must be avoided.

The reaction vessel employed is a creased flask *A* (Fig. 2)

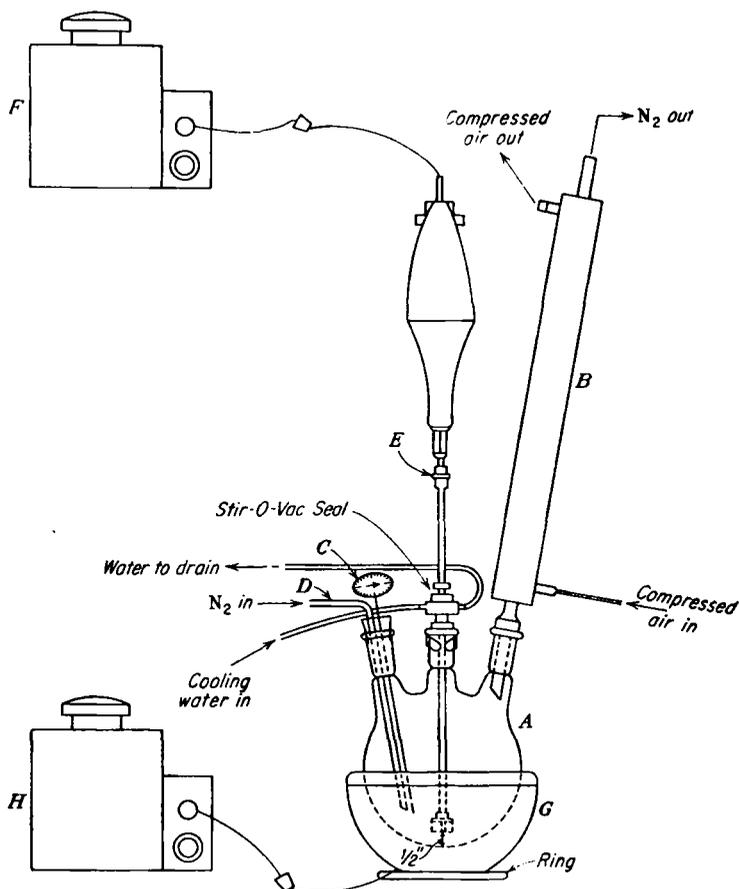


FIG. 2. Apparatus for the preparation of sodium dispersions.

of the Morton²⁻⁴ type without the bottom indentation, which is constructed from a 1-l. pyrex three-necked flask with 24/40 standard-taper joints.* To the flask are

* Baffles in the flask are necessary to eliminate vortex formation and ensure maximum agitation.

attached a condenser *B* of the waterless type, *e.g.*, Vigreux column or Liebig condenser with compressed air as coolant, etc.,* a mechanical-dial-type or oil-filled thermometer *C*,* an inlet tube *D* for admitting nitrogen, and a high-speed motor-driven stirrer *E* (capable of at least 10,000 r.p.m. in air, with sufficient power to maintain at least 7500 r.p.m. under load conditions).† The motor speed is controlled by a Variac *F*. The flask rests in a Glas-col heating mantle *G*, the temperature of which is controlled by a Variac *H*.

A solution of 0.25 g. of oleic acid (ca. 0.001 mol) in 100 g. of heavy *white* mineral oil (b.p. above 300°) is placed in the clean, dry, creased flask, and the stirrer assembly is adjusted so that the head is approximately $\frac{1}{2}$ in. from the bottom. Shaft and seal alignment are checked by noting the Variac voltage necessary to start the stirrer (between 10 and 25 volts if parts are properly aligned). A slow nitrogen purge, about 0.2 l./min., is started through the apparatus and maintained throughout all subsequent operations. The condenser is removed, and there is added 43 g. of sodium (1.87 mols) from which the oxide coating has been removed by scraping or cutting under mineral oil‡ and which has been freshly cut into small pieces and weighed in a tared beaker of mineral oil. The mineral oil in the flask should cover the sodium completely.

The condenser is immediately reattached to the flask, and the contents of the flask are heated to ca. 105° to melt the sodium. The stirrer is started, slowly at first but with increase to maximum speed in 1 to 2 minutes. Stirring is continued at this speed for approximately 15 minutes, the temperature being maintained in the range 105 to 125°.

* Potential hazards in the event of breakage are minimized by elimination of water and mercury.

† Such a stirrer assembly, consisting of a turbine- or cruciform-type head on a $\frac{3}{16}$ -in. stainless-steel shaft and supported by a water-jacketed vacuum seal, is sold as a unit by Labline, Inc., Chicago, Ill., under the name of Stir-O-Vac.

‡ The sodium may be cleaned by immersing in isopropyl alcohol for about 1 minute and then washing the residual alcohol from the metal with kerosene.

The resulting uniformly gray suspension* is allowed to cool to room temperature *without further agitation*. The yield is quantitative.

The cooled dispersion is either poured from the creased flask into a suitable container for further use or utilized directly in the dispersion flask (sodium hydride, synthesis 3).

Equipment Cleanup. If the dispersion is removed from the creased flask, the equipment should be decontaminated as soon as possible. Approximately 150 ml. of kerosine or similar hydrocarbon is added to the now-empty flask and swirled around to wash the residual sodium from the walls. A solution of 30 ml. of isopropyl alcohol in 100 ml. of kerosine is slowly added to the flask and permitted to react with the sodium residue. Similarly, the stirrer blade and shaft, seal, thermometer, and condenser are decontaminated by washing in a 25% solution of isopropyl alcohol in kerosine.

Properties

Sodium dispersions in mineral oil are gray in color and have approximately the same viscosity as the hydrocarbon medium, but they become more viscous as the oleic acid concentration is increased. The suspended sodium may tend to settle slightly under the influence of gravity on extended storage, but it can be redispersed by manual stirring. Dispersions containing more than 50% sodium tend to become increasingly viscous as the sodium concentration increases.

The protective hydrocarbon permits sodium dispersions to be poured or handled like any other liquid provided that the indicated necessary precautions are taken.

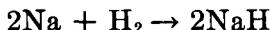
* Dispersions in mineral oil often develop a purple color; this color does not always indicate failure of the run but is sometimes associated with sodium dispersions that have broken into the component parts. Should this occur, the mixture should be heated to approximately 165° and the operation continued at this temperature.

Sodium dispersions may be used in almost any operation where sodium metal is employed. Specific applications include preparing alkoxides, reducing esters, and reducing metal halides. Such dispersions are useful because they are more reactive than massive sodium metal and thus give shorter reaction times at lower temperatures.

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3. SODIUM HYDRIDE



SUBMITTED BY G. W. MATTSON* AND T. P. WHALEY*

CHECKED BY C. C. CHAPPELOW, JR.†

Although sodium hydride can be obtained by the reaction of molten sodium metal with hydrogen at elevated temperatures,^{1,2} the procedure is too involved for practical laboratory synthesis. Yields are improved and techniques simplified by using dispersed sodium.³ Muckenfuss⁴ has described a procedure for hydrogenating sodium dispersions in oils, but superatmospheric hydrogen pressures are required. Hansley^{3,5} has found that sodium dispersed upon preformed inert surfaces by the use of small amounts of the sodium derivatives of anthracene, phenanthrene, or fluorene is readily hydrogenated at 250 to 350° by 1 atm. of the gas. The following synthesis is a laboratory procedure for hydrogenating sodium dispersions (synthesis 2) at atmospheric pressure.

Procedure

Caution. The same precautions outlined in the preparation of sodium dispersions (synthesis 2) must be observed.

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† Midwest Research Institute, Kansas City, Mo.

The apparatus employed for the preparation of sodium dispersions (Fig. 2) is used with the following modifications: (1) the gas inlet tube *D* is connected to a source of hydrogen in addition to a source of nitrogen, and (2) the condenser outlet tube is connected to a bubbler type of safety seal containing 1 l. of mineral oil to prevent suckback of air, which might result in an explosion. Electrolytically prepared hydrogen should be used because of the inhibiting effects of certain impurities (notably carbon monoxide) present in nonelectrolytic hydrogen.

The reaction vessel is flushed with dry nitrogen while the sodium dispersion in the 1-l. flask (synthesis 2) is slowly agitated and heated. When the temperature reaches 220°, the stirrer speed is increased to maximum value, the nitrogen source is shut off, and dry hydrogen is permitted to flow into the reactor at a flow rate of about 0.2 l./min. Heating of the reactor is continued until the temperature reaches 280°. At this temperature, hydrogen absorption will be quite rapid, as indicated by a marked decrease in the rate of bubbling in the mineral oil seal. The hydrogen flow rate is readjusted so that a small, positive flow of gas is always venting from the reactor through the safety seal. The temperature is maintained at 280 to 300°, and stirring is continued at maximum speed.

As the hydrogenation nears completion, the flow of gas through the safety seal will increase markedly. To test for completion of the reaction, the hydrogen flow to the reactor is momentarily stopped, and the gas outlet tube extending into the mineral oil bubbler is observed. If oil starts rising in the tube, hydrogenation is incomplete, and the hydrogen flow should be resumed immediately. If oil does not rise in the tube, hydrogenation can be considered complete (provided there is no leakage). Another simple confirmatory test of hydrogenation completeness is visual examination of the sodium hydride dispersion for free sodium. This is accomplished by withdrawing a drop of the dispersion and placing it between two glass

slides. The glass slides are pressed together with a slight grinding motion. If any free sodium is present, it can be readily detected visually by the appearance of the silvery dots of metal between the glass slides. The time required for complete hydrogenation is from 1 to 2 hours.

When hydrogenation is complete, the heating current is turned off, and the hydride dispersion is permitted to cool. The hydrogen flow rate is adjusted to several bubbles per minute and so maintained until the temperature has dropped to approximately 100°. Then the gas lead is switched back to a nitrogen purge, which is maintained until room temperature is reached. The sodium hydride dispersion can now be used as such or transferred into other equipment. From the dispersion, solid sodium hydride is obtained by diluting with an equal volume of hexane, decanting, and repeating the hexane addition and decantation several times. After several such additions, the solid product settles freely, and the hexane remaining after final decantation is removed by passing a stream of dry nitrogen over the product at room temperature. Because of its reactivity and pyrophoric nature, the dried product is stored under nitrogen. The yield, based upon the sodium used, is quantitative (ca. 44.8 g. from 43 g. of sodium).

Equipment Cleanup. The same procedure employed for sodium dispersions is used (synthesis 2).

Properties

Sodium hydride is a colorless to grayish-white, crystalline solid, consisting of sodium and hydride ions arranged in a lattice of the sodium chloride type ($a = 5.53$ A.).⁶ The density is 0.92_{20}^{20} and the heat of formation 13.8 kcal./mol. Heating causes the solid to dissociate to sodium and hydrogen, the pressure of the latter being expressed by the equation¹

$$\log p_{\text{mm.}} = \frac{-5700}{T} + 2.5 \log T + 3.956$$

Between 400 and 430° the hydrogen pressure reaches 1 atm. The melting point (under pressure) is above 800°. Sodium hydride dissolves in fused sodium hydroxide and in fused alkali halides. It is insoluble in liquid ammonia. Water decomposes it immediately and completely to hydroxyl ion and hydrogen. Although sodium hydride is said to be stable in dry oxygen to 230°, traces of elemental sodium present may cause its ignition at lower temperatures. Copper, lead, and iron oxides are reduced by the compound to the free metals. Sulfur dioxide, carbon monoxide, and the halogens are reduced by the hydride to dithionite, formate, and halide ions, respectively.

Dispersions of sodium hydride in oil are white or light gray and have roughly the same viscosity characteristics as sodium dispersions (synthesis 2). Such dispersions are useful as safe and convenient means of adding sodium hydride in such reactions as Claisen or Stobbe condensations, in preparations of complex hydrides, and in reductions of metal salts.

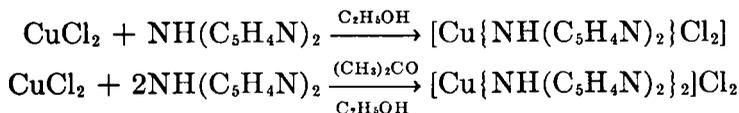
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CHAPTER IB

See also: Preparation of metal derivatives of 1,3-diketones, synthesis 29
Dichloro(di-2-pyridylamine)cobalt(II), synthesis 50

**4. DICHLORO(DI-2-PYRIDYLAMINE)COPPER(II)
AND BIS(DI-2-PYRIDYLAMINE)COPPER(II)
CHLORIDE**



SUBMITTED BY STANLEY KIRSCHNER*

CHECKED BY HENRY F. HOLTZCLAW, JR.,† AND JAMES P. COLLMAN†

The organic base di-2-pyridylamine, $\text{NH}(\text{C}_5\text{H}_4\text{N})_2$, can be prepared in the laboratory according to the method of Steinhäuser and Diepolder¹ and is commercially available.‡ The compound (m.p. 95°, b.p. 222°) is only slightly soluble in water (less than 0.5 g./100 g. at 20°) but dissolves readily in methanol, ethanol, and acetone. In its coordination compounds with metal ions di-2-pyridylamine appears to be bidentate, with coordination occurring through the pyridine nitrogen atoms and giving six-membered rings. Copper(II) compounds containing both one and two molecules of the base per copper ion are readily obtained by reactions in anhydrous media.

Procedure

A. DICHLORO(DI-2-PYRIDYLAMINE)COPPER(II)

Anhydrous copper(II) chloride is first prepared by heating the 2-hydrate at 125° for 12 hours. A solution of

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‡ Available from Reilly Tar and Chemical Corp., Indianapolis, Ind.

7.0 g. of the anhydrous compound (0.052 mol) dissolved in 150 ml. of absolute ethanol is filtered. To the filtrate, a solution of 8.56 g. of di-2-pyridylamine (0.050 mol) in 350 ml. of absolute ethanol is added slowly and with vigorous stirring. The resulting olive-green precipitate is removed by filtration, is washed with four successive 50-ml. portions of absolute ethanol, and is dried at 110° for 12 hours. The yield is at least 14.8 g. (97%). *Anal.* Calcd. for $[\text{Cu}\{\text{NH}(\text{C}_5\text{H}_4\text{N})_2\}\text{Cl}_2]$: C, 39.29; H, 2.97; N, 13.75; Cl, 23.20. Found:* C, 39.43; H, 2.96; N, 13.38; Cl, 22.64.

B. BIS(DI-2-PYRIDYLAMINE)COPPER(II) CHLORIDE

A solution of 7.0 g. of anhydrous copper(II) chloride (0.052 mol) in 25 ml. of absolute ethanol (the solvent may be warmed to effect solution of the salt, if necessary) is filtered, and the residue is washed with 5 ml. of absolute ethanol (the washing is added to the filtrate). The filtrate is then added slowly, and with vigorous stirring, to a solution of 18.5 g. of di-2-pyridylamine (0.108 mol) dissolved in 350 ml. of reagent-grade acetone. The resulting bright green precipitate is removed by filtration, washed with four successive 50-ml. portions of acetone, and dried at 110° for 12 hours. The yield is at least 23.8 g. (96%). *Anal.* Calcd. for $[\text{Cu}\{\text{NH}(\text{C}_5\text{H}_4\text{N})_2\}_2]\text{Cl}_2$: C, 50.37; H, 3.80; N, 17.63; Cl, 14.87. Found:† C, 50.31; H, 3.83; N, 17.26; Cl, 14.76.

Properties

Both complexes precipitate as extremely minute crystals. The olive-green mono(dipyridylamine) complex is stable in air up to a temperature of 290°, whereas the bis(dipyridylamine) complex is stable up to 235°. Both compounds are very slightly soluble in acetone, ethyl ether, benzene, chloroform, and carbon tetrachloride. The mono(dipyri-

* The checkers report C, 39.71; H, 3.23.

† The checkers report C, 51.30; H, 4.17.

dylamine) complex is very slightly soluble in absolute methanol and ethanol, whereas the bis(dipyridylamine) complex is soluble in both of these solvents.

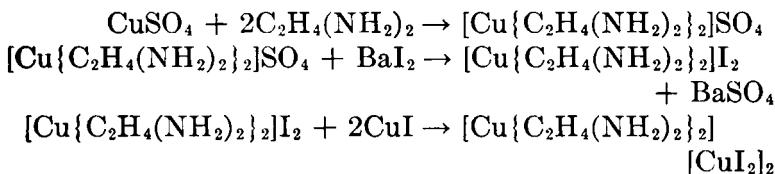
The very slightly soluble mono(dipyridylamine) complex reacts with excess dipyridylamine in methanol or ethanol to give the soluble bis(dipyridylamine) complex according to the equation



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5. BIS(ETHYLENEDIAMINE)COPPER(II) DIIDOCUPRATE(I)



SUBMITTED BY GEORGE W. POLLY,* DARRYL E. JACKSON,* AND BURL E. BRYANT*

CHECKED BY BODIE E. DOUGLAS†

Although the hydrated copper(II) ion is readily reduced to insoluble copper(I) iodide by iodide ion, the bis(ethylenediamine)copper(II) ion is not so reduced. Similarly, although water-soluble simple copper(I) salts cannot be isolated because of ready oxidation to copper(II) species, complex copper(I) species, such as the iodocuprate(I) ions,¹⁻³ $[\text{CuI}_2]^-$ and $[\text{CuI}_3]^-$, are resistant to oxidation. The compound bis(ethylenediamine)copper(II) diiodocuprate(I) is thus an interesting example of stabilization of both oxidation states of copper through coordination.⁴

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Bis(ethylenediamine)copper(II) iodide has been prepared by passing air through a mixture of ethylenediamine and copper(I) iodide heated at 60°. ⁵ Iodocuprate(I) compounds have been obtained by dissolving copper(I) iodide in concentrated alkali metal or ammonium iodide solutions. Bis(ethylenediamine)copper(II) diiodocuprate-(I) could be obtained by combining its components, but an adaptation of the procedure of Harris, ³ as given here, obviates isolation of the bis(ethylenediamine)copper(II) ion and is somewhat more rapid.

Procedure

Ten grams of practical (70 to 75%) ethylenediamine is added with stirring to a solution of 12.5 g. of copper(II) sulfate 5-hydrate (0.05 mol) in 50 ml. of water. To this solution, 21.4 g. of barium iodide 2-hydrate (0.05 mol)* dissolved in 50 ml. of water is added slowly with stirring. The precipitated barium sulfate is removed by filtration† and is washed twice with 25-ml. portions of distilled water. The washings and the filtrate are combined.

In a boiling solution of 120 g. of potassium iodide (0.72 mol) in 150 ml. of water,‡ 19.05 g. of copper(I) iodide§ (0.10 mol) is dissolved. The solution is filtered while hot, reheated to boiling, and then added with stirring to the boiling solution of bis(ethylenediamine)copper(II) iodide. Precipitation begins immediately. The suspension is allowed to cool to room temperature and the brown crystalline product removed by filtration. The crystals are washed with five 100-ml. portions of cold water and

* Barium iodide solution obtained by dissolving the carbonate in hydriodic acid can be used.

† Digestion on a steam bath for 1 hour increases the rate of filtration.

‡ This represents almost the minimum quantity of potassium iodide required to dissolve the copper(I) iodide. Larger amounts of potassium iodide increase the rate of solution.

§ Either commercially available copper(I) iodide or that obtained by reduction of a copper(II) salt solution with a soluble iodide in the presence of sodium thiosulfate to remove liberated iodine can be employed.

with 100 ml. of acetone and are then dried either in the air or in an oven at 110°. The yield is at least 33.6 g. (82%). *Anal.* Calcd. for $[\text{Cu}\{\text{C}_2\text{H}_4(\text{NH}_2)_2\}_2][\text{CuI}_2]_2$: N, 6.84; Cu(I), 15.53. Found: N, 7.04; Cu(I), 15.24.

Properties

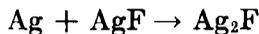
Bis(ethylenediamine)copper(II) diiodocuprate(I) is a chocolate-brown, crystalline compound which melts with decomposition at 267°. It is insoluble in cold water and in organic solvents such as ethanol, acetone, and ethyl ether. Boiling water decomposes it immediately to insoluble copper(I) iodide and a purplish-blue solution of bis-(ethylenediamine)copper(II) iodide. The solid instantaneously reduces a cold aqueous silver nitrate solution to elemental silver.

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6. DISILVER FLUORIDE

(Silver "Subfluoride")



SUBMITTED BY LEE POYER,* MAURICE FIELDER,* HUGH HARRISON,* AND BURL E. BRYANT*

CHECKED BY HERBERT H. HYMAN,† JOSEPH J. KATZ,† AND LLOYD A. QUARTERMAN†

Disilver fluoride (silver "subfluoride") has been prepared by the cathodic reduction of aqueous silver(I) fluoride solutions at low current densities¹ and by the reaction of elemental silver with silver(I) fluoride at tem-

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peratures of 50 to 90°.² The second of these procedures is the more convenient. An excess of silver(I) fluoride is used to ensure complete conversion of the elemental silver.

Procedure

To a solution of 18 g. of silver nitrate (ca. 0.11 mol) dissolved in 50 ml. of water, concentrated aqueous ammonia (sp. gr. 0.8980²⁴) is added slowly and with stirring until a clear solution results. A mixture of 5 g. of polyoxymethylene (metaformaldehyde)* with 100 ml. of water is boiled for 3 minutes and then added with stirring to the silver nitrate solution. The reaction mixture is allowed to stand for 1 hour, and the precipitated silver is removed by filtration. The product is washed with water, absolute ethanol, and ethyl ether and is then dried at 110°. The yield is ca. 11.4 g. (100%).†

A solution of 15 g. of sodium carbonate (0.14 mol) in 100 ml. of water is added with stirring to a solution of 35 g. of silver nitrate (ca. 0.21 mol) in 200 ml. of water.‡ The precipitated silver(I) carbonate is removed by filtration and washed with successive 100-ml. portions of water, absolute ethanol, and acetone with as little exposure to light as possible. Oven drying is not necessary.

The silver(I) carbonate is placed in a polyethylene§ container and treated with sufficient 47% hydrofluoric acid solution (ca. 30 ml.) to dissolve it completely. Slow addition of the acid is necessary to prevent frothing, although frothing can be minimized by decanting ethyl

* Although formalin can be employed, the submitters find the recommended procedure to give a better quality of elemental silver. Pure α -trioxymethylene (*sym*-trioxane) is not suitable.

† Analytical-reagent-quality precipitated silver obtainable from the Mallinckrodt Chemical Works, St. Louis, Mo., may be substituted for the product so prepared.

‡ If the silver nitrate solution is added to the carbonate solution, the precipitate will contain some silver(I) oxide.

§ Glass apparatus cannot be employed in this and in subsequent operations. Containers prepared by cutting the tops off 100-ml. polyethylene bottles are suitable.

ether fumes into the reaction vessel. Eleven grams of precipitated silver (0.1 mol) is added to the solution of silver(I) fluoride, and the mixture is placed upon a gently bubbling steam bath and permitted to evaporate slowly. When the liquid level reaches the solid material in the bottom of the container (12 to 18 hours), a second, exactly equal quantity of silver(I) fluoride solution is added. Evaporation is continued until the liquid level is just above the solid material.* The remaining liquid is decanted, and the solid is washed by decantation with at least four successive 30-ml. portions of absolute ethanol. The product is vacuum-dried at room temperature. The yield is at least 23 g. (96%). *Anal.* Calcd. for Ag_2F : F, 8.09. Found: F, 8.76.†

Properties

Disilver fluoride is a bronze-colored compound with a greenish cast when observed in bulk. It is an excellent electrical conductor. Crystal-structure determination³ shows the complete absence of elemental silver and silver(I) fluoride in the pure material and reveals the presence of successive layers of silver, silver, and fluorine in the lattice. The silver-silver distance is 2.86 Å. (nearly twice the metallic radius of 1.53 Å.), and the silver-fluorine distance is 2.46 Å. [as in ionic silver(I) fluoride]. The compound is regarded as being intermediate in structure between a metal and a salt.⁴

Thermal decomposition to elemental silver and silver(I) fluoride begins at 100° and is complete at 200°. Water effects the same decomposition almost instantaneously.

* If the liquid level falls below the solid material, decomposition of the exposed "subfluoride" may occur. The vessel should be shaken occasionally to break and submerge the film of solid which forms on the surface. Ordinary laboratory illumination causes no apparent decomposition, but direct sunlight does.

† Unreacted silver(I) fluoride gives high fluorine analyses and may give yields in excess of theoretical.

The compound may be kept dry in a stoppered container for weeks without evidence of decomposition. All common methods of purification cause decomposition.

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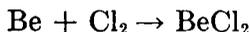
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CHAPTER IIA

See also: Chlorine(I) compounds, synthesis 44

Barium (ethylenediaminetetraacetato)cobaltate(III) 4-hydrate,
synthesis 52

7. BERYLLIUM CHLORIDE



SUBMITTED BY IRVING R. TANNENBAUM*

CHECKED BY S. YOUNG TYREE, JR., † AND DAVID L. VENEZKY, † AND BY
W. W. BEAVER ‡

Anhydrous beryllium chloride was first prepared by passing chlorine gas over a heated mixture of beryllium oxide and carbon.¹ A direct synthesis from the elements was reported in 1828.² Other syntheses described include heating the oxide at 800° in the vapor of sulfur(I) chloride,^{3,4} phosphorus(V) chloride,³ or carbon tetrachloride;⁵ heating beryllium carbide with chlorine^{6,7} or hydrogen chloride;⁶ passing hydrogen chloride over heated elemental beryllium;⁸ and calcining beryllium oxide, sulfate, or carbonate with ammonium chloride.⁹ An improved method based upon beryllium oxide, carbon, and chlorine has been described.¹⁰ The direct synthesis described here is recommended because of the availability of the elements in pure form, the simplicity and adaptability of the procedure, and the high purity of the product.

Procedure

The pyrex chlorination apparatus (Fig. 3) consists of a reaction tube *A*, which may be inserted into a 25-cm. sleeve-type electric furnace, and a collecting tube *B*, which

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† University of North Carolina, Chapel Hill, N. C.

‡ The Brush Beryllium Company, Cleveland, Ohio.

is attached by means of a three-way stopcock *E* to a 2-l. reservoir *F* and which ends in a breakoff seal *D*. As illustrated, the apparatus handles ca. 0.5 g. of beryllium and

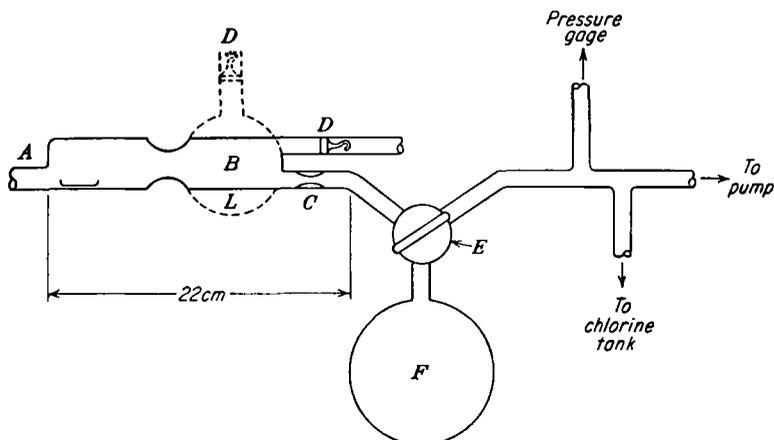


FIG. 3. Apparatus for the preparation of beryllium chloride.

yields 4.5 to 5.0 g. of beryllium chloride. For amounts of beryllium up to 2.5 g., the apparatus is modified to include a 100-ml. bulb *L* (indicated by dotted lines in Fig. 3). The constriction *C* is placed as far as possible from the heated zone to minimize plugging by the readily sublimable, glass-adherent product. The stopcock *E* is lubricated with a fluorocarbon grease, *e.g.*, Kel-F,* which remains usable after long contact with chlorine. Chlorine gas is admitted from a cylinder through a Teflon-packed stainless-steel needle valve, which is silver-soldered to a steel standard taper. To this is fitted a standard-taper glass joint, the union being made vacuum-tight with Apiezon W. A pressure gage constructed of stainless steel or monel metal is attached in the same fashion.

Five-tenths gram of beryllium powder or chips† (0.056 mol) is placed in a pyrex boat in reaction chamber *B*. The open end is then sealed at *A*. Both reaction chamber *B*

* Silicone fails after contact with chlorine for 2 to 3 days.

† Chips give a clean product more readily, but the yield is lower.

and reservoir *F* are evacuated and then filled with chlorine at a pressure of 1 atm. Stopcock *E* is manipulated to connect *B* and *F* and isolate the system from the chlorine source. The reaction chamber is inserted into the furnace just beyond the boat, and the temperature is raised slowly. At 300° a rapid rise in temperature indicates formation of beryllium chloride.* After the effect of the heat of reaction has subsided, the temperature of the reaction vessel is increased to 350°, and the reaction is continued for 40 hours. Consumption of chlorine may be followed by adjusting the stopcock and noting decrease in pressure

on the gage. More chlorine should be admitted periodically to maintain the pressure at 1 atm.

At the end of the reaction period, chamber *B* is evacuated and sealed off at *C*. The vessel is then sealed through *D* to the sublimation apparatus shown in Fig. 4. This amounts to a collection vessel *J*, which is separated from the initial sample by a coarse glass frit or plug of glass wool *G*. For amounts of beryllium up to 2.5 g., the

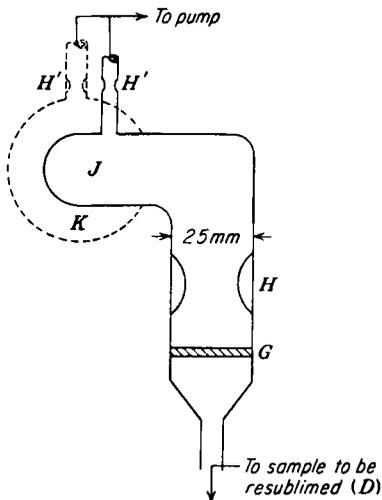


FIG. 4. Apparatus for the purification of beryllium chloride.

collector should be enlarged to a 100-ml. bulb *K* (indicated by dotted lines in Fig. 4). The entire system is evacuated, the seal at *D* is broken, and the entire apparatus up to *J* (or *K*) is heated at 350°, while pumping is maintained. Sublimation is complete in less than 1 hour. The product is isolated by sealing at *H* (and *H'*). The yield is 4 g. (91%).

* Beryllium samples containing iron (0.01 to 0.1%) yield yellowish iron(III) chloride at 250°. This material is readily removed by flaming the container with a brush flame.

Anal. Calcd. for BeCl_2 : Be, 11.28; Cl, 88.72. Found: Be, 11.33; Cl, 88.67.*

Properties

Anhydrous beryllium chloride is a white, crystalline solid, melting at 405° , boiling at 488° ,¹¹ and subliming *in vacuo* at 300° . When fused, its conductivity is about 0.001 that of sodium chloride. This suggests that about 1 molecule in 1000 is ionized.¹² The compound is very soluble in many organic solvents. It is extremely hygroscopic and dissolves readily in water with the evolution of large amounts of heat. The solid must be handled in a dry atmosphere. Anhydrous beryllium chloride can be used as a catalyst in organic syntheses much as anhydrous aluminum chloride is used.¹³

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* Losses of hydrogen chloride released by hydrolysis during direct solution of the product are avoided by placing a weighed sample in an open weighing bottle contained in a second weighing bottle to which some water has been added, stoppering, allowing to stand 1 day, mixing the resulting residue and hydrochloric acid solution, and analyzing.

CHAPTER IIIA

See also: Preparation of metal derivatives of 1,3-diketones, synthesis 29

8. BORON HALIDE-AMINE COORDINATION COMPOUNDS



SUBMITTED BY DALLAS T. HURD* AND ROBERT C. OSTHOFF*
CHECKED BY ALBERT W. LAUBENGAYER† AND DANIEL JACOBS†

The boron halides form a number of coordination compounds with various amines, the variety of such compounds decreasing from the trifluoride to the triiodide and from the tertiary amines to the primary.^{1,2} Preparation is usually effected by direct combination of boron halide and amine,³⁻⁵ often with provision for external cooling to remove heat released in the reaction. The following syntheses exemplify general methods that can be employed.

Procedure

A. BORON FLUORIDE-TRIMETHYLAMINE

Each of the side necks of a 1-l. pyrex three-necked flask is closed with a one-hole stopper carrying a piece of 6- or 9-mm. glass tubing which extends nearly to the bottom of the flask. A loose plug of glass wool is placed in the center neck of the flask, and then a one-hole stopper bearing a short length of glass tubing which does not extend below the bottom of the stopper is inserted. The flask is placed in an ice bath of sufficient size to immerse most of the flask, and the apparatus is transferred to a hood. One

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† Cornell University, Ithaca, N.Y.

of the tubes in a side neck is connected by means of Tygon or polyethylene tubing to a cylinder of boron fluoride and the other to a cylinder of trimethylamine.* The tube in the center neck is connected to a mercury or oil bubbler, in which the bubble tube is just below the surface of the liquid, to eliminate suckback.

A slow current of trimethylamine is admitted to the flask. Then the valve on the boron fluoride cylinder is opened slowly. The flask will fill immediately with dense white fumes of the product. The valve on the boron fluoride cylinder is adjusted so that the bubbler shows no appreciable net flow of gas out of the flask, and the reaction is allowed to continue until the desired quantity of product has accumulated in the flask. The flow of trimethylamine is discontinued, and then that of boron fluoride is stopped.† The white solid product can be recrystallized from benzene or ethanol. The yield for a reaction time of 40 minutes is ca. 12.5 g.

B. BORON CHLORIDE-TRIMETHYLAMINE

The apparatus used is the same as that described above, except that 200 ml. of dry benzene is placed in the flask and the gas delivery tubes are adjusted to project slightly below the surface of the benzene. The boron chloride delivery tube should be at least 9 mm. in diameter.‡ Trimethylamine is admitted to the reaction vessel at such a rate as to produce moderate bubbling in the bubbler. Boron chloride§ is then admitted, and its rate of flow is adjusted as before so that no net flow of gas out of the flask results. As the reaction proceeds, the product separates from the benzene layer as white crystals. The reaction is allowed to continue until the desired quantity of product is

* Obtainable from the Matheson Company, Inc., East Rutherford, N.J.

† The slight excess of boron fluoride so produced eliminates the objectionable odor of the amine.

‡ The solid product may clog the inlet of this tube and necessitate dismantling the apparatus and unplugging the tube.

§ Also obtainable from the Matheson Company.

obtained. The flow of trimethylamine is stopped first and then that of boron chloride. The contents of the flask are filtered through a Büchner funnel. A current of air is drawn through the solid on the filter until the material is dry. It is then recrystallized twice from hot ethanol. The yield for a reaction time of 1½ hours is ca. 45 g.

Properties

Boron fluoride-trimethylamine is a white, crystalline solid melting in a closed tube at 138°.³ The vapor pressure of the solid is given by the equation⁴

$$\log p_{\text{mm.}} = 10.240 - \frac{3600}{T}$$

and that of the liquid by the equation⁴

$$\log p_{\text{mm.}} = 8.735 - \frac{2963}{T}$$

From these relationships, the following values are obtained:⁴ heat of fusion, 3.5 kcal./mol; normal boiling point, 233°; Trouton's constant, 25.5 cal./deg. mol. The liquid and vapor are both associated.⁴ Cryoscopic measurements upon benzene solutions give apparent molecular weights ranging from 158 (mol fraction = 0.0016) to 230 (mol fraction = 0.0060).³ At room temperature the solubility of the compound in benzene is 0.995 g./100 g. of solvent.³

Boron chloride-trimethylamine is a white, crystalline solid melting at 242 to 243°.⁵ It is insoluble in benzene but soluble in hot ethanol. It sublimes in high vacuum.⁶

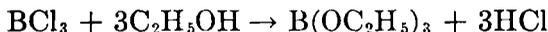
These two compounds are among the thermally more stable boron halide-amine compounds. Compounds derived from certain primary and secondary amines lose hydrogen halides at elevated temperatures to give condensed boron-imide or borazole (borazine) derivatives.

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9. ETHYL ORTHOBORATE



SUBMITTED BY S. V. URS,* CHARLES G. OVERBERGER,* AND EDWIN S. GOULD*

CHECKED BY HAROLD R. SNYDER,† EDWARD P. MERICA,† AND JOHN W. PANKEY†

Butyl orthoborate and esters of higher-molecular-weight aliphatic alcohols can be prepared by the reaction of orthoboric acid with an excess of the appropriate alcohol, the water formed and the alcohol that did not react being separated azeotropically.^{1,2} Although ethyl orthoborate has been prepared by treating absolute ethanol either with boric oxide^{3,4} or with borax and hydrogen chloride,⁵ the preparation from boron chloride and ethanol gives higher yields, is less troublesome, and involves no difficulties in separation of the product. The recommended procedure is a modification of that described by Ebelmen and Bouquet.⁶ Methyl orthoborate may be prepared by the same method, but synthesis from methanol and orthoboric acid, boric oxide, or borax⁷ is superior from the points of view of yield and convenience. Procedures involving reaction of an alcohol with either methyl orthoborate or sodium borohydride in the presence of acetic acid appear to be generally applicable.⁸

Procedure

Through the central neck of a 500-ml. three-necked round-bottomed flask provided with ground-glass joints is passed a mechanical stirrer provided with a simple rubber slip joint (glycerol-lubricated). The side necks are provided with one-hole rubber stoppers, through which

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pass small lengths of glass tubing. One of these sections of tubing is attached outside the flask to a 6-in. length of Tygon tubing for introducing boron chloride. The second tube is attached outside the flask to a rubber policeman having several small slits, in order to allow vapor to escape from the flask but prevent entrance of atmospheric moisture. The flask is cooled in a mixture of Dry Ice and acetone, and 151 g. of boron chloride⁹ (1.29 mol) is collected in the flask by condensation.* The inlet tube and its stopper are then quickly replaced by a 250-ml. dropping funnel equipped with a ground-glass joint.† The Bunsen-type valve in the other side neck of the flask is replaced by a vented "cold-finger" condenser, also equipped with a ground-glass joint.† The cold finger contains a mixture of Dry Ice and acetone, and its vent is protected by a drying tube containing calcium chloride. One hundred eighty-five grams of absolute ethanol (4.03 mols) is placed in the dropping funnel. The alcohol is allowed to drip into the flask, very slowly at first and over a total reaction period of 2½ to 3 hours. The contents of the flask are kept cold and are stirred vigorously during the entire reaction.

After all of the ethanol has been added, the mixture consists of two liquid phases. The denser of these is a mixture of dichloroethoxyborine, $B(OC_2H_5)Cl_2$, and chlorodiethoxyborine, $B(OC_2H_5)_2Cl$; the upper layer is largely ethyl orthoborate and ethanol. The mixture is allowed to warm slowly to room temperature. The mechanical stirrer is replaced by a well attached to a male ground-glass joint, and a thermometer is inserted through the well into the liquid. The vented cold-finger condenser is replaced by a Liebig condenser, again protected from atmospheric moisture by a calcium chloride drying tube. The tem-

* Commercial boron chloride (synthesis 8) can be used and run directly into the reaction vessel by inverting the cylinder. Condensation into the flask from the cylinder is slower but gives a better product.

† No lubricant is used on the ground-glass joints.

perature of the mixture is slowly raised and the mixture allowed to reflux. At the end of a 3-hour reflux period, the temperature of the mixture should be 115 to 120°, and only one liquid phase should remain. The desired ester (b.p. 120°) is separated from the small amount of excess alcohol (b.p. 78.5°) by distillation through a column having three or more theoretical fractionation plates. The yield is 146 to 150 g. (77.6 to 79.7%).

Properties

Ethyl orthoborate has a boiling point of 120°, a density of 0.864₂₆²⁶, and a refractive index (n_D^{25}) of 1.3721. It is readily hydrolyzed to ethanol and orthoboric acid. The ester may be analyzed for boron by dissolving a weighed sample in water, adding mannitol (about ten times the weight of sample taken), and titrating the boric acid to the phenolphthalein end point. This determination works best if the solution is protected from atmospheric carbon dioxide in the region of the end point.

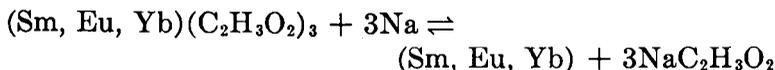
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CHAPTER IIIB

See also: Preparation of metal derivatives of 1,3-diketones, synthesis 29
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10. ISOLATION OF SAMARIUM, EUROPIUM, AND YTTERBIUM MATERIALS BY MEANS OF SODIUM AMALGAM



SUBMITTED BY J. K. MARSH*

CHECKED BY HOWARD E. KREMERS† AND DAVID FOSTER‡

In the dipositive state, the lanthanons‡ are chemically similar to the alkaline earth elements and, like the latter, give reciprocal replacement with alkali metal amalgams. This is best studied by the use of sodium amalgam and concentrated solutions of the lanthanon(III) acetates.¹⁻⁶ Acetates of all of the elements of the yttrium and cerium groups are capable of some metal exchange with sodium amalgam, but the samarium, europium, and ytterbium compounds react most readily, presumably because of the ease of reduction to the dipositive state with these materials. Amalgams of those lanthanons which do not yield dipositive ions form much less readily. In the cerium group, except for samarium and europium, metal exchange with sodium amalgam decreases rapidly from lanthanum to gadolinium. In the yttrium group, the decrease is so pronounced that the neighbors of ytterbium give essen-

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‡ Lanthanon is a general name applied to yttrium and any element in the region lanthanum through lutetium.

tially no exchange. Electrolytic reduction to amalgam has been used for the recovery of pure europium.⁷

Sodium amalgam extraction can thus be used to remove the whole of the samarium, europium, or ytterbium from mixtures with the other lanthanons. If the initial concentration of any of these is large, the efficiency of the reaction may exceed 75%. Low efficiencies characterize the removal of traces of these elements. Efficiency is enhanced by keeping the acetate solution as nearly free from sodium ion as possible and withdrawing much of the sodium amalgam before it can react. The extraction is an equilibrium process.

Procedure

A. GENERAL PROCEDURE

The lanthanon(III) oxide, which is best prepared by ignition at no more than a moderate red heat, is treated with 20% more than the theoretical requirement of 20% acetic acid solution, and the mixture is heated on the steam bath with occasional stirring until solution has occurred.* The filtered solution is boiled to remove carbon dioxide and evaporated below 70° until crystals start to form.† The suspension is then allowed to stand overnight to complete crystallization. The crystals are removed, and the mother liquor is added to the next batch of material prior to crystallization.

Acetate equivalent to 250 g. of the initial oxide mixture is placed in a 3-l. Florence flask‡ and dissolved by adding water and heating.§ Up to 750 ml. (10 kg.) of a 0.25 to 0.33% sodium amalgam⁸ is added, and the mixture is given a gentle rotary shake. A few milliliters of glacial acetic

* With samples rich in ytterbium, larger quantities of acid may be needed to effect solution.

† With samples rich in cerium earths, partial dehydration to products of small solubility occurs above 70°.

‡ Losses by frothing are avoided by use of a large flask of this type.

§ Ytterbium and samarium acetates require at least 1.5 and 2.5 parts of water, respectively, for solution.

acid is added from a buret to prevent frothing or hydroxide precipitation and to promote active reduction.* The quantity of acid required will vary inversely with the richness of the acetate with respect to samarium, europium, or ytterbium but should not exceed that necessary to react with 20 to 25% of the sodium (ca. 62 ml. for 750 ml. of 0.25% amalgam). After 1 to 2 minutes, most of the acetate solution is decanted into a second flask, and the remainder is removed from the amalgam with a separatory funnel. The aqueous solution is reserved for a second amalgam extraction. The amalgam is washed by passage through water in a second separatory funnel, both the separation and the washing being conducted as rapidly as possible to minimize loss by back-reaction. Large-bore stopcocks on the separatory funnels are desirable.

The amalgam is decomposed by covering it with 4 *M* acetic acid in a large crystallizing dish.† The dish is rocked gently to give the acid ample opportunity to attack the hydroxide that forms on the mercury surface, and the reaction is allowed to proceed for 1 to 2 hours.‡ The aqueous solution is then removed with a suction probe, evaporated until crystals begin to form, and allowed to crystallize overnight.§ The suspension is filtered, and the filtrate is diluted, made alkaline with sodium hydroxide, and boiled to recover the remaining lanthanon.

The original acetate solution is extracted with sodium amalgam a second time, and the above procedure is

* If the acetate is rich in europium or ytterbium, the yellowish or greenish colors of the dipositive ions may develop in solution. Similarly, material rich in samarium may give a reddish-brown solution. With material poor in these elements, color development indicates sodium exhaustion and solution of the lanthanon amalgam.

† The checkers suggest that when other reducible lanthanons are absent, the amalgam is more conveniently decomposed by covering it with 6 *M* hydrochloric acid and bubbling air through the amalgam.

‡ With samarium-europium samples, other cerium earths are extracted from the amalgam phase only after the bulk of it has decomposed. Fractional decomposition of the amalgam is thus desirable.

§ Sodium acetate does not crystallize until the bulk of the lanthanon acetate is removed.

repeated. Complete removal of the potentially dipositive species may require several additional extractions, but the quantities remaining after the second extraction are very small. The initial exchange efficiency of 70 to 90% decreases to a low value for removal of final traces of material.

B. SEPARATION OF SAMARIUM AND EUROPIUM^{4,5}

A concentrated acetate solution from the above procedure (98 to 99% samarium, 2 to 1% europium) is heated to 70° and rendered definitely acidic with a few drops of 30% sulfuric acid. A small volume of 0.1 to 0.2% sodium amalgam is added and the system stirred gently. The europium(II) sulfate which precipitates* is removed rapidly by suction filtration. The mother liquor is returned to the amalgam, and a second crop of europium(II) sulfate crystals is recovered. The process is repeated until red samarium(II) sulfate crystals appear,† each crop of europium(II) sulfate crystals being washed from the filter paper with water as soon as collected. All of the europium(II) sulfate (80 to 90% pure) is combined and oxidized with 6 *M* nitric acid to a solution of the tripositive species. This is converted successively to oxalate, oxide, acetate solution, and amalgam. The amalgam is then treated with successive small portions of 10 *M* hydrochloric acid in an inert nitrogen or carbon dioxide atmosphere in a dry box, and the precipitated europium(II) chloride 2-hydrate is removed as it forms.‡ The product is a pure europium compound. Pure samarium is then recovered by oxalate precipitation from the remaining europium-free solution.

* Traces of colloidal mercury impart a gray color and render the product very susceptible to oxidation.

† The last traces of europium are removed with the first crystals containing samarium(II) sulfate. These crystals are treated with 2 *M* nitric acid to oxidize and dissolve the samarium and leave behind white europium(II) sulfate.

‡ Samarium(III) chloride precipitates only at higher acidities, and samarium(II) chloride does not form.

Examples

The following examples represent results obtained for specific applications of these rather general procedures.

Separation of Samarium and Gadolinium. One hundred forty-three grams of mixed acetates (11% samarium, 89% gadolinium, trace of europium) in 325 ml. of aqueous solution was treated with 7.5 g. of sodium in 175 ml. of mercury and with 12 ml. of glacial acetic acid, added in small portions over a period of 2 to 3 minutes. Removal of the amalgam and recovery of its lanthanon content gave a yield of pure samarium(III) oxide of 86%. A second amalgam extraction, using 6.4 g. of sodium and 20 ml. of glacial acetic acid with the volume of aqueous solution doubled to avoid solubility reduction due to the presence of accumulating sodium acetate, gave an additional yield of 12.5%. Gadolinium recovered from the remaining aqueous solution was 99.85% pure with respect to samarium and europium.

Purification of Ytterbium and Lutetium. One hundred grams of crude lutetium-ytterbium acetate dissolved in 133 ml. of boiling water was treated with 22.7 g. of sodium in 250 ml. of mercury and with 7 ml. of glacial acetic acid. The resulting amalgam gave a yield of pure ytterbium oxide of 73%. Treatment of a similar sample with 28.4 g. of sodium gave a yield of pure ytterbium(III) oxide of 93%.

The crude lutetium acetate solution remaining was extracted with five successive portions of sodium amalgam, each consisting of 0.25 g. of sodium in 7 ml. of mercury. Sodium ion was eliminated through precipitation of the hydroxide and reconversion to acetate. Three more series of similar sodium amalgam extractions were made. Lutetium material recovered from the final aqueous solution was spectroscopically free from ytterbium.

Separation of Samarium and Europium. One hundred thirty-five grams of samarium-europium acetate in 450 ml. of solution at 60° was treated with 1.0 g. of sodium in 80 ml. of mercury. One-half milliliter of 30% sulfuric acid was added, and the precipitated europium(II) sulfate

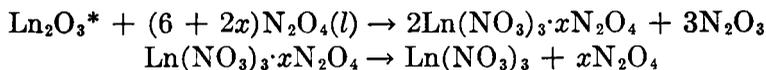
was removed by filtration. Six additional similar treatments gave mixed samarium(II) and europium(II) sulfate precipitates. Final decomposition of the remaining amalgam and recovery gave 54.3 g. of europium-free samarium(III) oxide. Total oxides recovered from the sulfate precipitates amounted to 5 g. The first sample contained no detectable samarium; the last only 0.003% europium.

Purification of Europium. An acetate solution obtained from 20 g. of europium(III) oxide (>99% pure) was treated with 260 ml. of 0.3% sodium amalgam, added in three separate equal portions. The resulting amalgam contained all but 0.09 g. of the europium. Treatment of the amalgam with 100 ml. of 10 *M* hydrochloric acid caused complete precipitation of europium(II) chloride 2-hydrate. Removal of the product followed by washing with ice-cold 10 *M* hydrochloric acid and ultimate conversion to europium(III) oxide gave a recovery of spectroscopically pure europium in excess of 90%.

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11. ANHYDROUS LANTHANON NITRATES



SUBMITTED BY THERALD MOELLER,† VICTOR D. AFTANDILIAN,† AND
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CHECKED BY GEORGE GIBSON‡ AND ILMAR KALNIN‡

Hydrated lanthanon (yttrium and rare earth metal) nitrates cannot be dehydrated by any recorded thermal

* Ln represents yttrium or a rare earth element.

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procedure because of hydrolysis to basic products. Anhydrous lanthanum nitrate has been obtained by reaction of fused ammonium nitrate with lanthanum oxide,¹ but with neodymium oxide the compound $\text{Nd}(\text{NO}_3)_3 \cdot \text{NH}_4\text{NO}_3$ was obtained and could not be freed from ammonium nitrate by thermal means without decomposition to a basic salt.¹ It is probable that the heavier and less basic members of the rare earth series would be even more prone to yield basic salts under such conditions. A general method for preparing anhydrous lanthanon nitrates, which is free from these difficulties and gives essentially quantitative yields, involves reactions of the sesquioxides with liquid nitrogen(IV) oxide under pressure at elevated temperatures and subsequent thermal decompositions of the solvated nitrates.² This procedure is an example of a general type of reaction applicable to the preparation of many anhydrous nitrates.³⁻⁹

Procedure

A pyrex glass and metal apparatus of the type indicated in Fig. 5 is assembled. A cylinder of nitrogen(IV) oxide is connected through Tygon tubing covered with Glyptal resin to a drying tower *A*, which is packed with phosphorus(V) oxide and glass beads. This tower is joined to a 200-ml.-capacity storage vessel *B* through a 6-mm. vacuum stopcock. Attached to *B* is a 60-cm. manifold of 6-mm. glass tubing, with connecting safety mercury manometer at *C*, trap and McLeod gage at *D*, and dividing vacuum stopcock. The reaction vessel *F*, a stainless-steel bomb of 150-ml. capacity,* is attached to the manifold

* Style No. HD150, Hoke Incorporated, Englewood, N.J. The cylinder, rated at 1800 p.s.i., is fitted with a needle valve (Hoke, Style 3002) at one end and a stainless-steel plug at the other end. Since the initial tapered threads are damaged by repeated tightening of the plug, the original hole is rebored with standard straight threads. Smooth shoulders are machined on both the cylinder around the hole and on the plug head, and a gastight seal is obtained by compressing a lead washer between plug and cylinder. The needle-valve outlet is fitted with a stainless-steel tube of the same diam-

at *E*.^{*} A trap *G* and an attachment to a high-vacuum pump at *H* complete the system.

Two grams of a rare earth metal (or yttrium) sesquioxide (ca. 0.006 mol), which has been ignited at 900° and cooled just prior to use,[†] is placed in the dry bomb through the

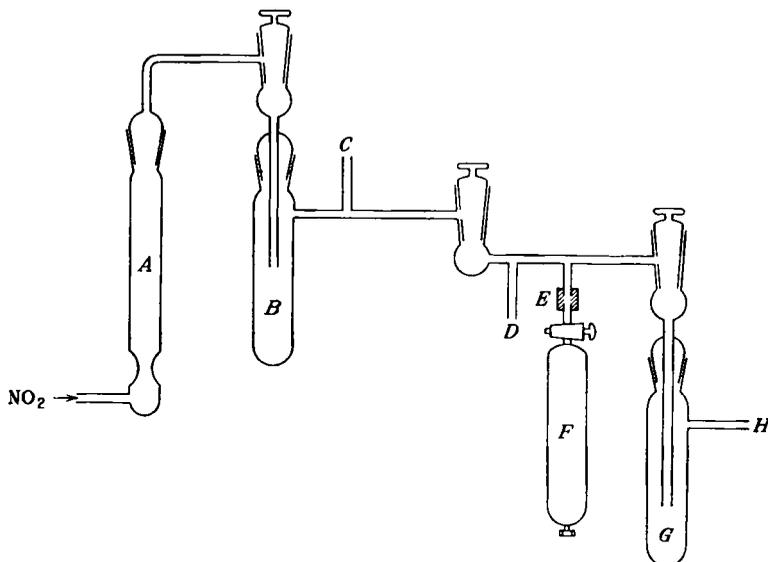


FIG. 5. Apparatus for the preparation of anhydrous lanthanon nitrates.

hole in the bottom. The hole is closed with the plug, and the bomb is connected to the glass manifold at *E* by wrapping a strip of aluminum foil around the glass-metal junction, covering with unvulcanized rubber tape, and

eter as the glass tube at *E*. A lead compression washer can be used between the needle valve and the cylinder to eliminate leakage.

^{*} The checkers employ a ball-and-socket joint with the socket portion attached to the needle valve through a thread and solder seal. Their bomb has no bottom plug, the top opening having the same diameter as the reaction region and the needle valve being held by an overlapping hex nut bearing on a compressible lead washer. Removal of product and cleansing are facilitated.

[†] Praseodymium(III) oxide is obtained by reducing the black oxide Pr_6O_{11} with anhydrous hydrazine, washing, and drying, first with ethanol and ether and then over nitrobenzene in an Abderhalden drying pistol.¹⁰

coating with Glyptal resin. The result is a gastight but easily broken seal. The system is evacuated to about 0.02 mm., and the stopcock dividing the manifold is closed. About 30 ml. of nitrogen(IV) oxide (ca. 0.49 mol) is condensed into vessel *B* by surrounding this vessel with liquid nitrogen. The system is then isolated by closing the two end stopcocks. The dividing stopcock is opened, and the nitrogen(IV) oxide is condensed into the bomb by cooling with liquid nitrogen while warming vessel *B* with water at 40°. The valve on the bomb is closed, the seal at *E* is cut, and the tube at the top of the bomb is closed with a stainless-steel cap at *E*. The bomb and its contents are then heated in an oven at 150° for 24 hours.

After being cooled to room temperature, the bomb is connected to a vacuum pump through a series of towers containing magnesium perchlorate and a trap cooled in liquid nitrogen. The bomb is warmed at 40 to 45° in a water bath, and the nitrogen oxides are bled off by careful manipulation of the needle valve while pumping is maintained. After ½ hour, the valve is closed and the bomb transferred to a dry box containing nitrogen. Nitrogen is admitted through the carefully opened needle valve. Then the stainless-steel plug is removed, and the solid contents are scraped into a weighed container.* The container is removed from the dry box and is heated to constant weight in an Abderhalden pistol at 137° over xylene. The container is then sealed for keeping. The yields, as determined by increases in weight during reaction, are quantitative, although mechanical losses during transfer may reduce

* Containers are constructed by sealing off one end of a 10-cm. length of 21-mm.-o.d. pyrex tubing and sealing to the other end the male member of a ground-glass joint (standard taper 24/40). The end of the female member is sealed off to make a cap with the ground glass on the inside. Samples can thus be added or removed from the containers without contacting the silicone grease used as lubricant. The checkers employ similar containers which are equipped with stopcocks and standard ball joints and are heated directly at 135° in an oil bath while attached through the ball joints to a vacuum pump.

them to 95 to 98%. With 2-g. oxide samples, quantities of anhydrous nitrates ranging from ca. 4.7 g. with yttrium to ca. 3.7 g. for gadolinium are obtained.

Analyses

Aliquots of solutions obtained by dissolving weighed quantities of the nitrates in water are analyzed for lanthanon content by evaporating to dryness, igniting, and weighing as oxide and for nitrate content by the gravimetric nitron procedure.¹¹ Typical results are as follows:

Oxide*	Product	Color of product	Nitrate		Lanthanon	
			Calcd.	Found	Calcd.	Found
La ₂ O ₃	La(NO ₃) ₃	White	57.26	56.67	42.75	42.99, 42.57†
Pr ₂ O ₃	Pr(NO ₃) ₃	Pale green	56.91	56.91	43.10	43.13
Nd ₂ O ₃	Nd(NO ₃) ₃	Violet	56.32	56.32	43.69	43.65, 43.64†
Sm ₂ O ₃	Sm(NO ₃) ₃	Cream	55.28	55.72	44.71	44.92, 45.05†
Gd ₂ O ₃	Gd(NO ₃) ₃	White	54.25	54.31	45.76	45.85
Y ₂ O ₃	Y(NO ₃) ₃	White	67.67	66.49	32.34	32.76, 32.78†

* Each oxide free from other lanthanons.

† Second value reported by the checkers.

Properties

The anhydrous nitrates are voluminous, powdery solids, with colors comparable to those of the metal ions present. They dissolve rapidly and completely to clear solutions in water, ethanol, or anhydrous ethylenediamine. In contact with moist air they absorb water readily and give the corresponding hydrated salts.

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CHAPTER IVA

- See also: Dichloro(di-2-pyridyl-amine)copper(II) and bis(di-2-pyridyl-amine)copper(II) chloride, synthesis 4
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12. CYANOGEN



SUBMITTED BY GEORGE J. JANZ*

CHECKED BY HENRY M. WOODBURN,† JAMES T. PECKA,† AND THOMAS J. DOLCE†

Cyanogen is most commonly prepared by adding an aqueous solution of sodium or potassium cyanide to an

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aqueous solution of copper(II) sulfate or chloride.¹⁻⁵ It is also obtained by the thermal decomposition of paracyanogen prepared by the reaction of alkali metal cyanides with phosphorus(V) chloride,⁶ by the vapor-phase reaction between hydrogen cyanide and chlorine,⁷ and by the dry distillation of mixtures of mercury(II) cyanide and mercury(II) chloride.⁸ The wet procedure is convenient for laboratory operations and gives a product of high purity if certain precautions are taken.

Procedure

Caution. This synthesis must be carried out in a well-ventilated hood.

The apparatus (Fig. 6) consists of a 2-l. resin kettle, reaction vessel *A*, to which are attached a water-cooled condenser *B*, a mechanically operated stirrer *C* with mercury-seal connection *D*, a thermometer, and a 1-l. dropping funnel *E* equipped with a pressure-equalizing connection *F* and attached to a nitrogen cylinder through a water bubbler *G*. The cyanogen outlet *H* is attached in series to two bubblers containing acidified silver nitrate solution, to two drying towers packed with phosphorus(V) oxide, and to a 250-ml. glass trap *I* (Fig. 7) cooled to -80° with Dry Ice in chloroform and carbon tetrachloride.

Five hundred grams of powdered copper(II) sulfate 5-hydrate (2 mols) is placed in the reaction vessel, and the latter is attached to the remaining apparatus with the stirrer just under the top of the solid. A saturated solution of sodium cyanide* (500 ml.), which has been freshly prepared and filtered, is placed in the dropping funnel, and the pressure equalizer is attached. A slow stream of nitrogen is passed through the apparatus, and the sodium cyanide solution is added sufficiently slowly so that the temperature in the reaction vessel is maintained at 50

* The carbon dioxide content of the product is reduced by adding barium chloride to the cyanide solution and removing precipitated barium carbonate.

to 55°.* Cyanide addition is continued until the copper-(II) ion is completely reduced.† The temperature of the

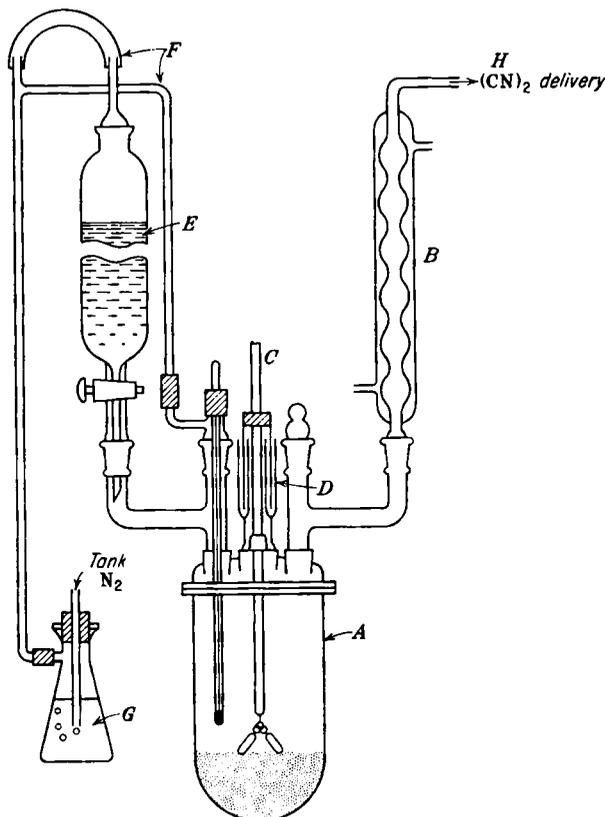


FIG. 6. Apparatus for the preparation of cyanogen.

reaction vessel is then increased to 70 to 75°, and the remaining cyanogen is swept into the trap *I* (Fig. 7) with

* This optimum temperature range should be maintained by controlled addition of the cyanide solution and external cooling of the reaction vessel with a water bath if necessary. Initial heating to 55° before adding the cyanide decreases the yield. Addition of copper(II) sulfate to the cyanide also decreases the yield.

† If additional sodium cyanide solution is required, it should be introduced into the dropping funnel without interrupting the nitrogen flow. The checkers suggest a side arm with stopcock on the dropping funnel for this purpose.

nitrogen.* An excess of iron(II) sulfate is then added to the reaction vessel to remove all cyanide ion before the reaction vessel is washed out.

For storage, the cyanogen is transferred to a 500-ml. stainless-steel cylinder *J*† (Fig. 7) by connecting the trap *I*

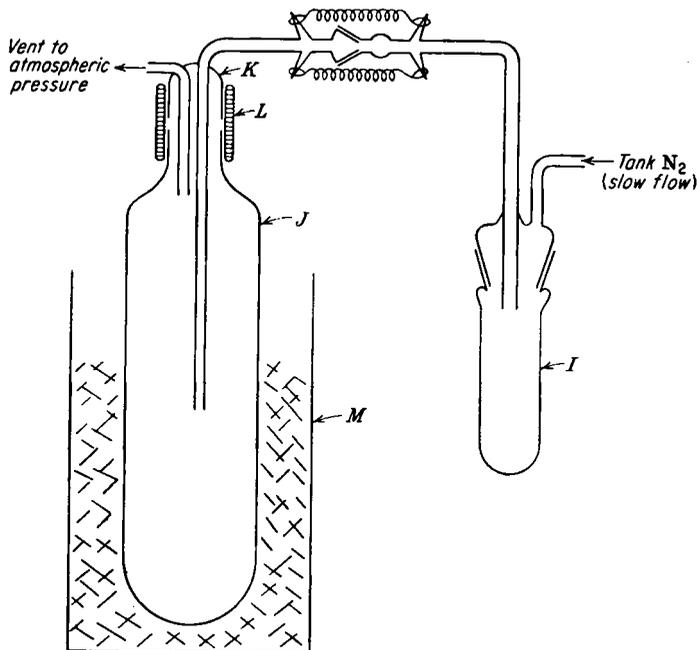


FIG. 7. Apparatus for the collection and storage of cyanogen.

through a wash-bottle-top fitting attached to the cylinder by means of a rubber joint *L*, immersing the steel cylinder in a 2-l. beaker *M* containing Dry Ice, chloroform, and carbon tetrachloride at -80° , and slowly withdrawing the trap from its freezing bath. A slow stream of dry nitrogen

* Addition of 12 *M* hydrochloric acid at the end of the reaction increases the yield by about 6%. However, so much silver nitrate is consumed in the scrubbers by the hydrogen chloride gas carried that this technique is not economically feasible.

† If the interior of the cylinder has been pickled in acid, washed, and thoroughly dried, cyanogen can be stored in it indefinitely without polymerization or decomposition.

is passed through the apparatus to facilitate the transfer. When distillation is complete, the cylinder is closed with a screw-type valve fitting and then allowed to warm to room temperature. Gas analysis^{9,10} shows the product to be better than 89 mol per cent cyanogen. Carbon dioxide is invariably present as a result of initial carbonate impurities and of hydrolysis of cyanate ion formed from cyanogen and the alkaline cyanide solution. The yield of cyanogen is about 21 g. (41%).

Properties

Cyanogen is a colorless gas, condensing to a colorless liquid boiling at -21.17° and freezing at -27.9° . The heat of vaporization of the liquid is 5.778 kcal./mol, and the density at the boiling point is 0.9537. One volume of water dissolves about 4 volumes of the gas.

Cyanogen is the dinitrile of oxalic acid and yields first oxamide and then oxalic acid upon hydrolysis. A number of resonance forms contribute to the linear structure,¹¹ the measured bond distances¹² being C-N, 1.16 Å. and C-C, 1.37 Å. The heat of dissociation of the molecule to CN groups is variously reported from 77 to 145 kcal./mol.¹³⁻¹⁵ The most probable value is around the upper limit.¹⁶ Chemically, cyanogen resembles the halogens. Thus, with hydroxyl ion it yields cyanide and cyanate ions. Above 500° it polymerizes to insoluble paracyanogen, $(\text{CN})_n$. Cyanogen is toxic, its physiological effect being comparable to that produced by hydrogen cyanide.

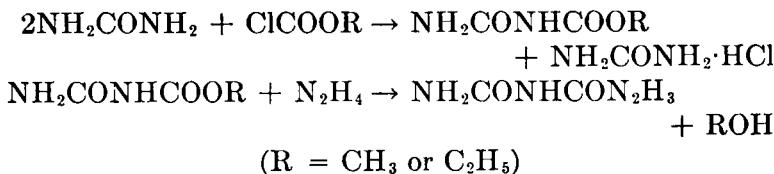
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13. ALLOPHANYL HYDRAZIDE

(1-Aminobiuret)



SUBMITTED BY PAUL G. GORDON* AND LUDWIG F. AUDRIETH*

CHECKED BY P. LENS†

Allophanyl hydrazide has been prepared previously as the hydrochloride by the zinc-hydrochloric acid reduction of 1-nitrobiuret.¹ The new procedure^{2,3} outlined here entails the hydrazinolysis of allophanic esters in alcoholic solution. Excellent yields (80 to 84%) of allophanyl hydrazide are obtainable with a minimum of difficulty using readily available starting materials. The methyl and ethyl allophanates are prepared from urea and the corresponding chlorocarbonic esters.⁴

* University of Illinois, Urbana, Ill. Experimental work was carried out under Ordnance Contract DA-11-022-ORD-33. Publication has been approved by the Office of Public Information of the Office of Chief of Ordnance.

† Chemical Research Division, Samuel Feltman Ammunition Laboratories, Picatinny Arsenal, Dover, N.J.

Procedure

A. ALKYL ALLOPHANATES

Methyl Allophanate. Three hundred five milliliters of methyl chlorocarbonate* (4.0 mols) and 480 g. of finely powdered urea (8.0 mols) are placed in a 2-l. standard-taper round-bottomed flask equipped with a 60-cm. reflux condenser. The mixture is heated on a steam bath for 90 minutes. Four hundred milliliters of water is added to the warm reaction cake to decompose any unreacted chlorocarbonic ester and to remove by solution both unchanged urea and urea hydrochloride.† Methyl allophanate remains behind as a relatively water-insoluble residue. The suspension is filtered and the white product washed with three 250-ml. portions of water, then with 95% ethanol (two 250-ml. portions), and finally with 500 ml. of ethyl ether. It is air-dried. The yield of product will vary from 227 to 274 g. (48 to 58%). The product thus obtained is pure enough to use as the starting material for other reactions. It can be further purified by recrystallization from hot water using 27.5 ml. of water per gram of compound (85% recovery; m.p. 215 to 216° with decomposition).

Ethyl Allophanate. A mixture consisting of 252 g. of finely powdered urea (4.2 mols) and 217 g. of ethyl chlorocarbonate (2 mols) is refluxed for 3 hours in a 1-l. round-bottomed flask equipped with a 60-cm. reflux condenser and heated by a steam bath. Two hundred milliliters of water is subsequently added to the warm reaction cake. After mechanical agitation to form an aqueous slurry, the suspension is filtered and the residue washed well with water (600 ml. in three portions), 95% ethanol (400 ml. in three portions), and ethyl ether (400 ml. in three portions).

* The chlorocarbonic esters are lacrimators; all operations must be carried out in a hood.

† Stirring of the mixture will help to convert it into an aqueous slurry, which will facilitate subsequent filtration and washing steps.

The product is then air-dried. Yields varying from 139 to 151 g. (51 to 57%) are obtained. The product melts at 190 to 191° with decomposition. It can be purified, if desired, by recrystallization from hot water using 30 ml. of solvent per gram of ester.

B. ALLOPHANYL HYDRAZIDE

From Methyl Allophanate. One hundred eighteen grams of methyl allophanate (1.0 mol), 100 ml. of 95% hydrazine (3.0 mols), and 1.5 l. of methanol are placed in a 3-l. standard-taper round-bottomed flask equipped with a reflux condenser and a heating mantle. A few charcoal boiling chips are introduced to prevent bumping of the reaction mixture. The solution is refluxed for 6 hours and chilled overnight in a refrigerator freezer (-14°). The white crystalline compound which has formed is collected on a sintered-glass funnel, washed with 95% ethanol and ethyl ether, and finally air-dried. The product weighs 95 g. (80.5% of theory) and decomposes at 166°. The filtrate is concentrated to 100 ml. under reduced pressure and chilled to produce an additional 4.4 g. of the hydrazide, bringing the over-all yield to 84% of theory.

The crude product can be recrystallized from hot water using 7 ml. of solvent per gram of hydrazide. On chilling the solution, 89.5 g. (90% recovery) of crystals is obtained. These melt at 166° with decomposition.

From Ethyl Allophanate. One hundred thirty-two grams of ethyl allophanate (1.0 mol), 100 ml. of 95% hydrazine (3.0 mols), and 1.5 l. of methanol are placed in a 3-l. standard-taper round-bottomed flask equipped with a reflux condenser and heating mantle. A few charcoal chips are added to prevent bumping. The reaction mixture is refluxed for 8 to 10 hours, after which it is cooled overnight in a freezer (-14°). The crystalline product is removed, washed with ethanol and ethyl ether, and air-dried. The yield is 63.7 g. (54% of theory) of allophanyl hydrazide, melting at 165 to 166° with decomposition.

The filtrate is then evaporated to about 70 ml. under reduced pressure and chilled to give an additional 32.1 g. (27% of theory) of product, melting at 161 to 162° with decomposition. The total yield is 95.8 g. (81%).

Low-melting fractions can be recrystallized from hot water (7 ml./g.) to remove any unreacted ester. In a typical experiment three fractions were obtained by cooling to 40, 30, and 5°. These melted with decomposition at 166 to 167, 167, and 163 to 164°, respectively.

Properties²

Allophanyl hydrazide is a white, crystalline, nonhygroscopic compound which melts at 166° with decomposition. It is soluble in water, methanol, and ethanol (at their boiling points) to the extents of 14, 3, and 1.4 g./100 ml. of solvent, respectively. It is a weak base, $K_B = 10^{-11}$. Melting points and formulas of typical salts are tabulated below. The compound is thermally unstable when heated at 110° for an extended period of time. As a typical hydrazine derivative, allophanyl hydrazide forms allophanyl hydrazones with carbonyl compounds. Among these, the water-insoluble benzaldehyde derivative (m.p. 208 to 209°) is easily prepared. Allophanyl hydrazide can also be treated with nitrous acid to give the water-insoluble azide, $\text{NH}_2\text{CONHCON}_3$, melting with decomposition at 193°.

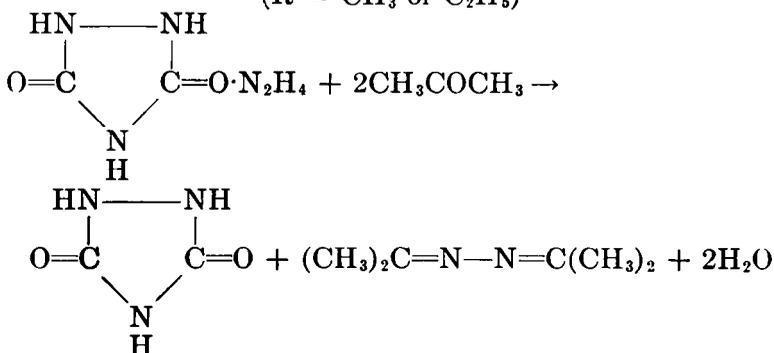
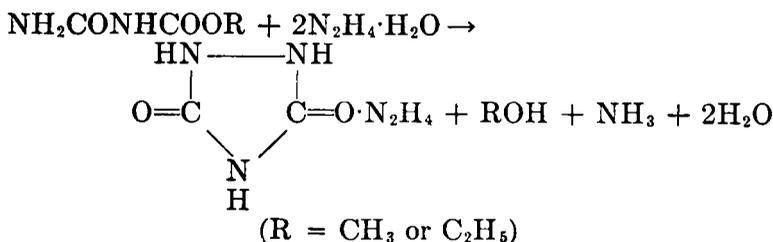
SALTS OF ALLOPHANYL HYDRAZIDE

$\text{NH}_2\text{CONHCON}_2\text{H}_2 \cdot \text{HX}$, where HX =	Melting point
HCl	185°
HNO_3	169°
$\frac{1}{2}\text{H}_2\text{C}_2\text{O}_4$	223°
$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$ (picric acid)	175°

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14. URAZOLE



SUBMITTED BY PAUL G. GORDON* AND LUDWIG F. AUDRIETH*

CHECKED BY P. LENSIT†

Urazole has been prepared by the thermal deammonation of biurea;¹⁻³ hydrazinolysis of biuret with hydrazine sulfate² and hydrazine hydrate;⁴ thermal cyclization-deammonation of allophanyl hydrazide hydrochloride and nitrate;⁵ treatment of diaminobiuret with dilute hydrochloric acid;⁶ heating carbamoyl azide;⁷ and hydrazinolysis of ethyl carbethoxythiocarbonate to give *O*-ethylurazole, followed by removal of the ethyl group by hydrolysis.⁸ The method described here^{9,10} involves (1) the preparation of methyl or ethyl allophanate¹¹ from urea and the cor-

* University of Illinois, Urbana, Ill. Experimental work was carried out under Ordnance Contract DA-11-022-ORD-33. Publication has been approved by the Office of Public Information of the Office of Chief of Ordnance.

† Chemical Research Division, Samuel Feltman Ammunition Laboratories, Picatinny Arsenal, Dover, N.J.

responding chlorocarbonic ester (synthesis 13), (2) hydrazinolysis of the allophanic ester in refluxing aqueous solution to form hydrazine urazolate (hydrazine salt of urazole), and (3) conversion of hydrazine urazolate to urazole by refluxing with acetone.

Procedure A

Preparation from Methyl Allophanate. One hundred eighteen grams of methyl allophanate (1.0 mol), 173 ml. of 85% hydrazine hydrate (3.0 mols), and 574 ml. of water are placed in a 2-l. three-necked round-bottomed flask equipped with a thermometer and a 30-cm. fractionating column packed with glass helixes. A Claisen head, thermometer, and condenser are attached to the column. The contents of the flask are refluxed for $3\frac{3}{4}$ hours, during which time the pot temperature rises from 25 to 101° and the still-head temperature rises from 25 to 93°. Approximately 60 ml. of distillate, consisting largely of methanol, is collected during the reaction period.

The reaction mixture is chilled to 0° in an ice-salt bath, and 2.9 g. of biurea (m.p. 245 to 246°) is filtered off. The filtrate is evaporated on a hot-water bath under reduced pressure (water aspirator) until a solid cake remains in the flask. The reaction cake is broken up and washed with 95% ethanol to give 110 g. (83%) of crude hydrazine urazolate (m.p. 195 to 196° with decomposition). The product can be purified with 86% recovery by dissolving it in hot water (2.5 ml./g.), filtering through a warm funnel, adding 95% ethanol to turbidity, and chilling.

The 110 g. of hydrazine urazolate and 1 l. of acetone are placed in a 2-l. three-necked standard-taper flask equipped with a stirrer and reflux condenser. The suspension is stirred and heated for 2 hours, after which the mixture is chilled and the insoluble product removed by filtration. The product is washed well with acetone and finally air-dried. The product weighs 78 g. and melts at 244 to 246° with decomposition. This represents a 94% con-

version of hydrazine urazolate to urazole and a 78% over-all yield of urazole based on the methyl allophanate used.

Procedure B

Preparation from Ethyl Allophanate. Thirteen and two-tenths grams of ethyl allophanate (0.1 mol), 15 ml. of 100% hydrazine hydrate (0.3 mol), and 100 ml. of water are placed in a 200-ml. three-necked flask equipped as in procedure A. The reaction mixture is heated for 3½ hours, during which the pot temperature rises from 25 to 101° and the still-head temperature rises from 25 to 99°. Fifteen milliliters of distillate is collected.

The reaction mixture is chilled to obtain 0.32 g. of a by-product, biurea (m.p. 244 to 246° with decomposition). The filtrate is concentrated to one-half its volume and chilled to give 4.34 g. of crystals (m.p. 188 to 190°). Further concentration of the filtrate to one-half its volume gives 3.55 g. of crystals (m.p. 194 to 195°). An excess of ethanol is added to the filtrate to produce an additional 1.41 g. of white crystals (m.p. 193 to 194°). The over-all yield of crude hydrazine urazolate is 9.30 g. (70%). Conversion to urazole is accomplished as described in procedure A.

Properties

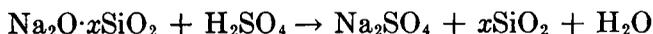
Urazole is a white, crystalline, nonhygroscopic compound which melts at 249 to 250° with decomposition. It does not decompose when heated at 110° for 48 hours.¹ The compound is soluble in water to the extent of 2.83 g./100 g. at 0° and 23.7 g./100 g. at 65°. An aqueous solution is acidic to litmus, the pH of a saturated aqueous solution being 3.15 at 25°. Urazole is a weak acid,⁹ $K_A = 1.6 \times 10^{-6}$, and forms stable alkali metal, ammonium, and amine salts.

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15. SILICA GEL (CORRECTION)¹



SUBMITTED BY ROBERT F. RUTHRUFF*

CHECKED BY H. S. BOOTH† AND ALBERT DOLANCE‡

Mr. William S. Heinaman‡ has called attention to the fact that the sulfuric acid added in the preparation of silica gel, synthesis 26 of Volume II,¹ should be 6 *M* rather than 6 *N* to be consistent with the submitter's statement that "twice the theoretical amount of acid is employed."

Reference

1. R. F. RUTHRUFF: *INORGANIC SYNTHESSES*, **2**, 95 (1946).

16. ORGANOSILAZANE COMPOUNDS

SUBMITTED BY ROBERT C. OSTHOFF§ AND SIMON W. KANTOR§

The preparation¹ and properties² of a great many organo-silicon compounds have been described. However, a relatively small amount of work has been done in the field of silazane chemistry, *i.e.*, the chemistry of compounds which contain at least one silicon-nitrogen bond.³⁻⁸ In general, this group of compounds has been found to be extremely sensitive to hydrolysis. The hydrolytic reaction forms the appropriate amine or ammonia and a silanol and/or a siloxane.

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An interesting structural analogy exists between compounds of the general formula $[(\text{CH}_3)_2\text{SiNH}]_x$ and the polydimethylsiloxanes, $[(\text{CH}_3)_2\text{SiO}]_x$. These silazanes differ from the cyclic polydimethylsiloxanes only in that the siloxane oxygen has been replaced by an NH group. However, the chemistry of the silazanes differs from that of the corresponding siloxanes in the ease of hydrolytic cleavage of the Si-N bonds. The silazanes are, in general, volatile, mobile liquids.

It is of interest to observe that the only tertiary amine containing three Si-N bonds that has been isolated to date is trisilylamine, $(\text{H}_3\text{Si})_3\text{N}$, which was prepared by Stock and Somieski⁹ by treating the vapor of chlorosilane with ammonia.

The following syntheses of specific compounds represent general procedures of preparation.

A. HEXAMETHYLDISILAZANE



CHECKED BY S. HASHMAN* AND CHARLES A. BROWN*

Hexamethyldisilazane has been prepared by Sauer and Hasek^{6,7} from the reaction of ammonia with trimethylchlorosilane in an inert solvent. When the reaction was carried out in liquid ammonia, a somewhat smaller yield of hexamethyldisilazane was obtained, along with appreciable amounts of trimethylsilanol and hexamethyldisiloxane⁶ owing to hydrolysis during recovery of the product. Presumably other trimethylhalosilanes could be employed in place of trimethylchlorosilane, but the ready availability of the latter favors its use.

Procedure

The reaction vessel is a 5-l. three-necked round-bottomed flask equipped with ground-glass joints. This flask is fitted with a water-cooled condenser bearing a drying

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tube packed with Drierite (nonindicating Drierite or Dehydrite may be used), a Tru-bore water-jacketed stirrer, and a gas inlet tube extending to about 3 cm. above the level of the liquid in the flask. A large-diameter tube (ca. 13 mm. o.d.) should be employed to prevent plugging with ammonium chloride. The gas inlet tube is connected directly to a tank of liquid ammonia through a suitable trap (to prevent backup) and a mercury blowoff.

Three hundred thirty-five grams of trimethylchlorosilane (3.1 mols) is added to 1500 ml. of anhydrous ethyl ether in the reaction flask, and stirring is commenced. A slow stream of ammonia is allowed to pass into the reaction vessel, and an immediate precipitate of ammonium chloride appears. Slow addition of ammonia is continued for 6 to 8 hours. During the early stages of the ammonia addition, a considerable amount of heat is evolved, and the ether refluxes.

After the addition of the ammonia is completed, the ether is refluxed for 5 hours to remove excess ammonia. The reaction flask is cooled to room temperature, and an additional 1 l. of anhydrous ethyl ether is added. At this time, the ether is removed by filtering, and the ammonium chloride is extracted with four 100-ml. portions of ether. It is desirable but not necessary to carry out these filtrations in a dry box. The combined filtrate is then dried overnight over anhydrous sodium sulfate. The ether is then stripped, and the hexamethyldisilazane is obtained by distillation at atmospheric pressure (b.p. 126°). The yield is 129 to 161 g. (52 to 65%, based upon the trimethylchlorosilane used).

Properties

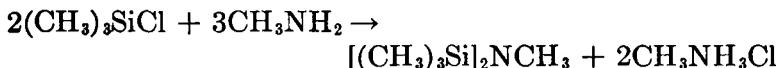
Hexamethyldisilazane is a colorless mobile liquid boiling at 126°; $n_D^{20} = 1.4080$, $d_4^{20} = 0.7741$.⁶ The molar refraction that is observed from these data is 51.44 cc. (calcd. $M.R._D = 51.44$ cc.).¹⁰ At 1000 c.p.s., the dielectric constant is 2.27 ± 0.01 at 20°,¹⁰ and the power factor is $\tan \delta = 0.0001$.¹⁰

These values give an Onsager dipole moment of 0.67 D.¹⁰ The Onsager dipole moment of the analogous siloxane, hexamethyldisiloxane, $[(\text{CH}_3)_3\text{Si}]_2\text{O}$, is 0.74 D. at 20°.¹¹

Hexamethyldisilazane is rapidly hydrolyzed in contact with the atmosphere.⁷ Under carefully controlled conditions, the hydrolysis can be carried out to give substantial yields of trimethylsilanol.⁶

The reaction of hexamethyldisilazane with boron trifluoride forms a white solid which sublimes *in vacuo* at 300 to 315° and reacts rapidly and violently with water.¹⁰ This material approximates $[(\text{CH}_3)_3\text{Si}]_2\text{NH}\cdot\text{BF}_3$ in composition.¹⁰ The presence of hexamethyldisiloxane formed by exposure of hexamethyldisilazane to atmospheric moisture can be detected readily by examination of the infrared absorption spectra, since the Si-O bond displays a strong absorption at 9.5 μ .¹² This absorption band is not present in the spectrum of pure hexamethyldisilazane.⁷

B. N-METHYLHEXAMETHYLDISILAZANE



CHECKED BY CHARLES A. BROWN*

N-Methylhexamethyldisilazane has been prepared by Sauer and Hasek⁷ by the reaction of trimethyl-*N*-methylaminosilane (*N*-1,1,1-tetramethylsilylamine) with trimethylchlorosilane. Larger quantities are more readily prepared by the direct reaction of trimethylchlorosilane with methylamine in an inert solvent.¹⁰

Procedure

To 2400 ml. of anhydrous benzene in a 5-l. round-bottomed flask equipped with a paddle stirrer, a water condenser, and a gas inlet tube is added 450 g. of trimethylchlorosilane (4.1 mols). The gas inlet tube extends to about 3 cm. above the surface of the reaction mixture

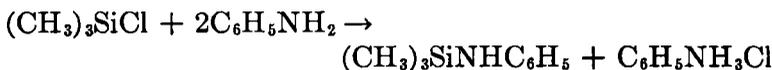
* Western Reserve University, Cleveland, Ohio.

and is of large size (ca. 13 mm. o.d.) to prevent clogging by amine hydrochloride. Methylamine is allowed to pass through a mercury blowoff and a trap to the gas inlet tube. As soon as a slow stream of amine is started, stirring is commenced. A white precipitate of methylammonium chloride forms at once. The amine is passed into the solution for 8 hours, and then the reaction mixture is refluxed for 18 hours. At the end of this time, the reaction mixture is filtered, and the methylammonium chloride is extracted with two 200-ml. portions of anhydrous benzene. These are filtered and combined with the original benzene solution. After the benzene has been stripped, *N*-methylhexamethyldisilazane is obtained by distillation (b.p. 150° at 1 atm. pressure). The yield is 153 to 175 g. (35 to 40%, based on the trimethylchlorosilane used).

Properties

N-Methylhexamethyldisilazane is a colorless liquid boiling at 150° at 1 atm. pressure; $d_4^{20} = 0.797$, $n_D^{20} = 1.4223$. The dielectric constant at 1000 c.p.s. at 20° is 2.25 ± 0.02 , and the power factor is $\tan \delta = 0.001$. From the above data the Onsager dipole moment is calculated to be 0.44 D. The molar refraction is calculated as 56.14 cc., and the observed value using the density and refractive index reported above is 55.92 cc.

C. TRIMETHYL(ANILINO)SILANE



CHECKED BY LEWIS J. SCHUPP* AND CHARLES A. BROWN*

Trimethyl(anilino)silane has been prepared by the reaction of hexamethyldisilazane with aniline.¹³ A more convenient preparation is the direct reaction of trimethylchlorosilane with aniline either in the absence of solvent¹⁴

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or in the presence of benzene.¹⁰ This reaction is reversible; so it is important to maintain an excess of trimethylchlorosilane.

The replacement of a chlorine by an anilino group has been carried out with chlorosilanes such as dimethyldichlorosilane, methyltrichlorosilane, triethylchlorosilane, and diphenyldichlorosilane. In each case, all of the chlorines are replaced by anilino groups, and yields of 60 to 80% are generally obtained. Whereas an aliphatic amine is readily substituted with 2 mols of trimethylchlorosilane (synthesis 16B), the substitution on aniline stops after one trimethylsilyl group has been introduced. Anilinosilanes are very labile compounds and are especially useful intermediates for the preparation of iodosalanes through the action of hydrogen iodide.^{15,16}

Procedure

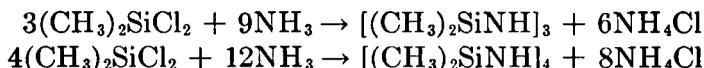
A solution of 396 g. of trimethylchlorosilane (3.64 mols, 21% excess) in 1500 ml. of anhydrous benzene is placed in a 5-l. round-bottomed flask equipped with a Tru-bore stirrer, a water-cooled condenser, and a dropping funnel, in which is placed a solution of 559 g. of aniline (6.0 mols) in 500 ml. of anhydrous benzene. The stirrer is started, and the aniline solution is added slowly over a period of 1½ hours, during which time a large precipitate of anilinium chloride forms. The reaction is maintained at room temperature by the use of an external ice-water cooling bath. At the end of the addition, the mixture is stirred for 2 hours and filtered. The anilinium chloride is washed with 500 ml. of benzene, and the washings are combined with the original benzene solution. After the benzene has been stripped, the residue is distilled under reduced pressure to give recovered aniline, boiling point 93 to 94° at 32 mm. (110 to 210 g., 20 to 38%) and trimethyl(anilino)silane, boiling point 106 to 107° at 24 mm. The yield of product is 230 to 280 g. (46 to 57%). Based on consumed aniline, the yield is 70 to 85%.

Properties

Trimethyl(anilino)silane, boiling point 106 to 107° at 24 mm. and 206° at 760 mm.,¹⁴ is a colorless, mobile liquid; $d_4^{20} = 0.931$ and $n_D^{20} = 1.5219$. The observed molar refraction is 54.15 cc. (calcd. M.R._D = 54.05 cc.).¹⁰ The dielectric constant at 1000 c.p.s. is 3.90 ± 0.02 at 20°, and the power factor is $\tan \delta = 0.014$.¹⁰ From these data the Onsager dipole moment is calculated to be 1.37 D.

Trimethyl(anilino)silane is readily hydrolyzed in contact with atmospheric moisture to form aniline. The anilino group is also readily cleaved by anhydrous hydrogen halides, which react instantaneously to form the corresponding trimethylhalosilane and the anilinium halide. Reactions with silicon, germanium(IV), and phosphorus(III) bromides also occur readily to give trimethylbromosilane and the corresponding tetraanilinosilane, tetraanilino-germane, and trianilinophosphine, respectively.¹⁴

D. HEXAMETHYLCYCLOTETRASILAZANE AND OCTAMETHYLCYCLOTETRASILAZANE



CHECKED BY VERNON ZEITLER* AND CHARLES A. BROWN*

Hexamethylcyclotrisilazane and octamethylcyclotetrasilazane have been prepared by Brewer and Haber⁸ from the reaction of dry, gaseous ammonia with dimethyldichlorosilane in benzene. When the ammonolysis was carried out in liquid ammonia, the combined yield of silazanes was only slightly less, but the trimer was formed in greater proportion than the tetramer. Although the yield of cyclic silazanes was always high, it was difficult to reproduce the proportions of the individual compounds. The procedure given here is an adaptation of that of Brewer and Haber.

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The ammonolysis of other alkylchlorosilanes has also been realized. Thus, the reaction of diethyldichlorosilane with liquid ammonia produces hexaethylcyclotrisilazane and octaethylcyclotetrasilazane. The reaction of methylchlorosilane with liquid ammonia also proceeds rapidly to yield high-molecular-weight silazanes from which no simple compounds have been obtained.⁸

Procedure

A solution of 500 g. of dimethyldichlorosilane (3.88 mols) in 3500 ml. of anhydrous benzene is placed in a 5-l. round-bottomed flask equipped with a Tru-bore paddle stirrer, a water-cooled condenser, and a gas inlet tube. The latter extends 12 mm. above the surface of the stirred reaction mixture. The gas inlet tube is connected to a tank of ammonia through a trap (to prevent backup) and a mercury blowoff. An external ice-water bath is used to keep the temperature of the reaction below 30°.

A slow stream of ammonia is allowed to pass into the reaction vessel, and an immediate precipitate of ammonium chloride appears. The addition of ammonia is continued for 8 to 10 hours. In the event that the precipitated ammonium chloride prevents stirring, it is advisable to add an additional 500-ml. portion of anhydrous benzene. After the addition of the ammonia is completed, the reaction mixture is refluxed for 3 hours to remove excess ammonia. The reaction flask is cooled to room temperature, and the copious precipitate of ammonium chloride is removed by filtration. The precipitate is stirred with an additional 500 ml. of anhydrous benzene and filtered. This filtrate is combined with the original benzene filtrate.

The benzene filtrate is stripped to leave 260 to 270 g. (92 to 95%) of crude silazanes. Fractionation of the silazanes gives 103 to 141 g. (36 to 50%) of hexamethylcyclotrisilazane, boiling point 110 to 112° at 85 mm.,¹⁰ and 73 to 120 g. (26 to 42%) of octamethylcyclotetrasilazane, boiling point 134 to 136° at 35 mm.¹⁰ The combined

yield of these two cyclic silazanes is usually 210 to 230 g. (74 to 81% of theory based on the dimethyldichlorosilane used).^{*} The octamethylcyclotetrasilazane solidifies in the receiver during distillation. One recrystallization from *n*-hexane (ca. 100 ml. of solvent for 75 g. of silazane) yields purified octamethylcyclotetrasilazane (m.p. 97°). The loss on recrystallization amounts to 10 to 15%.

Properties

Hexamethylcyclotrisilazane, boiling point 111 to 112° at 85 mm. and 188° at 756 mm., is a colorless, mobile liquid which freezes at -10°; $n_D^{20} = 1.4448$, $d_D^{20} = 0.9196$. The observed molar refraction from these data is 63.35 cc. (calcd. M.R._D = 63.48 cc.).¹⁰ At 1000 c.p.s., the dielectric constant is 2.57 ± 0.01 at 20°,¹⁰ and the power factor is $\tan \delta = 0.001$.¹⁰ These values give an Onsager dipole moment of 0.92 D.¹⁰ Hexamethylcyclotrisilazane is slowly hydrolyzed in contact with atmospheric moisture with the formation of ammonia and siloxanes.

Octamethylcyclotetrasilazane, boiling point 134.5 to 135.5° at 35 mm. and 225° at 756 mm., is a white solid which melts at 97°. Octamethylcyclotetrasilazane hydrolyzes in moist air to form ammonia and siloxanes.

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* The checkers, on fractionation of the final crude product, found 60 g. of a dark brown liquid which could not be distilled under reduced pressure. It is probable that this is a mixture of higher-molecular-weight silazanes.

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17. ORGANOGermanium COMPOUNDS

BY OTTO H. JOHNSON*

Organogermanium compounds are defined, by analogy with organosilicon compounds, as substances having at least one carbon atom attached to a germanium atom. Most of these carbon-containing compounds of germanium may be considered as derivatives of the simple germanes, namely, germane, GeH_4 ; digermane, Ge_2H_6 ; and trigermane, Ge_3H_8 . Organic derivatives of cyclotetragermane, Ge_4H_8 , are known, although cyclotetragermane itself has not yet been isolated.

Nomenclature

Considerable variation is found in the systems of naming organogermanium compounds discussed in the earlier literature. In order that these compounds may be named in compliance with modern standards of uniformity and clarity, the following recommendations are made:

1. Derivatives of germane, digermane, and trigermane are structurally analogous to the first three members of the alkane series and the accepted rules for the nomenclature of such organic compounds¹ should be followed as closely as possible in the naming of comparable germanium compounds.

2. Where organic nomenclature is ambiguous or inapplicable, the germanium compounds should be named in accordance with current recommendations for naming similar silicon compounds.^{2,3}

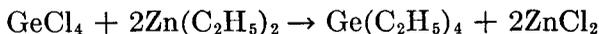
3. Inorganic nomenclature is recommended in accordance with present inorganic usage if such naming is simpler and more specific.

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4. The combining form "germ-" as used in germane, digermane, etc., is to be preferred to the combining form "german-" frequently found in earlier literature. Thus, the compound $(\text{CH}_3)_3\text{GeBr}$ becomes trimethylbromogermane, analogous to trimethylbromosilane.

General Methods of Synthesis⁴

1. Substitution by Dialkylzinc Compounds^{5,6}



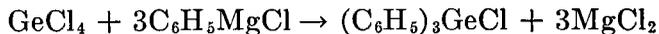
This was the method used by Winkler to prepare the first known organogermanium compound, tetraethylgermane. It is not commonly used at present.

2. Substitution by Diarylmercury Compounds⁷



Diphenylmercury combines with germanium(IV) chloride in a sealed tube at 140° to form phenyltrichlorogermane. Benzyltrichlorogermane, *p*-tolyltrichlorogermane, and (*p*-dimethylaminophenyl)trichlorogermane have been prepared in the same manner. No modifications of this method have come into common use.

3. Substitution by Grignard Reagents



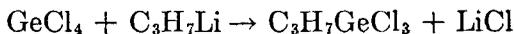
The Grignard reagent is prepared in the usual manner and then added to a stirred solution of germanium tetrachloride in ether. Magnesium chloride precipitates, and the substituted germanium compounds remaining in solution are then separated by distillation.

For sluggish reactions involving the higher arylmagnesium halides, the ether can be replaced by a higher boiling solvent such as toluene and the reaction mixture heated for a period of time. The organogermanium compounds can then be separated by destroying any excess Grignard reagent and recrystallizing the product from a suitable solvent.

All variations of the Grignard reaction or similar substitutions involving alkyls of different metals result in a mixture of products. With germanium tetrachloride the substitution products RGeCl_3 , R_2GeCl_2 , R_3GeCl , and R_4Ge are possible and form in varying percentages, so that if a specific intermediate is desired, the conditions yielding the highest percentage of that particular compound must first be investigated.

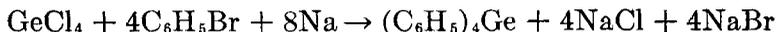
Mixed alkyl- or arylgermanes are obtained by the stepwise alkylation or arylation of halogen-substituted intermediates.

4. Preparation by Alkyl- or Aryllithium Compounds



The use of alkyl- or aryllithium techniques is advantageous in some cases. It has been observed⁸ that the use of organolithium compounds sometimes gives better yields in the preparation of tetrasubstituted germanes than are obtained with the standard Grignard procedure. The relative concentrations of the reactants are also of major importance, for it has been found⁹ that the product of the reaction between triphenylgermane and phenyllithium may be either tetraphenylgermane or hexaphenyldigermane, depending upon the sequence of mixing the reactants.

5. Coupling Reactions with Sodium

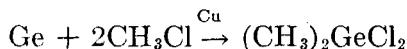


The Wurtz reaction as a method of alkylating germanium tetrachloride has never achieved the popularity of the Grignard reaction, chiefly because the difficulty of control makes it reasonably successful only as a means of preparing the fully substituted tetraalkyls or tetraaryl. The partially substituted germanium halides appear only in low yields since the reaction as usually conducted goes to complete substitution. One explanation is based upon the heterogeneity of the system. The sodium is unavoidably

present in relatively large masses. A molecule of germanium tetrachloride which comes in contact with the surface of a lump of sodium thus has an excess of sodium atoms immediately available and derives enough energy from the first substitution to continue with the substitution of the remaining germanium-chlorine bonds.

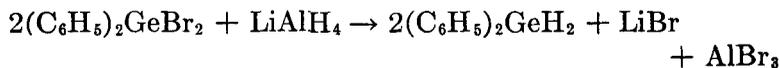
A two-stage synthesis,¹⁰ which has been successfully used with silicon and which should be applicable to germanium, allows better control. The sodium is first allowed to react with a halide such as chlorobenzene in an appropriate solvent to yield phenylsodium, similar to the usual aryllithium procedure. After the heat of the reaction is dissipated, the phenylsodium is mixed with the silicon halide in solution, and a milder reaction ensues. Thus phenyltrichlorosilane can be made by the reaction of phenylsodium with silicon tetrachloride. The use of a separately prepared alkyl- or arylsodium in this way provides about the same degree of control as in the Grignard synthesis.

6. Direct Synthesis from Elemental Germanium



The action of methyl chloride upon elemental germanium in the presence of a copper catalyst yields a mixture of related organogermanium chlorides, from which the individual substances can be separated by distillation. The composition of the mixture is influenced by the temperature of the reacting mass, the type of catalyst used, the manner in which the catalyst is associated with the germanium, and the possible time of contact. The method is best suited to the preparation of the lower dialkyldihalogermanes. Compounds of the type R_3GeCl and R_4Ge are present as only a small fraction of the total yield.

7. Reduction with Lithium Aluminum Hydride



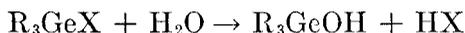
This procedure is now generally used for the preparation of the partially substituted germanes.⁸ It was originally used in the reduction of germanium tetrahalides to germane¹¹ and was employed for the preparation of the first diarylgermane to be described.¹² The technique serves as an important intermediate step in the preparation of some halogermanes. The alkyl- and aryl-substituted dihalogermanes and trihalogermanes are often exceedingly difficult to separate by fractional distillation. Subjecting the mixture of aryl mono-, di-, and trihalogermanes obtained by the halogenation of a tetraarylgermane to reduction with lithium aluminum hydride yields a mixture of the corresponding hydrides, which is readily separable by distillation. Since the hydrogen of partially substituted germanes is readily replaced by chlorine or bromine, this method gives a means of obtaining the corresponding chloro- or bromogermane.

Some Properties of Organogermanium Compounds

Compounds of the type R_4Ge , in which all the radicals are alkyl or aryl groups, are the most stable of the known organogermanium compounds. The tetraalkyl compounds are brominated by bromine or by hydrogen bromide in the presence of aluminum bromide. The tetraarylgermanes also are brominated readily, but generally substitution beyond the first aryl group is much more difficult than replacement of the first group. Tetrabenzylgermane is more resistant to reaction with bromine than are tetraarylgermanes.¹³ The following groups are arranged in order of decreasing ease of substitution by bromine: *p*-tolyl, *m*-tolyl, phenyl, benzyl. The germanium-germanium bond in hexaethyl- and hexaphenyldigermane and in octaphenyltrigermane is broken by bromination, indicating that the bond between neighboring germanium atoms is weaker than the carbon-germanium bond.

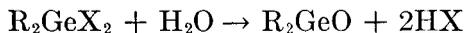
Hydrolysis of alkyl mono-, di-, and trihalogermanes yields the expected products with considerable variation in the

stability of the different hydroxides produced. The monohalo compounds react in accordance with the equation

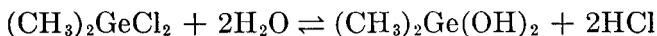


In the case of trimethylgermanol, $(\text{CH}_3)_3\text{GeOH}$, the compound may or may not condense with itself with the elimination of water. Triphenylgermanol, on the other hand, condenses readily.

Dialkyldihalogermanes hydrolyze readily with water and still more readily in hot aqueous alkali, forming dialkylgermanium oxides:



The trihalo compounds hydrolyze presumably to form acids of the type RGeOOH or the anhydrides. The fluoride is the most stable of the triphenylhalogermanes in that it hydrolyzes very slowly even when boiled with ethanolic potassium hydroxide. Triphenyliodogermane is very unstable. Rochow¹⁴ suggests the possibility of a readily reversible reaction in the case of dimethyldichlorogermane:



Laubengayer and Allen¹⁵ found the hydrolysis and subsequent condensation of methyltrichlorogermane to the highly polymeric methylgermanium oxide to be reversible. A comparison of dimethylgermanium oxide with its silicon analogs reveals wide differences in properties.¹⁴ Methyl silicones can be prepared by hydrolyzing the corresponding chlorosilanes, separating the water-insoluble methyl siloxane, and processing it to produce the desired polymer. Hydrolysis of dimethyldichlorogermane does not produce a water-repellent film on solids as does dimethyldichlorosilane; instead the compound dissolves completely in water.

The known carbon-containing compounds of germanium are too few in number and the numerical data on these known compounds are too limited to permit much generalization. It is evident, however, that there is considerable

variation in the strength of the carbon-germanium bond, depending principally upon the nature of the carbon radical. Halogens are readily replaced by hydrogen through reduction and by hydroxyl, with subsequent loss of water, through hydrolysis, particularly in alkaline media. Many resinous products are observed, but in general either the tendency of germanium to form polymers is less than that of silicon, or else the conditions favorable to polymer formation are not yet understood.

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18. TETRAPHENYLGERMANE



SUBMITTED BY DARREL M. HARRIS,* WILLIAM H. NEBERGALL,* AND OTTO H. JOHNSON*

CHECKED BY EUGENE G. ROCHOW† and NORMA TOLIVAISA†

Tetra-substituted germanes result when an excess of Grignard reagent is permitted to react with germanium(IV) chloride, unless the substituent is a sterically hindered one,

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as is the case with the cyclohexyl group. Treatment of germanium(IV) chloride with phenylmagnesium bromide yields tetraphenylgermane.

Procedure

To a 1-l. three-necked flask fitted with a reflux condenser, a motor-driven stirrer, and a dropping funnel are added 24.3 g. of magnesium turnings (1 mol) and 500 ml. of anhydrous ethyl ether. Through the dropping funnel 157 g. of redistilled bromobenzene (1 mol) is added dropwise, and the mixture is refluxed for 1 hour. A solution containing 21.4 g. of germanium(IV) chloride (0.1 mol)¹ in 250 ml. of toluene is added dropwise, and the ether is replaced immediately by toluene through distillation. The mixture is refluxed for 2 more hours and the excess phenylmagnesium bromide destroyed by the addition of 50% acetic acid.* The solution is then heated to boiling and the toluene layer separated while still hot. The toluene solution is cooled, giving crystals of tetraphenylgermane. The crystals are removed, and a second crop of crystals is obtained by concentrating the filtrate. The yield is 26.4 to 28 g. (67 to 72%).² A higher yield is obtained by using germanium(IV) bromide as starting material.³ The product melts at 225 to 228°.² It can be recrystallized from toluene.

Properties

Tetraphenylgermane is a white, crystalline substance, melting at 235.7°. It is readily soluble in hot benzene and toluene, the solubility decreasing greatly with a decrease in temperature. It is soluble in chloroform; moderately soluble in carbon tetrachloride, carbon disulfide, and acetone; and slightly soluble in ethanol, ethyl ether, and petroleum ether. Tetraphenylgermane is brominated easily, but substitution

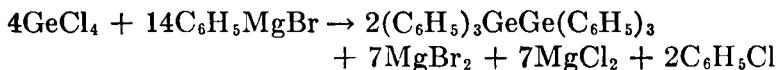
* The checkers recommend treatment with dilute hydrochloric acid (1 volume of 12 *M* acid to 10 volumes of water) to avoid formation of any solid products.

beyond one phenyl group is difficult, and replacement of two phenyl groups by direct bromination requires prolonged refluxing.⁴ Tetraphenylgermane reacts slowly with metallic sodium dissolved in liquid ammonia to form (triphenylgermyl)sodium, $(\text{C}_6\text{H}_5)_3\text{GeNa}$, sodium amide, and benzene.³ In concentrated solutions, a second phenyl group is replaced, giving the compound $(\text{C}_6\text{H}_5)_2\text{GeNa}_2$, which imparts a characteristic red color to the solution. Tetraphenylgermane is stable even at higher temperatures and can be volatilized without decomposition. It is insoluble in cold sulfuric acid but is sulfonated upon warming.⁵

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19. HEXAPHENYLDIGERMANE



SUBMITTED BY DARREL M. HARRIS,* WILLIAM H. NEBERGALL,* AND OTTO H. JOHNSON*

CHECKED BY EUGENE G. ROCHOW† AND NORMA TOLIVAISA†

Organogermanium reactions occasionally show considerable sensitivity toward minor changes in conditions,² and this property is illustrated by the preparation of hexaphenyldigermane. The method is almost identical with the method described in synthesis 18 for the preparation of tetraphenylgermane. The difference is that in the preparation of hexaphenyldigermane the ether is not removed immediately after the addition of the toluene solution of germanium(IV) chloride, and this slight change in conditions is sufficient to cause a major change in the principal products.

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Procedure

One hundred eighty-one grams of phenylmagnesium bromide (1 mol) is placed in 500 ml. of ethyl ether in a 1-l. three-necked flask fitted with a reflux condenser, a motor-driven stirrer, and a dropping funnel. To this solution is added dropwise a solution of 21.4 g. of germanium(IV) chloride (0.1 mol) in 225 ml. of toluene. The system is refluxed for 3 hours, and 200 ml. of toluene is added. The volume is reduced by distillation to about 600 ml. The excess Grignard reagent is destroyed with 50% acetic acid,* and the aqueous layer is removed by means of a rubber-bulb pipet. The organic layer with the residual solids is then washed five times with hot water by the same procedure. The toluene solution is heated to boiling to dissolve any tetraphenylgermane formed as a by-product and leave the relatively insoluble hexaphenyldigermane. The latter is removed from the hot solution by filtration, and a second crop is obtained by reducing the filtrate to a small volume and again filtering while hot. This procedure yields fairly pure hexaphenyldigermane (m.p. 325 to 327°). The principal impurity is tetraphenylgermane. This is removed through fractional sublimation, the tetraphenylgermane subliming at 210° under a pressure of 1 mm., leaving the hexaphenyldigermane. The sublimation is performed carefully since hexaphenyldigermane sublimes under the same conditions at about 275°. After removal of the tetraphenylgermane, the hexaphenyldigermane is sublimed and then recrystallized from chloroform to give a microcrystalline material with a melting point of 330 to 331°. The yield is 18 g. (59%).

Properties

Hexaphenyldigermane is only slightly soluble in ordinary organic solvents. It is almost insoluble in liquid ammonia.

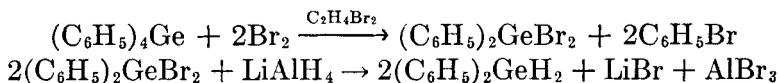
* The checkers recommend 200 ml. of 4 *M* hydrochloric acid to decompose the Grignard reagent.

When a suspension in liquid ammonia is treated with sodium, reaction takes place quite slowly with the formation of (triphenylgermyl)sodium.³ The bond between the germanium atoms is apparently quite stable, although the compound is converted to triphenylbromogermane by treatment with bromine in boiling carbon tetrachloride.

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20. DIPHENYLGERMANE



SUBMITTED BY OTTO H. JOHNSON* AND DARREL M. HARRIS*
CHECKED BY EUGENE G. ROCHOW† AND NORMA TOLIVAISA†

The usual procedure for preparing halogen-substituted alkylgermanes has been to prepare the tetraalkyl compound and then halogenate it under conditions that yield the maximum amount of the particular alkylhalogermane desired. The resulting mixture of mono-, di-, tri-, and tetrahalogermanes is then fractionated. However, the separation of diphenyldibromogermane from phenyltribromogermane is difficult owing to the similarity of their physical properties. These compounds are readily reduced by lithium aluminum hydride,^{1,2} and since triphenylgermane and diphenylgermane differ markedly in their boiling points, they are readily separated by distillation.²

Procedure

A 1-l. three-necked flask is fitted with a reflux condenser, a motor-driven stirrer, and a dropping funnel. In the flask are placed 52.5 g. of tetraphenylgermane (0.137 mol)

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(synthesis 18) and 300 ml. of ethylene bromide. The mixture is heated to reflux temperature. To the refluxing solution is added dropwise 46 g. of bromine (0.288 mol). The refluxing is continued until there is no visible evidence of bromine vapor (approximately $\frac{1}{2}$ hour after the last addition of bromine). The ethylene bromide, bromobenzene, and residual bromine are removed by distillation while the mixture is heated on a water bath under a pressure of 1 mm. The residue is diluted with 50 ml. of anhydrous ethyl ether and transferred to a separatory funnel which is fitted to a second 1-l. three-necked flask arranged similarly to the first. This flask contains 20 g. of lithium aluminum hydride (0.53 mol)* in 450 ml. of anhydrous ethyl ether and is swept out continuously with a current of dry helium, argon, or nitrogen to exclude air and moisture. The solution of the mixture of phenylbromogermanes is added dropwise at a rate which liberates sufficient heat to maintain slow refluxing. The refluxing is continued for 2 hours after addition is completed. Ether is then removed by distillation to a residual volume of 100 ml. The ethyl ether is replaced by adding 100 ml. of petroleum ether (b.p. 60 to 70°) and again distilling to a volume of 100 ml. Addition of petroleum ether with subsequent distillation is repeated several times (about four) until the boiling point indicates fairly complete removal of the ethyl ether. The resulting petroleum ether solution is then filtered through a dry Corning No. 39,533 coarse fritted-glass filter tube by pressure of helium, argon, or nitrogen gas. The remaining solids are washed with additional petroleum ether and filtered. The petroleum ether in the filtrate is removed by distillation, and the residue is then fractionated under reduced pressure. Distillation at 1 mm. pressure should yield only a few drops of distillate below 93°. Distillation is continued at 93° until practically all of the

* Lithium aluminum hydride may ignite in a humid atmosphere. The compound is conveniently weighed, pulverized, and added to the ether in the flask in a dry box swept out with dry nitrogen.

diphenylgermane is obtained, as indicated by a sudden increase in temperature. Very pure diphenylgermane is obtained by one distillation, any triphenylgermane present remaining in the distillation flask. The yield is at least 17.5 g. (55%).

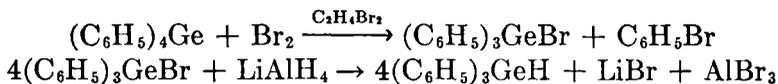
Properties

Diphenylgermane is a colorless liquid (b.p. 95° at 1 mm.) with a pleasant initial odor which rapidly changes to a burning sensation in the nose and in the eyes. The compound is fairly stable if held at temperatures below 0°. At room temperatures it is somewhat less stable, probably as a result of disproportionation, but the decomposition is not rapid enough to prevent purification of the substance by fractional distillation. Diphenylgermane can be brominated directly to diphenyldibromogermane, but direct iodination gives germanium(IV) iodide.

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21. TRIPHENYLBROMOGERMANE AND TRIPHENYLGERMANE



SUBMITTED BY OTTO H. JOHNSON,* WILLIAM H. NEBERGALL,* AND DARREL M. HARRIS*

CHECKED BY DENNIS HEARN† AND ALLAN FISH†

Aryl-substituted bromogermanes are readily reduced by lithium aluminum hydride to form the corresponding arylgermanes.¹ The bromogermane is usually formed from the tetra-substituted arylgermane, and since the first phenyl group is easily replaced by bromine whereas the

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second group is replaced only with difficulty, tetraphenylgermane is used as a starting material for this synthesis. Triphenylbromogermane is first formed and then reduced to triphenylgermane with lithium aluminum hydride.² This initial reaction differs from that in synthesis 20 in that a smaller mol ratio of bromine is employed.

Procedure

A solution of 58.4 g. of tetraphenylgermane (0.15 mol) (synthesis 18) in 400 ml. of ethylene bromide is placed in a 1-l. three-necked flask fitted with a reflux condenser, a dropping funnel, and a motor-driven stirrer. The solution is heated to boiling, and 25.6 g. of bromine (0.16 mol) is added dropwise. The mixture is then refluxed until the bromine vapor has almost disappeared (ca. $\frac{1}{2}$ hour). The solvent and unreacted bromine are then removed by distillation under reduced pressure, leaving about 50 ml. of residue, from which triphenylbromogermane crystallizes on cooling. The crude product is distilled under reduced pressure* and then recrystallized twice from glacial acetic acid. The crystals are finally collected by suction filtration and dried in the air. The yield of triphenylbromogermane is 44 to 48 g. (75 to 82%).

To a 1-l. three-necked flask fitted with a reflux condenser, a dropping funnel, and a motor-driven stirrer is added 400 ml. of an ethyl ether solution of 10 g. of lithium aluminum hydride (0.26 mol).† The flask is flushed with dry helium, argon, or nitrogen. Then 32.5 g. of triphenylbromogermane (0.085 mol) is added dropwise, and the reaction mixture is refluxed for 1 hour. The ethyl ether is replaced by 400 ml. of petroleum ether (b.p. 60 to 68°) by successive distillations (synthesis 20). The resulting suspension is filtered under pressure through a coarse fritted-glass filter tube (Corning No. 39,533) and

* The checkers recommend 210° at 6 mm.

† The precautions outlined in synthesis 20 should be observed.

the solid residue washed several times with petroleum ether. The washings are added to the initial filtrate. The petroleum ether is removed by distillation, and the resulting crude triphenylgermane is purified³ by distillation.* The yield is about 16.4 to 20 g. (about 61 to 79%). The product is further purified by recrystallization from methanol, from which solvent it separates as translucent, flaky crystals (m.p. 41.0 to 41.5°).²

Properties

Triphenylbromogermane is very soluble in ordinary organic solvents such as chloroform, carbon tetrachloride, benzene, and toluene. It hydrolyzes slowly in water and more readily in alkaline solutions. The product of the hydrolysis is not the hydroxide but the oxide, $(\text{C}_6\text{H}_5)_3\text{GeOGe}(\text{C}_6\text{H}_5)_3$. The bromide is readily soluble in liquid ammonia, and on evaporation of the solvent, tris(triphenylgermyl)amine, $[(\text{C}_6\text{H}_5)_3\text{Ge}]_3\text{N}$, is obtained. At higher temperatures triphenylgermane disproportionates rapidly, yielding tetraphenylgermane and diphenylgermane. When allowed to react with phenyllithium, it yields either tetraphenylgermane or hexaphenyldigermane, depending upon the conditions of the reaction.

References

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3. C. A. KRAUS and L. S. FOSTER: *ibid.*, **49**, 457 (1927).

* The checkers recommend 138° at 0.6 mm.

CHAPTER IVB

See also: Preparation of metal derivatives of 1,3-diketones, synthesis 29
Anhydrous metal chlorides, synthesis 43

22. EXTRACTION OF TITANIUM(IV) OXIDE FROM ILMENITE

SUBMITTED BY FOORD VON BICHOWSKY*
CHECKED BY SEPPO WILSKA†

Ilmenite is the most abundant and readily available of the titanium minerals. The composition of ilmenite is often given as $\text{FeO}\cdot\text{TiO}_2$ or FeTiO_3 , but iron(III) oxide is commonly present, and the ratio of titanium(IV) oxide to iron oxides is variable. It is convenient, therefore, to consider ilmenite as a mixture of titanium(IV), iron(II), and iron(III) oxides. Ilmenite is processed technically¹⁻³ by smelting with carbon and limestone and leaching with sulfuric acid, by leaching directly with sulfuric acid, or by heating with carbon and chlorine. In each case, the removal of iron is the major problem. The sulfuric acid leaching procedure is readily adaptable to laboratory practice, iron being removed best by crystallization as iron(II) sulfate 7-hydrate after reduction.⁴ The procedure described here is based upon decomposition of the mineral with fluoride.⁵

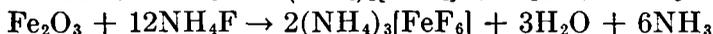
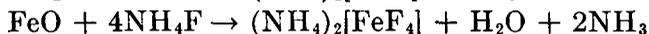
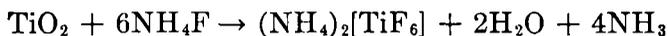
Procedure

Caution. Because of the cumulative corrosive effects of soluble fluorides on the skin,⁶ it is advisable to wear rubber gloves and to wash carefully after each operation.

* Wilmington, Del.

† Finland Institute of Technology, Helsinki, Finland.

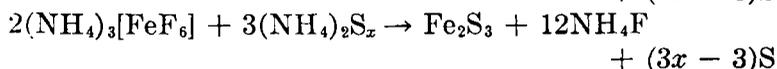
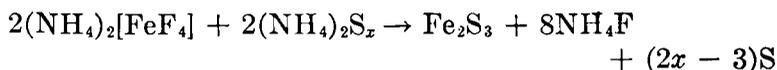
A. DECOMPOSITION OF THE MINERAL



One hundred grams of ilmenite,* ground so that 90% passes a 325-mesh screen, is mixed with 475 g. of dry ammonium fluoride† (12.8 mols) in a seamless 1-qt. iron bucket. Fifty milliliters of water is added, and the mixture is stirred into a mush with a steel rod or spatula. The mixture is then heated on a steam bath, with continued manual stirring, until the reacting mass becomes too thick for further mixing. The stirrer is removed, and the bucket and its contents are heated overnight at 160° in an oven. The resulting ashy-white residue weighs approximately 250 g.

The mass is cooled and leached in the bucket with 400 ml. of cold water. An iron pestle is used to break up lumps and improve contact. The resulting slurry is filtered rapidly using a Büchner funnel, a fast filter paper, and a paraffin-lined filter flask. The well-compressed filter cake is washed with 100 ml. of water, added in three or four portions. The combined filtrate and wash liquor is transferred to a polyethylene bottle for storage. About 65 to 75% of the titanium from the original mineral is present in the solution.

B. REMOVAL OF IRON

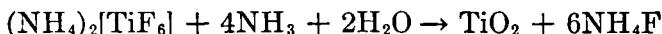


* The grade of starting material influences both the smoothness of the procedure and the yield. A high-grade ilmenite analyzing ca. 57% TiO₂ or better is recommended.

† If not available, ammonium fluoride can be prepared by neutralizing 375 g. of ammonium hydrogen fluoride with concentrated aqueous ammonia in the iron bucket and evaporating under an infrared lamp.

The fluoride solution from procedure A is placed in a polyethylene beaker and stirred either manually or with a plastic-coated magnetic stirrer. The pH is adjusted to, and maintained at, 5.8 to 6.2 by adding aqueous ammonia as needed.* Yellow ammonium sulfide (ammonium polysulfide)† solution⁵ is added drop by drop until precipitation is complete. The suspension is allowed to settle and then filtered, using a polyethylene funnel. The residue on the paper is washed with a few milliliters of water, and the filtrate and washings are combined. Any opalescence is removed by adding a quantity of 10% sodium carbonate solution equivalent to 1% of the titanium present and filtering.⁷ The resulting solution should be clear and colorless.

C. RECOVERY OF TITANIUM(IV) OXIDE



Concentrated (15 *M*) aqueous ammonia is diluted with an equal volume of water, and about 5% more than the theoretical quantity is placed in a polyethylene beaker. This solution is stirred vigorously, either manually or with a plastic-coated magnetic stirrer, and the clear fluoride solution from procedure B is added drop by drop. The resulting finely divided, white precipitate is removed by filtering, and the filter cake is washed by slurring with water and refiltering. The washed filter cake is about 80% water and represents 65 to 75% of the initial titanium-(IV) oxide content of the mineral.

Properties

Hydrous titanium(IV) oxide so obtained is nongelatinous and readily soluble in acids. It is represented as γ -TiO₂. Either the wet product or a material obtained by drying

* Frequent checks with indicator paper are recommended.

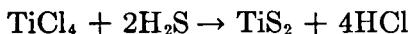
† Hydrogen sulfide can be used if the pH is first adjusted to 6.8. Excess yellow ammonium sulfide is avoided by testing the mother liquor from time to time with lead(II) acetate solution on a spot plate.

with ethanol and acetone can be used for preparing other titanium compounds.⁸ When calcined for 1 hour at 750°, the product yields anatase. Any faint discoloration after calcination is probably due to traces of manganese.

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23. TITANIUM(IV) SULFIDE



SUBMITTED BY RICHARD C. HALL* AND JOHN P. MICKEL*

CHECKED BY HENRY F. HOLTZCLAW, JR.,† AND A. GALUN†

The first attempt to prepare titanium(IV) sulfide was by Rose,¹ who obtained an impure product by passing carbon disulfide vapors over hot titanium(IV) oxide. An impure product was prepared by Ebelmen,² who passed titanium(IV) chloride vapors and hydrogen sulfide through a heated tube. Thorpe³ repeated the work of both Rose and Ebelmen but was unsuccessful in making the pure compound. Pfordten,⁴ whose work seems to be the best yet reported, produced pure titanium(IV) sulfide by passing oxygen-free hydrogen sulfide saturated with titanium(IV) chloride through a tube at a somewhat indefinite temperature described as red heat. The product was stable in air,

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in water, and in dilute acids and bases. The method of Pfordten has been simplified by using hydrogen sulfide from a tank supply to eliminate the necessity for passing the gas through chromium(II) chloride solution to remove the oxygen. Also, the use of carbon dioxide gas to sweep out the excess hydrogen chloride gas has been eliminated by using an excess of hydrogen sulfide for this purpose.

Procedure

The apparatus is shown in Fig. 8. A T-tube *A* for blending nitrogen and hydrogen sulfide is attached to a drying

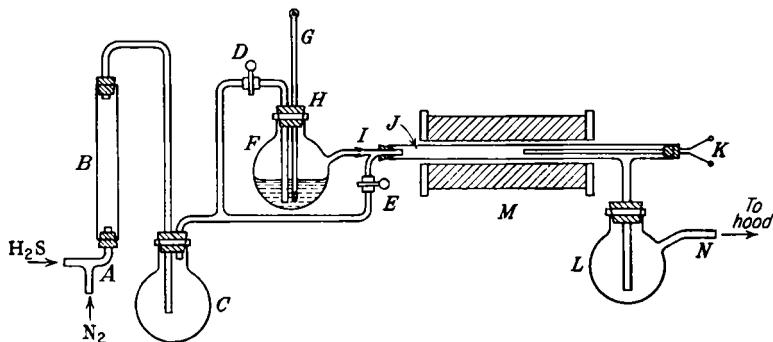


FIG. 8. Apparatus for the preparation of titanium(IV) sulfide.

tube *B* constructed from a 30-cm. length of 20-mm. glass tubing and packed with Drierite. The mixing flask *C* is connected by a by-pass arrangement containing pinch clamps *D* and *E* to a 500-ml. round-bottomed flask *F* and a reaction tube *J*. Both delivery tube* and thermometer *G* reach nearly to the bottom of flask *F*. The 6-mm. delivery tube from flask *F* has a ground-glass joint at *I* to facilitate removal of the flask at the completion of the reaction. Reaction tube *J* is a 64-cm. length of 30-mm.-i.d. pyrex tubing, which is connected by a side arm to a 500-ml. trap *L* and is provided with an enclosed thermocouple *K*. The reaction tube is placed in a 32-cm.

* The tubing should be at least 10 mm. i.d. to eliminate clogging by by-product titanium(II and III) chlorides.

tube furnace *M* so that 7 cm. projects before the heating area and 25 cm. after it. Dried rubber stoppers are employed. The entire reaction is run in a hood or is vented to a hood at *N*.

A slow stream of tank nitrogen, freed from oxygen by passing over hot copper at 400° or through alkaline pyrogallol, is passed through the assembled apparatus, and all of the glass portions from *D* to *N* are flamed. This drying procedure is continued for 30 minutes. The flow of nitrogen is increased, flask *F* is opened, 50 ml. of titanium(IV) chloride (0.46 mol) is introduced, and the flask is closed quickly with the stopper *H* containing the thermometer and connecting tubing. The pinch clamp *D* is closed and the flask *F* immersed halfway into a wax bath. The tube-furnace temperature is then increased, and the wax-bath temperature is raised to 100°. When the temperature of the furnace has reached 650°, the wax-bath temperature is then increased to 145 to 150°. The nitrogen stream is then shut off, and hydrogen sulfide is introduced into the system at a rate of 2 bubbles/sec., as seen in the flask *F*, with pinch clamp *D* open and *E* closed. The hydrogen sulfide saturated with the vapors of titanium(IV) chloride is swept into the reaction tube *J*, where titanium(IV) sulfide forms. The reaction is continued for 70 to 75 minutes.

The reaction is stopped by removing the wax bath and shutting off the tube furnace. The pinch clamp *D* is closed, and *E* is opened. The rate of hydrogen sulfide flow is increased to prevent air from entering as the flask is loosened at the ground-glass joint *I*. A stopper is placed in the opening created by disconnecting the joint *I* to prevent air from entering tube *J* and causing an explosion in the hot furnace, which contains hydrogen sulfide. Hydrogen sulfide is passed through the furnace until the temperature has dropped to 200°. At this temperature, the hydrogen sulfide flow is stopped and the nitrogen stream started again. When the furnace reaches room

temperature, the titanium(IV) sulfide is removed by breaking the cake with a glass rod, by pouring water through the tube, or if necessary by breaking the tube. The product is air-dried and pulverized.

The yield varies with the temperature of the furnace as shown by the following data:

Furnace temperature	Yield, g.
350	None
400	4.0
450	6.5
500	8.1
550	16.2
600	21.0
650	27.7

The 27.7 g. obtained at 650° is 55% of the theoretical based upon the titanium(IV) chloride used. Reactions run above 650° would require Vycor tubing.

Analysis

Titanium(IV) sulfide is analyzed for titanium by igniting the sample in air and weighing as the dioxide. The ignition temperature must be held below 800° since titanium tends to form nitrides at higher temperatures. *Anal.* Calcd. for TiS_2 : Ti, 42.75. Found: Ti, 43.49. The high titanium value is due to the presence of a small quantity of titanium(III) sulfide.

Properties

Titanium(IV) sulfide is a crystalline solid much resembling green gold. When rubbed between the fingers, it produces a graphitelike feeling. When viewed in an ordinary microscope, the crystals resemble gold in color and brilliance and show a laminated hexagonal-plate structure. Under an electron microscope the hexagonal-plate structure is clearly defined. Titanium(IV) sulfide is insoluble in water, in dilute acids or bases, and in the ordinary organic solvents. It is stable in air and maintains

its green-gold appearance after long exposure to laboratory conditions. It serves as a convenient solid intermediate for the syntheses of other titanium compounds.

References

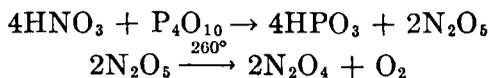
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3. T. E. THORPE: *J. Chem. Soc.*, **47**, 491 (1885).
4. O. F. PFORDTEN: *Ann.*, **234**, 257 (1886).

CHAPTER VA

- See also: Dichloro(di-2-pyridyl-amine)copper(II) and bis(di-2-pyridyl-amine)copper(II) chloride, synthesis 4
 Bis(ethylenediamine)-copper(II) diiodocuprate(I), synthesis 5
 Boron halide-amine coordination compounds, synthesis 8
 Anhydrous lanthanon nitrates, synthesis 11
 Cyanogen, synthesis 12
 Allophanyl hydrazide, synthesis 13
 Urazole, synthesis 14
 Organosilazane compounds, synthesis 16
N-Nitrosohydroxylamine-*N*-sulfonates, synthesis 31
 Hydroxylamine-*O*-sulfonic acid, synthesis 32
 Aquopentamine- and acidopentaminechromium(III) salts, synthesis 36
 Polyhalogen complex salts, synthesis 46
 Typical polyhalogen complex salts, synthesis 47
 Dichloro(di-2-pyridylamine)cobalt(II), synthesis 50
 Nitrosylpentamminecobalt(II) chloride, black, and nitrosylpentamminecobalt(III) chloride, pink(correction), synthesis 51
 Barium (ethylenediaminetetraacetato)cobaltate(III) 4-hydrate, synthesis 52
 Potassium hexacyanodinickele(I), synthesis 57
 Ammonium hexabromoosmate(IV), synthesis 59
 Ammonium hexachloroosmate(IV), synthesis 60

24. NITROGEN(IV) OXIDE

(Dinitrogen Tetroxide)



SUBMITTED BY A. PEDLER* AND F. H. POLLARD*

CHECKED BY GEORGE GIBSON† AND ILMAR KALNIN†

Nitrogen(IV) oxide can be prepared by reducing nitric acid, but it is difficult to obtain a pure product. Pure

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† Illinois Institute of Technology, Chicago, Ill.

nitrogen(IV) oxide has been obtained by oxidizing nitrogen(II) oxide with oxygen¹ or by heating lead(II) nitrate,² but complete separation of the product from nitrogen(II) oxide impurities requires involved manipulation. The method of Hackspill and Besson,³ described here, is more convenient for preparing small quantities (up to 50 ml.) of pure liquid nitrogen(IV) oxide.

Procedure

The apparatus is shown in Fig. 9. A 125-ml. dropping funnel *A* is connected to a 750-ml. round-bottomed dis-

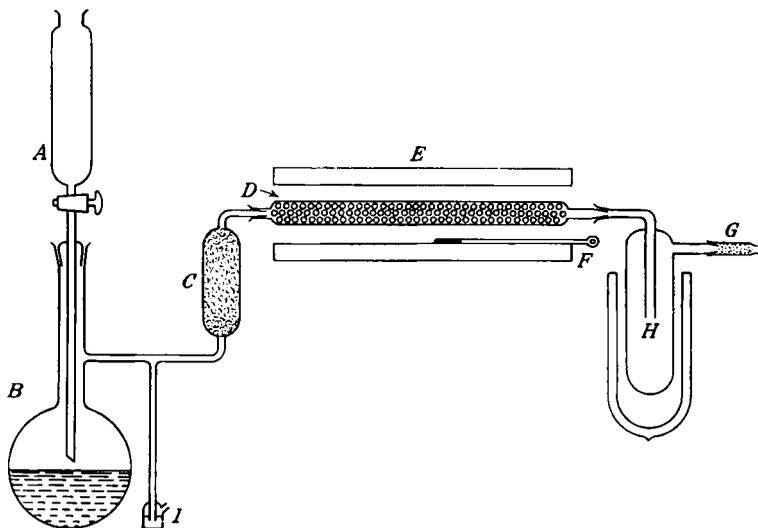


FIG. 9. Apparatus for the preparation of nitrogen(IV) oxide.

tilling flask *B* through a ground-glass joint. The side arm of the flask is sealed to a 20-cm. length of 30-mm. glass tubing *C*, which is loosely filled with phosphorus(V) oxide. This tube is connected through a standard-taper joint to a 40-cm. length of 20-mm. pyrex tubing *D* resting in a tube furnace *E*. Decomposition tube *D* is connected through another standard-taper joint to a 140-ml. trap *H*,* which is attached in turn to a drying tube *G* filled

* The central tube should be at least 1 cm. in diameter and not over 2 cm. in length to avoid blockage by condensing product.

with phosphorus(V) oxide. A safety bubbler *I* filled with silicone oil and a thermometer *F* complete the apparatus. All ground-glass joints are lubricated with Dow-Corning silicone grease.

Two hundred fifty grams of phosphorus(V) oxide (0.88 mol) is placed in flask *B*,* and 105 ml. of fuming (95% or more, water-white) nitric acid (2.25 mols) is placed in the dropping funnel. The temperature of the furnace is adjusted to 260° and maintained at this value by means of a suitable Variac.† The nitric acid is then added drop by drop, the addition being sufficiently slow to avoid observed distillation of the acid into the connecting tubes. The reaction is allowed to proceed for 15 to 30 minutes to flush the apparatus completely. Trap *H* is then surrounded by a Dewar flask containing a mixture of Dry Ice and acetone to condense nitrogen(IV) oxide as a white solid. The reaction is continued until 100 ml. of the acid has been added, and then addition of acid is stopped.

The product is purified in the apparatus shown in Fig. 10. A 250-ml. Dewar flask *A* containing liquid oxygen and equipped with a safety tube *B* is attached through a ground-glass joint to vessel *C*, which is attached in turn through a drying tube *D* filled with phosphorus(V) oxide to a 100-ml. trap *E*. Trap *E* is protected by phosphorus(V) oxide at *F*. The solid nitrogen(IV) oxide in trap *H* (Fig. 9) is melted by warming to room temperature and poured into vessel *C* or distilled into *C* by using a vacuum system and cooling *C* with liquid oxygen. Vessel *C* is attached immediately to the apparatus, and the nitrogen(IV) oxide is evaporated by the slow stream of dry oxygen from the

* The level of the solid should be about 5 mm. below the outlet tube of the dropping funnel, and a cavity about 3 cm. wide and 3 cm. deep should be made just below this tube. Alternatively, the nitric acid may be added under the phosphorus(V) oxide if glass beads are packed around the tip of the dropping funnel to prevent blockage.

† Decomposition to nitrogen(II) oxide and oxygen is appreciable above this temperature.

boiling liquid in *A*.* The apparatus is swept out for a few minutes, and trap *E* is then cooled with a Dry Ice-

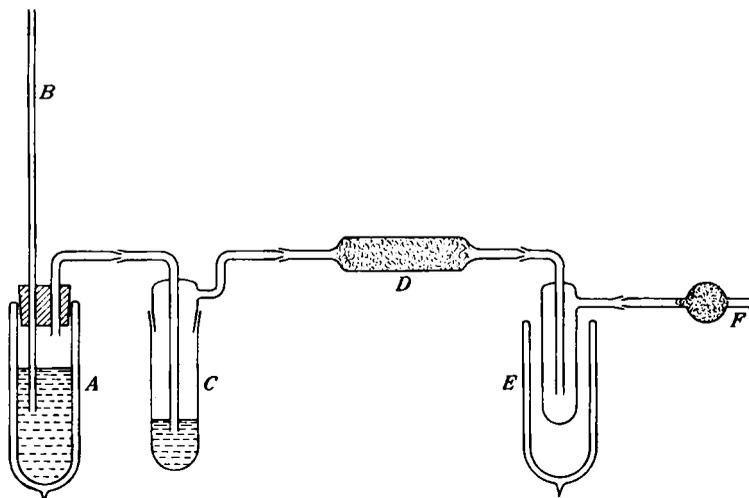
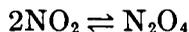


FIG. 10. Apparatus for the purification of nitrogen(IV) oxide.

acetone bath. To avoid cooling due to evaporation in *C*, this vessel is heated with a warm-water bath. The product is either preserved frozen in vessel *E* or distilled into a thick-walled glass tube,† which is sealed. The yield is about 50 ml. of the liquid (25% of theoretical for 100 ml. of 95% nitric acid).

Properties

Nitrogen(IV) oxide is a brown, paramagnetic gas, which condenses to a brownish, paramagnetic liquid boiling at 21.3°. When cooled, the liquid becomes lighter in color and freezes to a white diamagnetic solid melting at -11°. Changes in color and magnetic behavior upon cooling are associated with conversion from the NO₂ monomer to the N₂O₄ dimer,⁴ as



* Trap *H* may be incorporated directly into the purification apparatus if properly constructed.

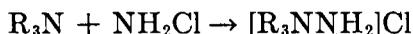
† Such tubes should be allowed to warm to room temperature only if very carefully sealed.

Dissociation of the tetroxide to the dioxide increases from 20% at 27° to 90% at 100°. Above 600° the dioxide decomposes extensively to nitrogen(II) oxide and oxygen.^{5,6} Solid nitrogen(IV) oxide crystallizes in the cubic system ($a = 7.77$ A.) with six N_2O_4 groups to the unit cell.⁷ Liquid nitrogen(IV) oxide is an electrolytic solvent.^{8,9} Nitrogen(IV) oxides dissolve in anhydrous nitric and sulfuric acids and react with water to give nitrous and nitric acids.

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25. 1,1,1-TRISUBSTITUTED HYDRAZONIUM CHLORIDES



SUBMITTED BY HARRY H. SISLER* AND GEORGE OMIETANSKI*
 CHECKED BY CHARLES J. A. VOLZ† AND BERNARD RUDNER†

1,1,1-Trisubstituted hydrazonium chlorides have been prepared by reaction of 1,1-disubstituted hydrazines with alkyl chlorides,¹ by alkylation of hydrazine with alkyl chlorides,² by metathesis of the corresponding bromide³ or iodide⁴ with silver chloride, and by neutralization of the corresponding hydrazonium hydroxide with hydrochloric acid.⁵ For many of these compounds, however, the direct reaction of chloramide (chloramine), NH_2Cl , prepared by the gas-phase reaction of ammonia with chlorine,⁶ with the corresponding tertiary amine⁷ is the most convenient

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method. The following 1,1,1-trisubstituted hydrazonium chlorides have been prepared in this way: trimethyl-, triethyl-, triisopropyl-, tri-*n*-heptyl-, dimethyl(phenyl)-, diethyl(phenyl)-, diethyl(2-hydroxyethyl)-, dimethyl(2-hydroxyethyl)-, dimethyl(*p*-tolyl)-, cyclohexyldiethyl-, and diethyl(3-hydroxypropyl)hydrazonium chloride. The preparations of 1,1,1-trimethyl- and 1,1,1-triethylhydrazonium chlorides are given as representative of the method.

Procedure

A. THE CHLORAMIDE GENERATOR



The apparatus used⁶ is illustrated in Fig. 11. The glass reactor tube *A* is approximately 65 cm. in length and

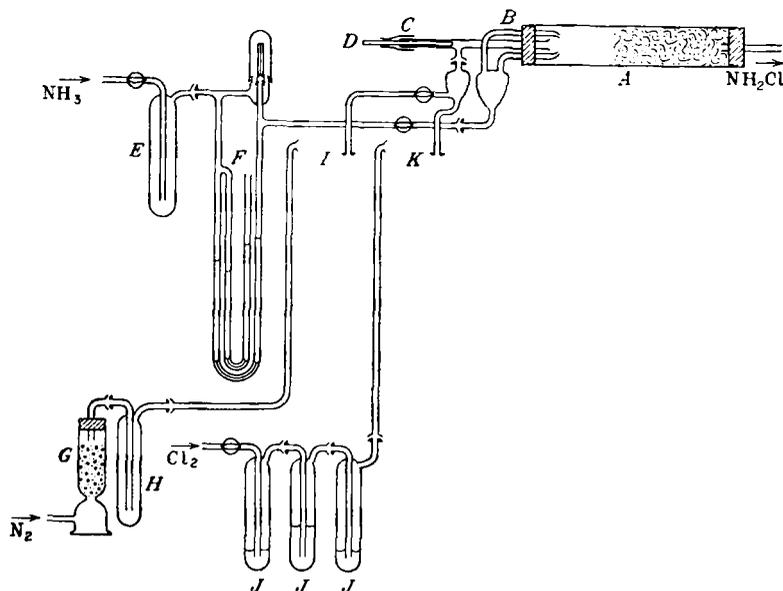


FIG. 11. Apparatus for the generation of chloramide.

50 mm. in diameter and is fitted at each end with rubber stoppers. At one end the rubber stopper is fitted with five 8-mm. glass tubes *B*, one through the center and the

other four symmetrically distributed around it. The center tube is flared slightly, and the outer tubes end in jets bent to point into the effluent gas stream from the center tube. The outer tubes are for the introduction of ammonia gas, whereas chlorine and nitrogen are introduced through the center tube. The center tube is fitted with a rubber collar *C*, through which a glass rod *D* is inserted. This is used to remove plugs of ammonium chloride which build up in the end of the chlorine inlet. The reactor tube is packed with glass wool, loosely in the fore part and more tightly near the outlet end. This serves to remove completely the ammonium chloride from the effluent gas stream. The apparatus is arranged for introduction of cylinder ammonia through expansion chamber *E* and a differential-manometer-type flowmeter *F*; of cylinder nitrogen through an Anhydrone-Ascarite tower *G*, an expansion chamber *H*, and a similar flowmeter inserted at *I*; and of cylinder chlorine through sulfuric acid bubblers *J* and a flowmeter at *K*. Connections within the system are made with ball-and-socket-type ground-glass joints.

Chlorine, nitrogen, and ammonia are introduced in the mol ratio 1:3:30, with a chlorine flow rate of 0.01 to 0.05 mol/hr.* The quantity of ammonium chloride produced in *A* as a by-product from the reaction of chlorine with ammonia can be used to calculate the yield in terms of the expression

$$\% \text{ yield} = \frac{2(a - b)}{a} \times 100$$

where *a* is the total weight of chlorine introduced and *b* is the weight of chlorine recovered as ammonium chloride. The yield varies from 75 to 95% over generation periods of 60 to 90 minutes.†

* Neither the proportions of reagents nor the flow rate is absolutely critical as long as a large excess of ammonia is employed and the rate is not too slow.⁶ The checkers note that the nitrogen may be replaced by a large excess of ammonia without reduction in yield.

† The checkers note that each generator has its own optimum operating characteristics and that the yield of chloramide varies accordingly. Their

B. 1,1,1-TRIMETHYLHYDRAZONIUM CHLORIDE

The gaseous effluent of the chloramide generator (at a flow rate of ca. 0.04 mol of chloramide per hour)* is passed directly into 100 ml. of anhydrous trimethylamine (ca. 1.1 mols), maintained at a temperature of about -30° by intermittent addition of Dry Ice to a chloroform-carbon tetrachloride cooling bath. As the chloramide is passed into the amine, crystallization of 1,1,1-trimethylhydrazonium chloride begins to occur. The reaction is continued for 1 hour. After the chloramide stream is shut off, the reaction mixture is allowed to warm to room temperature and the excess amine (and ammonia) allowed to evaporate. The residue is thoroughly washed with ethyl ether to remove adhering amines. The washed residue (2 to 4 g.) consists of 1,1,1-trimethylhydrazonium chloride contaminated with 1 to 2% of ammonium chloride. The yield of the crude hydrazonium salt, as based upon the chloramide retained in the reaction mixture,† is at least 95%. If a product of higher purity is desired, the above residue can be recrystallized from an ethanol-ether mixture or from anhydrous ethanol. *Anal.* Calcd. for $(\text{CH}_3)_3\text{NNH}_2\text{Cl}$: C, 32.58; H, 10.03; N, 25.33; Cl, 32.06. Found: C, 31.77; H, 9.91; N, 25.12; Cl, 32.81.

C. 1,1,1-TRIETHYLHYDRAZONIUM CHLORIDE

The chloramide-ammonia mixture from the generator is passed into 100 ml. of triethylamine (0.7 mol) maintained at about 20° . After about 30 minutes, the trap containing the reaction mixture becomes choked with the solid triethylhydrazonium chloride. The solid is filtered

best yields (90% for 60- to 90-minute periods) were obtained with apparatus permitting flow rates of 0.1 mol/hr. or greater, using a chlorine-to-ammonia mol ratio of 1:50 and no nitrogen.

* The higher flow rate employed by the checkers gives less loss of trimethylamine by evaporation and permits a longer reaction period.

† The total chloramide retained in the reaction mixture is equivalent to the chloride ion present in the reaction mixture at the end of the process.

off (2 to 3 g.), washed with ethyl ether, and vacuum-dried at room temperature. The product thus obtained is completely soluble in ethanol and in chloroform, indicating that little, if any, ammonium chloride is present. The yield is quantitative. 1,1,1-Triethylhydrazonium chloride can be recrystallized from chloroform-ethyl ether mixtures. *Anal.* Calcd. for $(C_2H_5)_3NNH_2Cl$: C, 47.20; H, 11.22; N, 18.35; Cl, 23.22. Found: C, 47.30; H, 11.23; N, 18.21; Cl, 23.38.

Properties

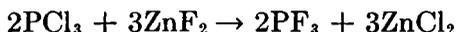
The 1,1,1-trisubstituted hydrazonium chlorides are colorless, crystalline compounds which are very soluble in water, many being highly hygroscopic. They are also soluble in ethanol but are only slightly soluble in ethyl ether. 1,1,1-Trimethylhydrazonium chloride melts at about 245° in a sealed capillary with decomposition. 1,1,1-Triethylhydrazonium chloride melts at about 177 to 178° in a sealed capillary.

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26. PHOSPHORUS(III) FLUORIDE

(Phosphorus Trifluoride)



SUBMITTED BY A. A. WILLIAMS*

CHECKED BY ROBERT W. PARRY† AND HOWARD DESS†

Phosphorus(III) fluoride can be prepared by the reaction of phosphorus(III) chloride with arsenic(III) fluoride,^{1,2}

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lead(II) fluoride,³ or antimony(III) fluoride;^{4,5} by the reaction of copper phosphide with lead(II) fluoride;⁶ by the reaction of phosphorus(III) bromide with zinc fluoride;⁷ or by the thermal reaction of the mixed phosphorus(V) halide, PF_3Cl_2 , with hydrogen, mercury, aluminum, tin, lead, iron, nickel, or phosphorus.⁸ The reaction of phosphorus(III) chloride with zinc fluoride has the advantages of employing inexpensive and readily available reagents and of giving an easily controlled supply of pure product.⁹

Procedure

Powdered anhydrous zinc fluoride is dried overnight at 140 to 150°. Fifty to sixty grams of the warm solid (0.48 to 0.58 mol) is placed in a 300-ml. distilling flask which is equipped with a dropping funnel and attached in series to two traps cooled with Dry Ice in acetone, a sulfuric acid bubbler, and either a container for storing the gaseous product or a trap cooled with liquid nitrogen.¹ About 45 ml. of phosphorus(III) chloride is placed in the dropping funnel. This reagent is added initially at a rate of 1 drop in 3 seconds for a period of 1 to 2 minutes. After an induction period of slow phosphorus(III) fluoride evolution,* the product is released rapidly in a strongly exothermic reaction. The rate of phosphorus(III) fluoride production, as indicated by the bubbler, is then controlled by adjusting the rate of phosphorus(III) chloride addition and by immersing the flask in a cold water bath to condense phosphorus(III) chloride in droplets on the cooler parts of the flask. The reaction is continued until 40 ml. of phosphorus(III) chloride has been added over a period of 1½ to 2 hours. In the final stages of the synthesis, the reaction vessel is heated in a warm-water bath. Any entrained phosphorus(III) chloride is removed in the Dry Ice-acetone traps. It is recommended that the reaction

* If rapid evolution of phosphorus(III) fluoride is not noted within 5 minutes, more phosphorus(III) chloride is added, and time is allowed for the induction period.

be run on the scale indicated and that larger quantities of phosphorus(III) fluoride be produced by use of additional generators, all operating on the same scale.

Properties

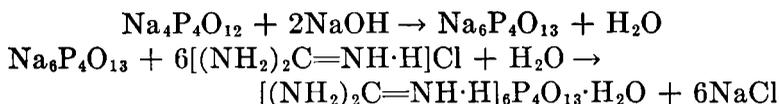
In addition to the properties listed previously,¹ the following are characteristic:⁵ heat of vaporization, 3489 cal./mol; Trouton's constant, 30.2 cal./deg. mol; critical temperature, -2.05° ; critical pressure, 42.69 atm.; vapor pressure,

$$\log p_{\text{mm.}} = 7.310 - \frac{761.4}{T}$$

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27. HEXAGUANIDONIUM TETRAPHOSPHATE 1-HYDRATE



SUBMITTED BY OSCAR T. QUIMBY* AND FRANK P. KRAUSE*
CHECKED BY FRED MCCOLLOUGH†

In the series of chain compounds known as the polyphosphates, $\text{M}_{n+2}\text{P}_n\text{O}_{3n+1}$ (where M stands for univalent cations), mono-, di-, and triphosphates are readily obtainable as crystalline compounds of high purity. Until

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† Victor Chemical Works, Chicago Heights, Ill.

recently¹ tetraphosphates have not been available as crystalline laboratory reagents of reasonable purity. Although tetraphosphate ions are present in aqueous solutions of sodium phosphate glasses^{2,3} containing 59 to 64% phosphorus(V) oxide and of condensed phosphoric acids³ containing 82 to 86% phosphorus(V) oxide, a more convenient starting material is the tetrameric ring compound, tetrametaphosphate.^{4,5} The anion ring is opened by hydrolysis in an excess of aqueous sodium hydroxide solution at or near room temperature. The resulting tetraphosphate is induced to crystallize by double decomposition with excess guanidonium chloride in a formamide-rich solvent (formamide-to-water volume ratio 3:1 to 4:1).

Procedure

A. PURIFICATION OF SODIUM TETRAMETAPHOSPHATE

Three hundred grams of crude sodium tetrametaphosphate 4-hydrate* (ca. 0.63 mol) is dissolved in 2 l. of water at room temperature and the solution filtered if necessary. The solution is stirred vigorously, and a total of 1 l. of 95% ethanol is added, the first part of the alcohol in a steady stream until precipitation begins and the remainder more slowly over a period of at least 30 minutes. The crystals are removed by filtering and are washed successively with 300 ml. of 35% ethanol and 300 ml. of 50% ethanol. Ethanol on the crystals is allowed to evaporate, and the crystals are dissolved in 1 l. of water.† The compound is reprecipitated as before by adding 500 ml. of 95% ethanol.‡ Two such precipitations eliminate phosphate impurities which give multiple end points in acid-base titrations.¹ The yield of the air-dried product is 195 to

* Sold under the trade name Cyclophos by Victor Chemical Works, Chicago Heights, Ill.

† More water is required if the ethanol is not completely removed first.

‡ If more than 1 l. of water was added, 1 ml. of ethanol is added for each 2 ml. of water used.

231 g. (65 to 77%).* *Anal.* Calcd. for $\text{Na}_4\text{P}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$: P, 25.8; H_2O , 15.0. Found: P, 26.0, 25.8; H_2O (by loss of weight in 2 hours at 400°), 15.6, 15.4. The x-ray diffraction pattern is identical with that reported for the low-temperature form of the 4-hydrate.⁵

B. HYDROLYSIS OF TETRAMETAPHOSPHATE TO TETRAPHOSPHATE

A 10 to 15% aqueous solution is prepared from the purified sodium tetrametaphosphate. The solution is cooled to room temperature, and sufficient cold concentrated sodium hydroxide solution to give a final concentration of 8.5 to 10% tetrametaphosphate and a mol ratio of hydroxide to tetrametaphosphate of 3:1 is added. The temperature is not permitted to rise above 40° during this addition. The resulting solution is stored at constant temperature, and aliquots are titrated periodically for excess sodium hydroxide to pH 10. When 1.90 to 1.95 mols of sodium hydroxide has been consumed,† giving a 9.8 to 11.5% solution of sodium tetrphosphate, an equal volume of 95% ethanol is added and the system allowed to stand until two clear liquid layers are formed. The upper layer is discarded, and the sirupy lower layer, containing about 46% sodium tetrphosphate, is reserved for procedure C.‡

* The initial material varies in purity.

† About 3 weeks is required at 32° . Any temperature between 20 and 40° is satisfactory, but degradation of the tetrphosphate is appreciable above 40° . The rate of cleavage of the P-O-P bond increases about threefold for a 10° rise in temperature, permitting calculation of the time required from the data at 32° . As the reaction approaches completeness (consumption of 2.00 mols of sodium hydroxide), the rate of opening the tetrametaphosphate ring is so decreased that subsequent degradation of the tetrphosphate chain becomes significant. Both yield and purity of product can be decreased if the reaction is continued until exactly 2.00 mols is consumed.

‡ It is unnecessary to remove sodium hydroxide remaining in the sirupy liquid. This can be done, if desired, by retreating once or twice with 3 volumes of water and 4 volumes of ethanol and separating the layers.

C. PRECIPITATION OF HEXAGUANIDONIUM TETRAPHOSPHATE

To 100 g. of the sirupy liquid (ca. 44 g., or 0.094 mol, of sodium tetraphosphate), 121 g. of guanidonium chloride (1.27 mols) and 121 ml. of water are added. The solution is maintained at 25 to 28° and stirred vigorously while formamide is added until a faint turbidity results. At least 530 ml. of formamide (3 volumes per volume of water) is required.* Nucleation is usually noted within 15 minutes, but may require 30 minutes or more,† and is aided by rubbing the inside walls of the container with a stirring rod.‡ Stirring is continued for about 1 hour after crystallization begins. The crystals are removed by suction filtration and are washed three times with 50-ml. portions of formamide and then three times with 50-ml. portions of anhydrous ethanol. After the addition of each quantity of wash liquid, the crystals are stirred with the liquid before suction is applied. During the ethanol washes, care is taken not to draw air through the crystals after the bulk of the liquid is removed to minimize agglomeration. The product is air-dried at 25 to 28° at a relative humidity not in excess of 50%. The yield is about 46.6 to 51.2 g. (about 70 to 77%).

The product is purified by dissolving 45 g. of it and 5 g. of guanidonium chloride in 75 ml. of water, diluting with sufficient formamide (ca. 70 ml.) to produce permanent turbidity, and crystallizing as outlined above.

* The quantity of formamide added is critical. Insufficient formamide to cause turbidity gives solutions that crystallize very slowly; excess formamide gives persistent gelatinous precipitates that hinder filtration.

† If crystallization does not occur in 30 minutes, the formamide-to-water ratio is increased to 4:1 by adding some water and then formamide until the solution remains turbid but does not give a gelatinous precipitate. At water contents of 5% or less, no amount of formamide will induce cloudiness or crystallization. Speedy crystallization is effected under these conditions by adding 95% ethanol. Small quantities of seed crystals are easily obtained in this manner.

‡ Seeding is less effective in inducing crystallization.

The product is washed and dried as in its preparation. About 85% of the guanidonium tetrphosphate is recovered in each recrystallization. *Anal.* (after one recrystallization). Calcd. for $[(\text{NH}_2)_2\text{C}=\text{NH}\cdot\text{H}]_6\text{P}_4\text{O}_{13}\cdot\text{H}_2\text{O}$: P, 17.46; N, 35.5; H_2O , 2.54; $[(\text{NH}_2)_2\text{C}=\text{NH}\cdot\text{H}]_6\text{P}_4\text{O}_{13}$, 97.5. Found: P, 17.2, 17.7; N, 34.6, 36.0; H_2O ,* 2.8, 2.9; $[(\text{NH}_2)_2\text{C}=\text{NH}\cdot\text{H}]_6\text{P}_4\text{O}_{13}$,† 97.98. An acid-paper chromatogram‡ on a sample 2 years old indicated 2% of the total phosphorus as orthophosphate, 2% as pyrophosphate, none as triphosphate, and 96% as tetrphosphate. An alkaline-paper chromatogram‡ revealed no ring compounds.

Properties¹

Though somewhat hygroscopic, hexaguanidonium tetrphosphate 1-hydrate does not change weight appreciably during the time needed for weighing under laboratory conditions (25 to 28°, 30 to 50% relative humidity). Its water solubility is about 63% at 27°. In 1% solution in carbon dioxide-free water, its pH is 9.64 to 9.68 at 27°. It has proved chemically stable over a period of at least 2 years. Drying for 2 hours at 100° does not change the x-ray pattern. It can be oven-dried for 2 hours at 110° without much loss of water. At 120°, however, the compound loses 80% of its water in 20 hours; the water not volatilized has become water of constitution and can be determined by acid-base titration.¹ This hydrolysis during dehydration recalls the similar behavior of sodium triphosphate 6-hydrate.¹

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* By drying for 20 hours at 120° and adding water indicated by titrating the residue to pH ca. 10.

† By titrating from pH 4 to 9.5.

‡ The solvents used were essentially those employed by Ebel.* The apparent pH values were 1.8 and 11.4, respectively.

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28. SODIUM MONOTHIOPHOSPHATE

(Sodium Phosphorothioate)



SUBMITTED BY STANLEY K. YASUDA* AND JACK L. LAMBERT*

CHECKED BY L. E. NETHERTON† AND VINCENT R. WIEDERKEHR†

Sodium monothiophosphate 12-hydrate has been prepared by treating phosphorus(V) sulfide with sodium hydroxide solution, hydrolyzing the dithiophosphate recovered as a major product, and crystallizing.^{1,2} The anhydrous salt has been obtained by fusing sodium metaphosphate glass with anhydrous sodium sulfide.³ However, the direct reaction of phosphorus(V) sulfochloride with aqueous sodium hydroxide solution^{4,5} provides a simpler procedure and one that does not give contaminating di-, tri-, and tetrathiophosphates. Potassium monothiophosphate, previously obtainable only in solution,⁶ can be prepared in impure form by the same general procedure if the potassium hydroxide solution used is sufficiently concentrated.

Procedure

Three hundred milliliters of a cool aqueous solution containing 40 g. of sodium hydroxide (1 mol) is added to 17.5 ml. of phosphorus(V) sulfochloride (0.17 mol)⁶ in a 1-l. three-necked round-bottomed flask equipped with a reflux condenser, a thermometer, and a motor-driven stirrer. The mixture is heated at 103 to 109° for 15 to 20 minutes, until the phosphorus(V) sulfochloride layer has disappeared. The solid hydrated sodium monothio-

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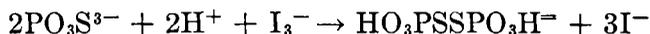
† Victor Chemical Works, Chicago Heights, Ill.

phosphate and sodium chloride, which separate out on cooling in an ice bath, are removed by filtration and dissolved in a minimum quantity of warm (40 to 45°) water. For each 100 ml. of salt solution, approximately 185 ml. of anhydrous methanol is added to precipitate the sodium monothiophosphate 12-hydrate, which is removed by filtering. This recrystallization procedure is repeated, and the hydrated salt is dehydrated by suspending with constant stirring for 1 hour in 200 ml. of anhydrous methanol. The anhydrous sodium monothiophosphate crystals are removed by suction filtration at room temperature, heated at 100° for 1 hour, and stored in a tightly stoppered bottle. The yield is about 17 g. (about 57% of the theoretical). The exact yield depends on the purity of the sodium hydroxide. *Anal.* Calcd. for $\text{Na}_3\text{PO}_3\text{S}$: S, 17.83; P, 17.27. Found: S, 17.90, 17.78, 17.90, 17.68, 18.06; P, 17.09, 17.38, 17.25. Sulfur was determined by oxidizing to the sulfate and weighing as barium sulfate. Phosphorus was converted to the phosphate and weighed as magnesium ammonium phosphate. Titration of the trisodium salt with standard iodine solution in the pH range 0.5 to 0.8, using a potentiometric end point,⁷ gave consistent results between 99.9 and 100.0% of calculated purity.

Properties

Anhydrous sodium monothiophosphate is a white, crystalline solid which decomposes without melting at 120 to 125° to release a volatile compound that discolors lead acetate paper. The anhydrous salt does not absorb moisture from the air at relative humidities below 31%. The solid 12-hydrate evolves hydrogen sulfide slowly at room temperature and decomposes rapidly at 60°. Solubilities in grams of anhydrous salt per liter of saturated solution at various temperatures are 4°, 21.2; 18°, 79.2; 28°, 132.7; 38°, 241.5. Solutions of the sodium salt decompose only very slowly when stabilized with added

sodium carbonate. Titration with iodine solution proceeds quantitatively under strongly acidic conditions as⁷



The end point is best obtained potentiometrically using polarized platinum electrodes.

Cobalt(II) ion forms a deep blue solution with an excess of monothiophosphate ion in a solution made slightly alkaline with sodium acetate. This reaction can be used as a qualitative identification test for cobalt(II) ion in the presence of nickel(II) ion.⁸ Monothiophosphate ion reacts with lead ion in cool solution to form a white precipitate, which turns brown to black when the suspension is heated.

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CHAPTER VB

29. PREPARATION OF METAL DERIVATIVES OF 1,3-DIKETONES

BY W. CONARD FERNELIUS* AND BURL E. BRYANT†

The structures, types, properties, uses, nomenclature, and general methods of preparation of metal derivatives of 1,3-diketones have been discussed in a previous volume.¹ It now seems desirable to consider in somewhat more detail the various factors involved in the preparation and purification of these substances.

Preparation of Metal Derivatives of 1,3-Diketones. Methods of preparation may be grouped into several general classes.

1. Direct Reaction of 1,3-Diketones with Metal Salts.

a. In Aqueous Solution. Unless the metal chelate is extremely insoluble, the reaction between a 1,3-diketone and a metal salt will come to an equilibrium short of completed reaction because of the increase in concentration of free acid in the solution. One obvious way of overcoming this difficulty is to control the pH of the solution by buffering it. For this reason, the use of metal acetates is widely recommended for such preparations.^{2,3} Another method of controlling the pH of the solution is by gradually adding a base,⁴⁻⁶ preferably a weak one such as ammonia^{3,7} and preferably in such a manner as to maintain the pH below a critical value where a metal hydroxide or basic salt might contaminate the product.⁷⁻¹⁰

The use of a buffer has the disadvantage of adding extraneous ions, which in turn may contaminate the

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product. Even the controlled addition of ammonia may result in high local concentrations which cause the precipitation of metal hydroxides or of basic diketone derivatives. These may be so slightly soluble that they are only slowly converted to the normal diketone derivatives. This difficulty can be avoided by the homogeneous generation of ammonia (adding urea to the solution and heating)¹¹ (see synthesis 35).

The direct reaction between a 1,3-diketone and a salt in water is limited by the small solubilities of many 1,3-diketones. This difficulty can be overcome in part by using a partially nonaqueous solvent (a mixture of water with ethanol or dioxane)¹¹ or by adding the 1,3-diketone in ethanolic (or similar) solution to the aqueous solution of the metal salt.³

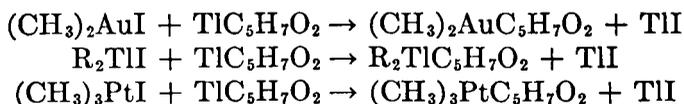
The effect of the limited water solubility of a 1,3-diketone can also be overcome by dissolving the compound in a water-immiscible organic solvent and then shaking with an aqueous solution of a salt of the appropriate metal.^{9,12,13} Ideally, this procedure necessitates one of two situations: (i) insolubility of the metal derivatives in water and in the immiscible solvent or (ii) complete extraction of the product into the immiscible solvent (see 3 below). If such conditions do not prevail, the solids must be removed by filtration and the solvent evaporated. Because neither (i) nor (ii) is encountered in most cases, procedures which assume that one or the other prevails often give low yields.

b. In Nonaqueous Solution. In those instances where both a metal halide (such as the compounds BCl_3 , AlCl_3 , SiCl_4 , GeCl_4 , ZrCl_4 , ThCl_4 , NbCl_5 , TaCl_5) and the 1,3-diketone are soluble in an inactive organic solvent such as benzene, reaction can be brought to completion by warming, since the hydrogen halide formed is insoluble in the reaction medium.¹⁴⁻¹⁶ A somewhat different reaction is that between calcium carbide and a benzene solution of a 1,3-diketone.¹⁷ Here the escape of acetylene and the solubility of the calcium salt make possible the reaction

with the insoluble carbide. Were the particles of carbide to become coated with an insoluble calcium salt, the reaction would not proceed to completion.

2. Reaction of a Soluble Salt of a 1,3-Diketone with a Soluble Salt of a Metal. Although this category is very similar to method 1, it involves the preliminary formation of the diketone salt. The usual technique involves dissolving the 1,3-diketone in water by adding the minimum necessary amount of aqueous ammonia or sodium carbonate.¹⁷⁻²⁶ This amounts to carrying out the reaction at a higher pH than by the use of the 1,3-diketone alone but lacks the pH control which may be essential. Under these conditions a number of substances other than the desired neutral chelate can be formed. Among these are (a) a mixed compound, *e.g.*, MChX (Ch = 1,3-diketone)²⁶ resulting from the presence of insufficient 1,3-diketone in the region of reaction or to the formation of unusually insoluble compounds; (b) metal hydroxide or basic chelate, *e.g.*, MChOH,²⁶ resulting from too high a pH; or (c) complex anions, *e.g.*, MCh₃⁻,^{20,26} resulting from the presence of excess 1,3-diketone. Formation of substances of these types would result in contamination of the neutral complex. The desired product would then require careful purification. Procedures leading to such relatively impure initial products should be avoided whenever possible since generally applicable purification measures may fail in a specific case.

A potentially very useful variant of this "salt + salt" procedure is the use of selected salts that will produce a soluble 1,3-diketone derivative and an insoluble by-product. Such procedures are illustrated by the equations^{27-30,33}



thallium(I) iodide being precipitated in each instance.

The syntheses of acetylacetone (2,4-pentanedione) derivatives of beryllium,¹⁸ aluminum,²³ zirconium,¹⁴ and thorium⁶ are representative of this general method.

3. Incorporation of Solvent Extraction with Method 1 or 2. Some investigators have suggested the addition of an immiscible liquid to an aqueous reaction mixture to extract the metal 1,3-diketone compound as it is formed.^{5,21,34,35} Since metal hydroxides and such species as $MChX$, $MChOH$, MCh_3^- are seldom soluble in an organic medium, the extraction liquid separates the desired compound from these contaminants. It must be remembered that, unless the distribution ratio is unusually favorable, several extractions may be necessary to remove all of the product. Careful adjustment of the pH in such extractions often permits the separation of one metal from others.³⁵

4. Reaction of a 1,3-Diketone with a Metal Oxide, Hydroxide, Carbonate, or Basic Carbonate. *a. In Aqueous Solution.* The reaction between a 1,3-diketone and a suspension of a hydrous oxide or hydroxide,³⁶ although often slow, may present the advantage of introducing minimum amounts of impurity. Furthermore, this procedure permits the preparation of metal derivatives in oxidation states that are relatively unstable under other conditions.

b. In Inert Solvent. An excess of a liquid 1,3-diketone or a solution of a solid 1,3-diketone in an inert solvent can be refluxed with an oxide, carbonate, or basic carbonate of a metal.^{19,21,22,37-44} This procedure has many advantages: (i) it introduces no foreign ions; (ii) if the complex is soluble, it permits easy separation of product from unreacted oxide, etc.; (iii) it requires no special attention or control; (iv) only very minor differences of procedure are required for a wide variety of 1,3-diketones and metals; and (v) the metal compounds required are readily available and easily stored. On occasion, the metal in the oxide, etc., need not be in the same oxidation state as that desired in the 1,3-diketone chelate because the diketone used may act

as a mild reducing agent and lower the oxidation state, or the oxygen of the air (or added oxidizing agent) may raise the oxidation state.

This general procedure is illustrated in the preparation of vanadium(IV) oxy(acetylacetonate) (synthesis 30B).

5. Reaction of a 1,3-Diketone with a Metal. This procedure is usually carried out in an anhydrous inert medium. It has been used for obtaining derivatives of the alkali metals,^{13,45,46} alkaline earth metals,¹³ copper (in the presence of air),⁴⁷ aluminum (as an amalgam),⁴⁸ and lead.⁴⁰

This procedure is particularly useful for obtaining (a) compounds of very active metals, (b) anhydrous compounds, or (c) compounds of metals in lower states of oxidation.

6. Miscellaneous Methods. Some of the reactions that have been used for the preparation of metal derivatives of 1,3-diketones cannot be classified as any of the above general types. Derivatives of metals in lower oxidation states have been prepared by the reduction of materials exhibiting higher oxidation states, *e.g.*, uranium(IV) acetylacetonate by reduction of the uranium(VI) compound with hydrogen sulfide,⁴⁹ manganese(III) acetylacetonate by reduction of manganese(IV) chloride with acetylacetone.⁵⁰ Derivatives of metals in higher oxidation states have been obtained by oxidation in the presence of excess 1,3-diketone, *e.g.*, cobalt(III) acetylacetonate by oxidation of cobalt(II)⁴⁸ (synthesis 53), manganese(III) acetylacetonate by oxidation of manganese(II).⁴⁸ Derivatives of metals in intermediate states of oxidation have been made by reaction between a lower and a higher oxidation state in the presence of 1,3-diketone, *e.g.*, manganese(III) acetylacetonate by reduction of permanganate ion with manganese(II) ion.⁵¹

Purification of Metal Derivatives of 1,3-Diketones. Despite all care in the preparation of metal derivatives, it may still be necessary to purify such compounds after they are formed. Distillation, sublimation, and crystallization (particularly the last) are the methods generally available

for this purpose. Considering the techniques available, it is surprising that so few data are available on the boiling points, temperature sensitivities, and solubilities of 1,3-diketone chelates. The following information is that recorded in the literature.

The molecular weights of beryllium⁵² and aluminum^{53,54} acetylacetonates have been determined by vapor-density measurements. The boiling points of metal acetylacetonates are given as follows: Be(II), 270°;¹⁵ Al(III), 314 to 315° (decomp.);⁵⁴ Th(IV), 260 to 270 (8 to 10 mm.);²⁵ Cr(III), ca. 340°;¹⁶ and Ni(II), 220 to 235° (11 mm.).⁴⁸ The acetylacetonate of vanadium(III) in small quantities distills without decomposition.⁵ Data on sublimation behavior of acetylacetonates are as follows: (CH₃)₂Au⁺, noticeable vapor pressure at room temperature;²⁷ Zn(II), partial sublimation 124°;⁴⁸ Sc(III), sublimes easily;²¹ Al(III), purified by sublimation;²³ Ga(III), 140° (10 mm.);⁵⁵ In(III), 260 to 280°;⁵⁶ (CH₃)₂Tl⁺, 170°; (C₃H₇)₂Tl⁺ and (C₄H₉)₂Tl⁺, sublime in air on heating;²⁹ Hf(IV), 82° (0.001 mm.);⁴ Th(IV), 160° (8 to 10 mm.);²¹ purified by sublimation;²⁵ Co(II), sublimes without melting;⁴⁸ Rh(III), 240° (1.0 mm.);⁸ and Ir(III), 260° (1.0 mm.).⁸

The solvents most frequently mentioned as dissolving the metal acetylacetonates are benzene, ethanol, chloroform, carbon tetrachloride, carbon disulfide, and petroleum ether. Since the solubility in petroleum ether is much less than in benzene, the former is frequently added to a saturated solution in the latter to effect crystallization. Hatch and Sutherland¹³ give data on the solubilities of sodium, potassium, magnesium, beryllium, and aluminum acetylacetonates in benzene, cyclohexane, and *n*-hexane from 0 to 100°. Other solubility measurements are as follows: copper(II) acetylacetonate, 0.00338 mol/l. in benzene at 25°;⁵⁷ zirconium acetylacetonate, 200, 34, 47, and 56 g./l. in absolute ethanol, carbon disulfide, carbon tetrachloride, and acetylacetone, respectively, at 25°.⁴ Recent data by Blanch⁵⁸ are assembled in the following table.

SOLUBILITY OF ACETYLACETONATE
 (g./100 g. solvent)*

Solvent	Temperature	Aluminum	Chromium (III)	Cobalt(III)	Iron(III)	Lanthanum	Manganese(III)	Cobalt(II)	Copper(II)	Magnesium	Manganese(II)	Palladium(II)
Benzene	20°	35.9 ₁	30 ₁	14.4	52.1	0.5 ₇	0.08 ₆	1.2 ₄
	30°	41.5 ₈	34 ₀	16.3	57.7 ₁	0.048	34.84	0.5 ₆	0.1 ₅	0.023	0.01	1.6 ₇
	40°	47.6 ₇	38.4 ₂	18.6	66.3	0.6 ₂	0.2 ₁	2.2 ₂
Toluene	20°	15.9 ₇	11.6 ₆	4.1 ₅	21.5 ₈	0.05 ₅	0.65 ₅
	30°	18.3 ₁	13.6	26.8	0.039	0.09 ₅	0.016
	40°	22.0 ₅	16.2	6.8	29.9	0.14 ₅	1.4 ₅
Acetylacetone	20°	6.6 ₆	6.2 ₁	1.9 ₅	12.7 ₇	2.0	0.2 ₁	0.8 ₇
	30°	8.1 ₃	7.1 ₅	18.1 ₄	0.2 ₇	1.2 ₄
	40°	10.3 ₉	7.6 ₁	2.9 ₁	17.7 ₅	0.054	2.3	0.4 ₂	0.02	1.5 ₆
Methylcyclohexane	30°	0.23 ₁	0.062	0.27 ₅	0.05 ₅
	20°	0.09 ₁	0.04	0.02 ₅	0.11	0.06 ₅	0.009 ₅	0.01 ₅
	30°	0.1 ₃	0.05 ₃	0.03 ₁	0.1 ₅	0.019	0.1 ₆	0.02 ₅	0.01	<0.01	0.02 ₉
m-Xylene	40°	0.2 ₃	0.09 ₁	0.04 ₆	0.21	0.1 ₆	0.02 ₁	0.05 ₅
	30°	5.0 ₃	1.9 ₆	0.1 ₄	0.6 ₆
	30°	5.2 ₁	1.9 ₆	0.1 ₄	0.5 ₅
Phenylcyclohexane	30°	1.34	0.7 ₂

* J. E. Blanch, master's dissertation, The Pennsylvania State University, 1956.

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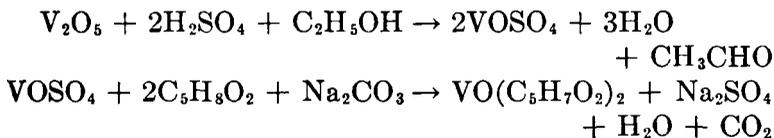
30. VANADIUM(IV) OXY(ACETYLACETONATE)

[Bis(2,4-pentanediono)oxovanadium(IV)]

Vanadium(IV) oxy(acetylacetonate) has been prepared by direct reaction of acetylacetonone (2,4-pentanedione) with either hydrous vanadium(IV) oxide or an aqueous solution of an oxovanadium(IV) salt.¹⁻³ Procedure A is an adaptation of this approach. The facts that acetylacetonone can reduce vanadium(V) oxide to vanadium(IV) oxide, react as an acid^{4,5} with the latter to give the desired product, and behave as a solvent for that product are combined in procedure B to give a synthesis based directly upon readily available starting materials.

Procedure A

Preparation from Vanadium(V) Oxide through Prior Reduction to Oxovanadium(IV) Ion



SUBMITTED BY RICHARD A. ROWE* AND MARK M. JONES*
CHECKED BY PETER BLOCK†

To 20 g. of pure vanadium(V) oxide (0.11 mol) in a 1-l. beaker are added 50 ml. of distilled water, 35 ml. of 96% (by weight) sulfuric acid, and 100 ml. of ethanol. The mixture is heated to boiling on a hot plate or steam bath and stirred. As the reaction proceeds, the initial slurry of vanadium(V) oxide darkens, becomes light green, and finally turns dark blue. The solution of vanadium(V) oxide and its reduction to vanadium(IV) are complete in 30 minutes. The solution is filtered and the filtrate returned to the 1-l. beaker. Then 50 ml. of freshly distilled acetylacetone (ca. 0.49 mol) is added, and the solution is neutralized by adding a solution of 80 g. of anhydrous sodium carbonate dissolved in 500 ml. of distilled water. The sodium carbonate solution is added slowly with continuous stirring to avoid excessive frothing.‡ The precipitated product is removed by filtration on a Büchner funnel and dried by drawing air through the filter cake. The yield of crude vanadium(IV) oxy(acetylacetonate) is 48 to 53 g. [75 to 83%, based upon vanadium(V) oxide used]. The product is recrystallized from chloroform.

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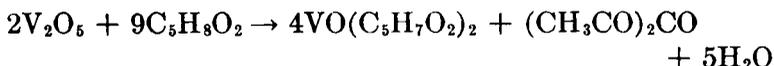
† The Pennsylvania State University, University Park, Pa.

‡ The reaction is conveniently followed with a pH meter, precipitation beginning at pH 3.5 and being complete at pH 5.5. At the end point, addition of more sodium carbonate solution causes no more frothing.

Anal. Calcd. for $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$: C, 45.28; H, 5.28; V, 19.25.
Found: C, 45.1; H, 5.37; V, 19.2.*

Procedure B

Direct Preparation from Vanadium(V) Oxide



SUBMITTED BY BURL E. BRYANT† AND W. CONARD FERNELIUS†
CHECKED BY DARYLE H. BUSCH,‡ R. CARL STOUFER,‡ AND WILMER
STRATTON‡

Five grams of technical vanadium(V) oxide (ca. 0.03 mol)§ is placed in a 200-ml. round-bottomed flask which is attached to a reflux condenser through a ground-glass joint. One hundred milliliters of commercial acetylacetone (ca. 0.98 mol)|| is added, and the mixture is refluxed gently for 24 hours. The suspension is filtered while hot,¶ and the filtrate is cooled. About 5 g. of product separates as tiny blue crystals. The remaining acetylacetone is removed by evaporation in a stream of air. The solid product is washed with acetone and ethyl ether and dried at 110°. The yield is 10 g. (68%). *Anal.* Calcd. for $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$: C, 45.28; H, 5.28; V, 19.25. Found: C, 45.09;** H, 5.33;**

* Vanadium is determined by destroying the organic material with sulfuric acid and igniting to vanadium(V) oxide.⁶

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‡ The Ohio State University, Columbus, Ohio.

§ The reaction apparently proceeds without difficulty with any quantity of vanadium(V) oxide if the specified ratio of reactants is maintained. Larger ratios of vanadium(V) oxide give large crystals or crystal aggregates of product in the reaction flask because the solubility of the product is exceeded. Vanadium(V) oxide prepared by decomposition of pure ammonium metavanadate at 250° gives higher yields of product but no increase in its purity.

|| If the material is colored, it should be distilled before being used.

¶ Resinous material may form and clog the filter. The addition of a small quantity of acetone before filtration alleviates this difficulty. The nature of the organic oxidation product is indefinite and is represented in an idealized fashion in the equation as $(\text{CH}_3\text{CO})_2\text{CO}$.

** Data supplied by the checkers.

V, 19.32. Material of analytical-reagent purity is obtained by recrystallization from acetone or acetylacetone, with a recovery of 50 to 80%.

Properties

Vanadium(IV) oxy(acetylacetonate) is a blue to blue-green compound, crystallizing in the monoclinic system with refractive indexes of α , 1.520; β , 1.676; γ , 1.739.⁷ The compound was originally believed to be a 1-hydrate but is now known to be anhydrous. It forms addition compounds with pyridine, methylamine, and other amines.⁸ Vanadium(IV) oxy(acetylacetonate) decomposes at elevated temperatures and has no definite melting point. The compound is soluble in ethanol, benzene, chloroform, and acetylacetone but is only moderately soluble in acetone or ethyl ether.

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CHAPTER VIA

See also: Lithium hydroperoxide 1-hydrate, lithium peroxide, and lithium oxide, synthesis 1	Titanium(IV) sulfide, synthesis 23
Silica gel (correction), synthesis 15	Nitrogen(IV) oxide, synthesis 24
Extraction of titanium-(IV) oxide from ilmenite, synthesis 22	Uranyl chloride, synthesis 41
	Anhydrous metal chlorides, synthesis 43
	Chlorine(I) compounds, synthesis 44

31. *N*-NITROSOHYDROXYLAMINE-*N*-SULFONATES

(Dinitrososulfites)

A series of salts containing the nitrosohydroxylamine-sulfonate (dinitrososulfite) ion can be prepared by the reaction of nitrogen(II) oxide with sulfite ion in alkaline solution. The initial investigation,¹ which established the composition of the potassium salt,¹ has been extended by Weitz and Achterberg² to the synthesis of several other salts. The potassium salt is conveniently obtained by the modification of the original procedure as given here (procedure A). The somewhat less stable and more soluble sodium salt is prepared by additional modification of the same general procedure (procedure B). Salts less soluble than the sodium compound are obtained by metathetical reactions involving the latter (procedure C).

Procedure A

Potassium *N*-Nitrosohydroxylamine-*N*-sulfonate



SUBMITTED BY RONALD S. NYHOLM* AND L. RANNITT*

CHECKED BY RUSSELL S. DRAGO†

Fifty grams of pellet potassium hydroxide (ca. 0.89 mol) is dissolved in 100 ml. of distilled water in a 500-ml. filter

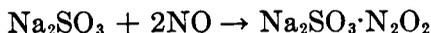
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flask. The solution is saturated with sulfur dioxide, and 50 g. of pellet potassium hydroxide is then added cautiously. Any small amount of undissolved solid is brought into solution by the addition of a small volume of water. The flask is vented to a hood and is fitted with a one-hole stopper carrying a delivery tube, the lower flared end of which reaches just below the surface of the solution. The other end of this tube is attached to a three-way stopcock. One inlet of the stopcock is connected to a source of nitrogen or hydrogen; the other is connected to a source of nitrogen(II) oxide.* A rapid stream of nitrogen or hydrogen is passed through the reaction flask for about 10 minutes to remove all air. The stopcock is adjusted to admit nitrogen(II) oxide, which is passed through the solution, with vigorous stirring or shaking, for 40 to 60 hours.† Excess nitrogen(II) oxide is then removed by flushing the flask with a rapid stream of nitrogen or hydrogen. The white solid product and the mother liquor are transferred from the flask to an open dish, and the caked product is broken up with a glass rod. The mixture is filtered on a sintered-glass funnel and the solid washed several times with 5- to 10-ml. volumes of ice-cold water. Washing is continued until the pH of the wash liquid becomes constant (ca. 8). The product is then washed with a small volume of ethanol and twice with ethyl ether. It is dried in a vacuum desiccator over solid potassium hydroxide. The yield is about 125 g. (about 60 to 65%). *Anal.* Calcd. for $K_2SO_3 \cdot N_2O_2$: K, 35.8; SO_4^- , 44.0; N, 12.8. Found: K, 35.9; SO_4^- , 43.9; N, 12.9.

* Either nitrogen(II) oxide prepared from sodium nitrite and iron(II) sulfate³ or that from commercial cylinders can be used. The gas is passed through 10 M sodium hydroxide and through a tower packed with sodium hydroxide pellets before entering the flask.

† At nitrogen(II) oxide pressures of 50 to 60 cm. of water, about 1 l. of gas is absorbed per hour at room temperature. Each liter of gas absorbed yields about 5 g. of product. If stirring is sufficiently vigorous, the reaction can be completed in 8 hours.

Procedure B**Sodium *N*-Nitrosohydroxylamine-*N*-sulfonate**

SUBMITTED BY RUSSELL S. DRAGO*

CHECKED BY HAROLD M. STATE†

A 500-ml. three-necked flask with ground-glass necks is fitted with a sealed stirrer, an inlet tube attached to a three-way stopcock and extending nearly to the bottom of the flask, and an outlet tube vented through a water bubbler to a hood. Seventy grams of anhydrous sodium sulfite (0.555 mol) and 160 ml. of 0.5 *M* sodium hydroxide (0.008 mol) are placed in the flask, and the resulting heterogeneous mixture is stirred vigorously. The flask is flushed with oxygen-free nitrogen for several minutes and then is immersed in an ice bath. Nitrogen(II) oxide, either prepared³ or obtained from a cylinder and purified by bubbling through 10 *M* sodium hydroxide, is passed through the vigorously stirred cold suspension at a rate of about 1 bubble each 10 seconds. The reaction is allowed to continue for 30 to 35 hours. Stirring and the flow of nitrogen(II) oxide are then stopped, and the system is flushed with nitrogen. The solution in the flask is cooled to -12 to -15° with an ice-salt mixture until a quantity of solid with a volume approximately one-half that originally added crystallizes. This solid (mainly sodium sulfate) is removed by filtration using a filter previously cooled with ice water. The filtrate is cooled at -12 to -15° until a quantity of solid equivalent in volume to one-fourth that initially present crystallizes. This sodium sulfate is also removed by filtration. The resulting filtrate is treated with 85 ml. of absolute ethanol and shaken vigorously. Two liquid layers are obtained, and the lighter, alcohol layer is removed by decantation. The heavier layer is

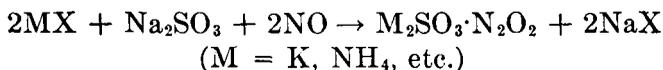
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† Allegheny College, Meadville, Pa.

treated with 50 ml. of absolute ethanol, and the mixture is shaken and stirred until a white solid crystallizes.* The mother liquid is removed by decantation,† and the solid is washed successively with absolute ethanol, acetone, and ethyl ether. The product is dried over solid potassium hydroxide in a vacuum desiccator. The yield is about 28 g. (about 27%). *Anal.* Calcd. for $\text{Na}_2\text{SO}_3 \cdot \text{N}_2\text{O}_2$: Na, 24.73; N, 15.01. Found:‡ Na, 24.61; N, 14.38.

Procedure C

N-Nitrosohydroxylamine-*N*-sulfonates by Metathesis



SUBMITTED BY RUSSELL S. DRAGO§

CHECKED BY HAROLD M. STATE||

Nitrosohydroxylaminesulfonates which are less soluble than the sodium salt are obtained by the reaction of sodium sulfite with nitrogen(II) oxide in alkaline medium in the presence of a salt of the desired cation. If the hydroxide of that cation is a strong base, it is used directly. If the hydroxide is a weak base, sodium hydroxide is added. Syntheses of the potassium and ammonium compounds are typical.

Potassium Salt. A suspension of 40 g. of potassium chloride (0.537 mol) and 30 g. of sodium sulfite (0.238 mol) in 100 ml. of 0.5 *M* potassium hydroxide (0.05 mol) is treated as in procedure B. As the reaction proceeds, the original solid dissolves, and potassium nitrosohydroxylaminesulfonate precipitates. The solid is removed, washed, and dried as indicated in procedure A. The yield is 21.3 g. (41%, based on the sodium sulfite used). *Anal.* Calcd. for $\text{K}_2\text{SO}_3 \cdot \text{N}_2\text{O}_2$: K, 35.8; N, 12.8. Found: K, 35.7; N, 12.2.

* If no solid is obtained, the alcohol layer is decanted, and another 50 ml. of absolute ethanol is added with shaking.

† The solid should be separated as soon as crystallization is complete.

‡ Sodium is determined by weighing as sodium sulfate. Nitrogen is determined by the Dumas method.

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Ammonium Salt. A solution of 50 g. of ammonium chloride (0.935 mol), 30 g. of anhydrous sodium sulfite (0.238 mol), and 15 ml. of 15 *M* aqueous ammonia in 100 ml. of 0.5 *M* sodium hydroxide (0.05 mol) is treated as in procedure B. The product is removed and purified as in procedure A. The yield is 21.8 g. (52%, based on the sodium sulfite used). *Anal.* Calcd. for $(\text{NH}_4)_2\text{SO}_3 \cdot \text{N}_2\text{O}_2$: N (total), 31.82. Found: N (total), 31.80.

Properties

Sodium, potassium, and ammonium nitrosohydroxylaminesulfonates are white, diamagnetic, crystalline compounds. The potassium salt is soluble in cold water to the extent of 8 to 10 g./100 ml. The ammonium salt is comparable, but the sodium compound is very soluble. In aqueous solution, decomposition to sulfate and nitrogen(I) oxide occurs slowly in the cold and rapidly upon heating. The same decomposition takes place rapidly and quantitatively in acidic solution. The compounds are comparatively stable when kept over potassium hydroxide in a desiccator. Compounds containing complex anions of the type $[\text{M}^{\text{II}}(\text{SO}_3 \cdot \text{N}_2\text{O}_2)_3]^{4-}$ ($\text{M}^{\text{II}} = \text{Zn}, \text{Mn}, \text{Co}$) have been prepared. These compounds have stabilities comparable to the simple salts. Reducing agents convert nitrosohydroxylaminesulfonates to hydrazine derivatives.

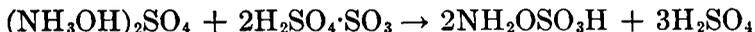
X-ray diffraction data,⁴⁻⁶ molecular-orbital considerations,⁷ and the fact that the potassium and thallium(I) salts are obtained by the reaction of the corresponding hydroxylaminemonosulfonates with alkyl nitrites⁸ are all in agreement with the suggestion⁹ that these compounds are salts of *N*-nitrosohydroxylamine-*N*-sulfonic acid, $\text{HON}(\text{NO})\text{SO}_3\text{H}$.

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32. HYDROXYLAMINE-O-SULFONIC ACID



SUBMITTED BY HAROLD J. MATSUGUMA* AND LUDWIG F. AUDRIETH*
CHECKED BY H. L. WEHRMEISTER†

Hydroxylamine-*O*-sulfonic acid, $\text{NH}_2\text{OSO}_3\text{H}$, has been prepared by heating a mixture of a hydroxylammonium salt with an excess of chlorosulfonic acid for several hours at 100° ,¹ by allowing bis(hydroxylammonium) sulfate to react with fuming sulfuric acid at room temperature,^{2,4} and by bubbling gaseous hydrogen azide through fuming sulfuric acid maintained at 60 to 80° .³ The second method is the most convenient and gives excellent yields of product of high purity.

Procedure

Two hundred twenty-five grams of 30% fuming sulfuric acid (oleum) is placed in a clean, dry 500-ml. three-necked pyrex flask. The central neck of the flask is fitted with a paddle stirrer having a ground-glass bearing.† A thermometer holder, having a vent connected to a drying tower filled with calcium chloride, is inserted into one of the necks of the flask. The thermometer is immersed in the liquid to a level slightly above the bulb. Sixty-two grams of dry, well-ground bis(hydroxylammonium) sulfate (0.37 mol) is then added slowly, with continuous stirring, to the oleum. The solid should be added in small portions to prevent it from caking on the sides of the flask. Addition of the hydroxylammonium salt is accompanied by a marked temperature rise (to temperatures as high as

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‡ Ground-glass standard-taper equipment lubricated with concentrated sulfuric acid should be used throughout.

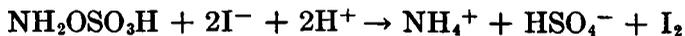
100°). After all the solid has been added, a dropping funnel is inserted into the other neck of the flask, and the reaction mixture is allowed to stand at room temperature for 1 hour with continuous stirring. The flask is then cooled to 0° in an ice-salt bath.

One hundred fifty milliliters of c.p. anhydrous ethyl ether, which has been cooled previously for 1 hour in an ice-salt bath, is then added through the dropping funnel. As the ether is added, another rise in temperature is observed, and the rate of addition must be so controlled that the temperature of the mixture does not exceed 50°.* After the resulting white suspension has cooled to about 15°, the mixture is poured into a medium-porosity sintered-glass funnel on a suction flask. The reaction flask is rinsed with 100 ml. of cold, dry ether, and the rinse solution is added to the contents of the funnel. The bulk of the liquor is removed by suction, but a sufficient quantity to keep the solid moist is allowed to remain.

The moist solid is then washed with seven 110-ml. portions of cold, anhydrous ethyl ether, care being taken that the solid is not allowed to drain free of ether between washings. Vigorous stirring of the ether with the solid, with the suction off, is necessary to remove all traces of sulfuric acid. After washing, the product is allowed to drain dry for 5 minutes and is then dried for 12 to 14 hours *in vacuo* and stored in a vacuum desiccator over concentrated sulfuric acid.

The yield varies from 83 to 85 g. (98 to 99%). The final product has a purity of 92 to 98%, as judged by its oxidation of iodide ion.

Analysis



The purity of the product may be influenced by moisture with which it has come into contact during the course of

* Continuous stirring must be maintained during this operation, preferably by hand to minimize fire hazards.

the synthesis. Therefore, it is necessary that the product be analyzed for its hydroxylamine-*O*-sulfonic acid content.

Samples (0.1 to 0.2 g.) are weighed into small thin-walled glass ampoules. The ampoules may be stoppered with small corks during weighing, but the stoppers must be removed before solution is effected. Each analytical sample is dissolved in a solution prepared by adding 2 g. of potassium iodide and 0.5 g. of sodium hydrogen carbonate to 150 ml. of water and 10 ml. of 9 *N* sulfuric acid in a glass-stoppered 500-ml. Erlenmeyer flask. The solution is allowed to stand for at least 1 hour and 40 minutes, after which the liberated iodine is titrated with standard sodium thiosulfate solution using a starch indicator. The equivalent weight of hydroxylamine-*O*-sulfonic acid is 56.55 g./g.-equiv.

Properties

Hydroxylamine-*O*-sulfonic acid is a white, hygroscopic, microcrystalline solid, melting with decomposition at 210 to 211°. The solid acid is stable for long periods of time if it is stored in a moisture-free atmosphere, but the compound decomposes very slowly in aqueous solutions below 25°. It is rapidly destroyed in solutions above this temperature. The decomposition is also markedly affected by pH and by the presence of traces of copper ion.⁴ Decomposition in acidic media yields hydroxylammonium and hydrogen sulfate ions. In alkaline solution the products are nitrogen, ammonia, and sulfate ions. Hydroxylamine-*O*-sulfonic acid is soluble in cold water and methanol, slightly soluble in ethanol, and insoluble in chloroform, ethyl ether, and carbon tetrachloride. It reacts with ammonia and amines to give hydrazine and substituted hydrazines, respectively.

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33. SELENIUM(IV) CHLORIDE



SUBMITTED BY HENRY G. NOWAK* AND JOHN F. SUTTLE*

CHECKED BY WILLIAM E. PARKER† AND JACOB KLEINBERG†

Selenium(IV) chloride has been prepared by direct chlorination of either elemental selenium or selenium(I) chloride (diselenium dichloride), Se_2Cl_2 .^{1,2} Elemental selenium is first converted to selenium(I) chloride, which then combines with more chlorine to give selenium(IV) chloride.

Procedure

An all-pyrex apparatus of the type shown in Fig. 12 is constructed. Bulb A, of 125 ml. capacity, has sealed to it

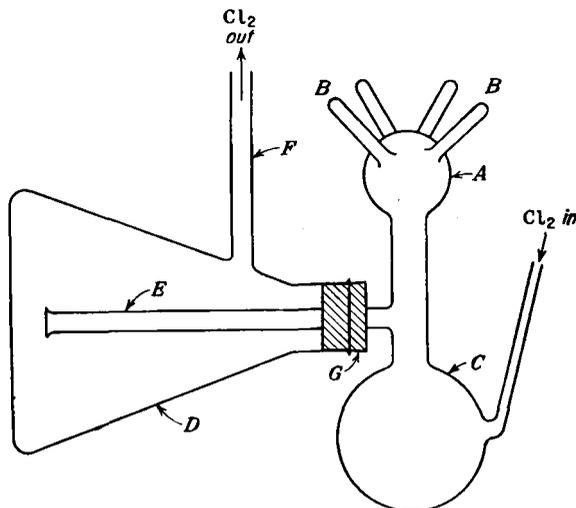


FIG. 12. Apparatus for the preparation of selenium(IV) chloride.

four ampoule tubes *B*, each 12 mm. in diameter and 12 cm. in length. This bulb is sealed as shown to a 250-ml.

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distilling flask *C*, to which a 6-mm.-i.d. chlorine inlet tube is attached in the position indicated. These bulbs vent into a 500-ml. Erlenmeyer flask *D* through a common 20-mm.-i.d. tube *E*, the end of which is 2.5 cm. from the bottom of the flask. A 20-mm. side arm sealed to the flask vents to a hood at *F*. The stopper *G* is rubber.

The apparatus is dried thoroughly, and 5 g. of powdered selenium (0.063 mol) is introduced through *E* into flask *C* by means of a long-stemmed funnel. Flask *D* is attached as indicated, and a slow current of chlorine gas, dried by passage through 18 *M* sulfuric acid, is introduced.* An immediate reaction, evolving sufficient heat to liquefy the contents of *C*, takes place. The flask is then heated intermittently† with a microburner to maintain its contents in the liquid state while the flow of chlorine is continued. When the contents of flask *C* become yellow, the reaction is complete, and the chlorine addition is stopped. The exhaust is clamped off at *F*, and the entire apparatus is inverted. The selenium(IV) chloride produced is transferred into the ampoules *B* by gentle tapping, any product sticking to the walls of the flask being removed by gentle heating with the burner. The ampoules, in which an atmosphere of chlorine is maintained, are then sealed off. The yield is quantitative.

Analysis

A weighed ampoule is broken in a closed flask containing aqueous sodium hydroxide solution. Chlorine is determined by the Mohr method, and selenium is weighed as the metal after reducing an aliquot with hydroxylammo-

* To minimize entrainment of sublimed selenium(IV) chloride, a flow rate not in excess of 1 or 2 bubbles of chlorine every 2 seconds through a 6-mm. orifice in the exhaust line is maintained.

† Continuous heating with the microburner causes loss of about 5% of the product by sublimation. Heat is best applied until the sublimation cloud approaches the side arm *E* and then stopped until the cloud has fallen back into the flask *C*.

nium chloride and sodium dithionite. Results for chlorine are high because of the chlorine atmosphere in the ampoule. *Anal.* Calcd. for SeCl_4 : Se, 35.76; Cl, 64.24. Found: Se, 35.71, 35.60, 35.49; Cl, 64.65, 64.69, 64.69.

Properties^{1,2}

Selenium(IV) chloride is a bright yellow, crystalline solid which sublimates at 196° . The solid contains $[\text{SeCl}_3]^+$ and Cl^- groups.³ In the vapor state, it is completely dissociated into selenium(II) chloride and chlorine, the vapor density being half that for selenium(IV) chloride, and the vapor pressure of the solid being depressed in the presence of excess chlorine.² The heat of formation of the solid is 46.12 kcal./mol at 18° . Selenium(IV) chloride hydrolyzes readily in moist air but is stable indefinitely in an atmosphere of dry chlorine. With anhydrous aluminum chloride it forms an addition compound which has the structure $[\text{SeCl}_3]^+[\text{AlCl}_4]^-$.⁴

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CHAPTER VIB

See also: Preparation of metal derivatives of 1,3-diketones, synthesis 29
Anhydrous metal chlorides, synthesis 43

34. CHROMIUM(III) IODIDE



SUBMITTED BY N. W. GREGORY* AND LYMAN L. HANDY*
CHECKED BY S. YOUNG TYREE, JR. †

Pure chromium(III) iodide can be prepared by the direct reaction of powdered chromium metal with iodine.¹ The procedure given here can be used conveniently to prepare quantities up to 25 g.

Procedure

A reaction vessel is constructed of 28-mm.-o.d. pyrex tubing as shown in Fig. 13. This is attached through a

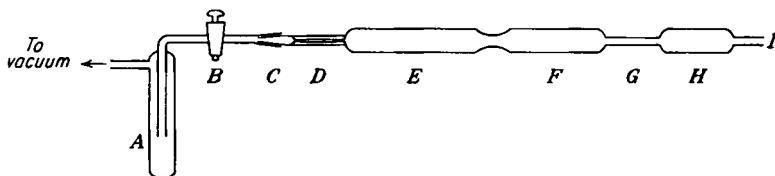


Fig. 13. Apparatus for the preparation of chromium(III) iodide.

capillary *D* and a trap *A* to a high-vacuum pump, with a standard-taper ground-glass joint at *C* and a stopcock at *B*. Three grams of powdered chromium metal (0.058 mol) of at least 98% purity is introduced into chamber *E* by means of a long-stemmed funnel inserted at *I*. Thirty grams of iodine (0.12 mol) is similarly introduced into chamber *H*. The opening at *I* is sealed off, and the apparatus is evacuated (to ca. 10^{-5} mm.) for 10 minutes,

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with intermittent flaming.* The iodine is then sublimed into chamber *F* by cooling this vessel with Dry Ice and warming the iodine reservoir, stopcock *B* being opened intermittently during this sublimation. The reaction vessel is sealed off *in vacuo* at *G* and finally at *D*. Vessel *E* is placed in one tube furnace and vessel *F* in a second tube furnace. Vessel *E* is heated to 475° and vessel *F* to 225° (vapor pressure of iodine ca. 3 atm.), and these temperatures are maintained for 24 hours.

The tube is cooled, and excess iodine is removed from chamber *E* by heating at 100° and maintaining chamber *F* at room temperature.† The tube is cracked at the center and opened in a dry box. The product is transferred to a pyrex tube equipped with a standard-taper ground-glass joint and a stopcock, and the tube is evacuated to remove any remaining iodine. The yield is essentially quantitative. Further purification can be effected by transferring the product to a quartz tube, heating *in vacuo* at 500° for several hours, subliming the resulting chromium(II) iodide *in vacuo* at 700°, and reiodinating to chromium(III) iodide by the technique outlined above.

Analysis

Iodine is determined by igniting a sample in air with the full flame of a Bunsen burner and comparing the weight of the chromium(III) oxide produced with the initial weight of the sample. Chromium is determined in the usual manner by fusing the oxide with sodium peroxide and measuring the quantity of chromate ion produced. *Anal.* Calcd. for CrI₃: Cr, 12.02; I, 87.98. Found: Cr, 12.03, 11.73; I, 85.47, 87.65.

Properties

Chromium(III) iodide is a black, crystalline compound, isomorphous with chromium(III) chloride.² When pure,

* Sufficient iodine is present to compensate for losses during this procedure.

† Traces of red or white materials are due to impurities in the chromium used.

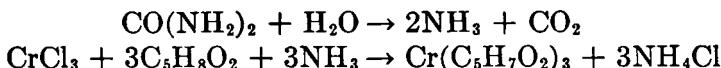
it does not dissolve readily in water, but if chromium(II) iodide is present, solution is rapid. Chromium(III) iodide is stable in contact with oxygen or moisture at 25°. At elevated temperatures it reacts quantitatively with oxygen, liberating iodine. At high temperatures *in vacuo* or in an inert atmosphere it decomposes to chromium(II) iodide and iodine. The equilibrium pressure of iodine is 7 mm. at 500° and 1 atm. at ca. 670°.³ The heat of formation at 25° is 47.8 kcal./mol.⁴

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35. CHROMIUM(III) ACETYLACETONATE

[Tris(2,4-pentanediono)chromium(III)]



SUBMITTED BY W. CONARD FERNELIUS* AND JULIAN E. BLANCH*

CHECKED BY BURL E. BRYANT† AND KAZUJI TERADA,† AND BY RUSSELL S. DRAGO‡ AND JOHN K. STILLE‡

Previous preparations of chromium(III) acetylacetonate have involved the treatment of freshly precipitated hydrous chromium(III) oxide with acetylacetone.^{1,2} The preparation presented here was suggested by Cooperstein³ and involves exact pH control through the homogeneous generation of ammonia (by the hydrolysis of urea) in a solution of a chromium(III) salt and acetylacetone. The operations involved are simple and easy to perform.

Procedure

To 100 ml. of water are added 2.66 g. of chromium(III) chloride 6-hydrate (0.01 mol) and, after complete solution,

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20 g. of urea and 6 g. of acetylacetone (0.06 mol). The reaction mixture is covered with a watch glass and heated overnight on a steam bath. As the urea hydrolyzes to release ammonia, deep maroon platelike crystals form. These are removed by suction filtration and dried in air.

The crude air-dried compound is dissolved in 20 ml. of hot benzene, and 75 ml. of hot petroleum ether is added slowly. The mixture is cooled to room temperature, chilled in a mixture of ice and salt, and filtered. The crystals are air-dried. The yield is at least 2.9 g. (83%); the melting point is 216°. *Anal.* Calcd. for $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$: Cr, 14.90; C, 51.57; H, 6.06. Found: Cr, 15.06; C, 51.70; H, 6.08.*

Properties

Chromium(III) acetylacetonate is a red-violet, crystalline material ($d = 1.34$,⁴ m.p. 216°).³ It boils at ca. 340°¹ to form a green vapor² but sublimes even at 100°. Molecular-weight determinations in such solvents as amyl benzoate show that the compound is not associated.

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36. AQUOPENTAMMINE- AND ACIDOPENTAMMINECHROMIUM(III) SALTS

SUBMITTED BY M. MORI†

CHECKED BY JOHN C. BAILAR, JR.,‡ AND JOHN W. PANKEY‡

Aquopentammine- or acidopentamminechromium(III) salts have been prepared by the reaction of liquid ammonia with anhydrous chromium(III) chloride;¹ by the oxidation

* Data supplied by checkers Drago and Stille.

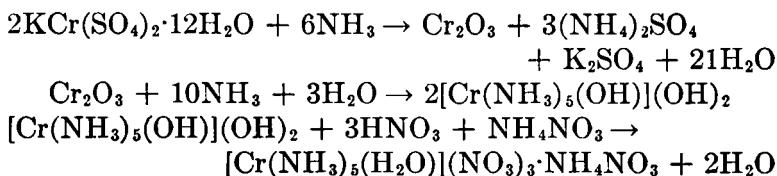
† Osaka City University, Minami-Ogi-machi, Osaka, Japan.

‡ University of Illinois, Urbana, Ill.

of chromium(II) compounds in aqueous ammonia solutions;² by the reaction of ammonium pentachloro-aquo-chromate(III) and ammonia, the latter being condensed on ammonium nitrate at 0°;³ and by the reaction of hydrous chromium(III) oxide with aqueous ammonia in the presence of large quantities of ammonium salts.⁴ The last of these methods is the basis for the procedure given here for the preparation of aquopentamminechromium(III) ammonium nitrate. This fairly stable compound is readily changed into other pentamminechromium(III) salts.

Procedure

A. AQUOPENTAMMINECHROMIUM(III) AMMONIUM NITRATE

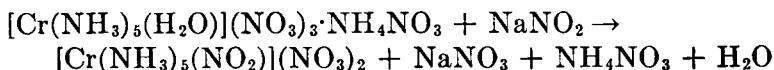


One hundred grams of potassium chromium(III) sulfate 12-hydrate (0.2 mol), pulverized to pass a 60-mesh sieve,* is mixed in a flask with 250 ml. of 15 *M* aqueous ammonia. Then 250 g. of ammonium nitrate (3.125 mols) is added, and the flask is loosely stoppered with a cork carrying a thermometer. The mixture is warmed to 55 to 60° and maintained at this temperature for 1 hour with occasional shaking. The mixture is then cooled to below 20°, and a vigorous current of air is passed through it for 30 minutes. The solution is poured slowly into a mixture of 100 g. of cracked ice and 250 ml. of nitric acid (sp. gr. 1.38), the temperature being maintained below 30° by means of an ice bath. The red suspension is kept in the ice bath for 1 hour, with occasional stirring, to complete crystallization. The resulting orange crystals are collected on a Büchner

* Clogging of the sieve is minimized by adding a small quantity of the coarsely powdered salt to the finely powdered material and shaking.

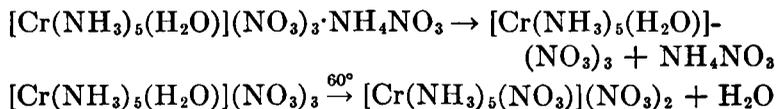
funnel and dissolved in 200 ml. of water. The suspension is filtered, and the filtrate is treated with a filtered solution of 200 g. of ammonium nitrate in 200 ml. of water. The mixture is stirred and cooled with ice. The orange crystals which form are removed by filtration and washed first with 200 ml. of a filtered saturated ethanolic solution of ammonium nitrate and then with 200 ml. of a 1:1 mixture of ethanol and ethyl ether. The yield is 17 to 19 g. (20 to 25%, based upon the chromium compound used). The salt is sufficiently pure to be used for other syntheses, but it can be purified further by dissolving and recrystallizing with ammonium nitrate. *Anal.* Calcd. for $[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{NO}_3)_3 \cdot \text{NH}_4\text{NO}_3$: Cr, 12.3; NH_3 (total), 24.2; NO_3^- , 58.8. Found: Cr, 12.3; NH_3 , 24.0, 24.3; NO_3^- , 58.9.

B. NITROPENTAMMINECHROMIUM(III) NITRATE*



Four and two-tenths grams of aquopentamminechromium(III) ammonium nitrate (0.01 mol) is dissolved in 40 ml. of water containing 1 ml. of 1 *M* nitric acid. A filtered solution of 4 g. of sodium nitrite in 6 ml. of water is added, and the mixture is allowed to stand for several minutes. The orange crystals thus formed are removed by filtration and washed with a 1:1 solution of 95% ethanol and water. The yield is 2.4 g. (88%). *Anal.* Calcd. for $[\text{Cr}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$: Cr, 16.9; NH_3 , 27.7; N as NO_2^- and NO_3^- , 13.7. Found: Cr, 17.1; NH_3 , 27.2; N as NO_2^- and NO_3^- , 13.8.

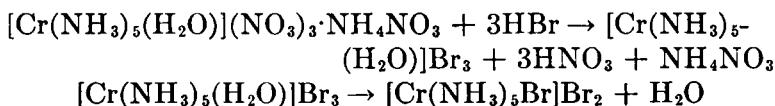
C. NITRATOPENTAMMINECHROMIUM(III) NITRATE



* Some evidence that the cation contains the nitrito group rather than the nitro group has been offered.⁷

Four and two-tenths grams of aquopentamminechromium(III) ammonium nitrate (0.01 mol) is dissolved in 40 ml. of water, and 20 ml. of nitric acid (sp. gr. 1.38) is added. The mixture is cooled in an ice bath, and then 20 ml. of 95% ethanol is added. After several minutes, the orange leaflets of aquopentamminechromium(III) nitrate thus formed are collected on a filter and washed with 95% ethanol. The yield is 2.8 g. (82%). This compound is heated in an oven at 60° for 8 hours to give the flesh-colored nitratopentammine salt. The conversion is quantitative. *Anal.* Calcd. for $[\text{Cr}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)_2$: Cr, 16.3; NH_3 , 26.3; NO_3^- , 57.6. Found: Cr, 16.3; NH_3 , 25.9; NO_3^- , 57.2.

D. BROMOPENTAMMINECHROMIUM(III) BROMIDE



Four and two-tenths grams of aquopentamminechromium(III) ammonium nitrate (0.01 mol) is dissolved in 8 ml. of water containing 2 ml. of 15 *M* aqueous ammonia. Ten milliliters of 48% hydrobromic acid and 10 ml. of 95% ethanol are added, and the mixture is cooled to 0°. The precipitate is collected on a filter, washed with 95% ethanol, and dissolved in 20 ml. of water. The resulting solution is filtered, treated with 20 ml. of 48% hydrobromic acid, and cooled to 0°. The crystallized aquopentamminechromium(III) bromide is removed by filtration and washed with 95% ethanol. The yield is 3.3 g. (83%). *Anal.* Calcd. for $[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Br}_3$: Cr, 13.2; NH_3 , 21.6; Br, 60.7. Found: Cr, 13.5; NH_3 , 21.8; Br, 60.6.

These crystals are dissolved in 20 ml. of water, and 5 ml. of 48% hydrobromic acid is added. The mixture is digested on a steam bath for 30 minutes, while three 5-ml. portions of 48% hydrobromic acid are added at intervals of several minutes. The mixture is cooled to room temperature and filtered. The precipitate of bromopentam-

minechromium(III) bromide is washed with 95% ethanol and air-dried. The yield is 2.9 g. (76%, based on the double nitrate). *Anal.* Calcd. for $[\text{Cr}(\text{NH}_3)_5\text{Br}]\text{Br}_2$: Cr, 13.8; NH_3 , 22.6; Br, 63.6. Found: Cr, 13.8; NH_3 , 22.4; Br, 62.4.

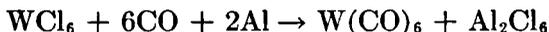
Properties

The color and solubilities of these chromium(III) amines are very similar to those of the corresponding cobalt(III) complexes.⁵ The chlorides, bromides, nitrates, and perchlorates in the acidopentamminechromium(III) series are not very soluble in water, whereas the analogous aquopentamminechromium(III) salts are soluble. In aqueous solutions, these chromium(III) amines are much more readily decomposed than the corresponding cobalt(III) amines. Decomposition may be perceptible within a few minutes. The absorption spectra of aqueous solutions of some acidopentamminechromium(III) salts have been studied.^{6,7}

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37. TUNGSTEN HEXACARBONYL



SUBMITTED BY DALLAS T. HURD*

CHECKED BY EUGENE O. BRIMM†

For many years, the only available procedure for preparing the hexacarbonyls of chromium, molybdenum, and

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tungsten involved reduction of a metal chloride in the presence of carbon monoxide and in an ethyl ether-benzene medium by the slow and steady addition of an aryl Grignard reagent.¹ The chromium and tungsten compounds were obtained in yields of 14 and 17 to 23%, respectively, by this technique.¹ A modification of this procedure gives higher yields of the chromium compound under high carbon monoxide pressure.^{2,3} However, tungsten hexacarbonyl has been obtained in yields up to 70% by reducing tungsten(VI) chloride with zinc dust in the presence of ethyl ether and under carbon monoxide pressures of 100 to 120 atm.^{4,5} Further improvements in yield are effected by use of aluminum as outlined in the following procedure.

Procedure

The apparatus consists of an Aminco Micro Series* reaction vessel of 300 ml. capacity, † a heating jacket, a rocking mechanism, and a hydraulic booster pump to give increased gas pressure. ‡ The reaction vessel is connected through a combined inlet and exit valve and high-pressure tubing to a source of carbon monoxide under pressure and to a vent line leading into a good hood. A pressure gage is included in the inlet system. Ten grams of tungsten(VI) chloride (0.025 mol)⁶ is placed in a thin-walled fragile ampoule of about 2.5 cm. diameter blown on the end of a 15-cm. length of 10-mm. pyrex tubing. The neck of the ampoule is drawn out to ca. 1.6 mm. diameter at a point 2 to 5 cm. above the bulb and cut off but not sealed. A steel ball of 2.0 to 2.5 cm. diameter is placed in the pressure vessel. Then 10 g. of 40- to 60-mesh aluminum (0.37 mol) or, better, 20 g. of 60-mesh Devarda's alloy, and 100 ml. of anhydrous ethyl ether are poured into the vessel, and the ampoule of tungsten(VI) chloride is inserted gently. The

* American Instrument Co., Superpressure Division, Silver Spring, Md. The gas inlet tube should be shortened to 1 in.

† The checker emphasizes that operation with apparatus of greater capacity than 300 ml. is *dangerous*.

‡ Other pressure reactors can be used if they meet safety requirements.

reaction vessel is closed carefully and placed gently in the heating and shaking mechanism. The valve and tubing systems are attached.

Carbon monoxide is admitted slowly and the pressure boosted to ca. 1600 p.s.i.* The vessel is allowed to stand connected to the gas line for 10 minutes, and the valve is then closed. The shaking mechanism is adjusted for widest possible oscillation to allow the steel ball to roll back and forth to shatter the ampoule and mix the reactants. The vessel is heated to 100° and maintained at this temperature for 4 to 6 hours.† The vessel is allowed to cool, and then with the valve at the top the contained gas is bled off through the vent line. The pressure vessel is opened in a hood, and its contents are transferred into a 1-l. distilling flask containing ca. 500 ml. of water. The ether is distilled off at low temperature. When the ether has been removed, the receiver is changed and the water in the flask boiled. The tungsten hexacarbonyl is carried over into the receiver with the steam.‡ Water is removed on a Büchner funnel, and the product is purified by redistillation from 3 to 5% sodium hydroxide solution, by vacuum sublimation at 60 to 70°, or by crystallization from ethyl ether. The yield varies from 6 to 8 g. (68 to 90%), depending upon conditions.§

Properties

Tungsten hexacarbonyl is a colorless, diamagnetic, crystalline solid, in which the CO groups are arranged

* If no gas booster pump is available, the full tank pressure of ca. 900 to 1000 psi may be used, but with some reduction in yield.

† The reaction can be run at room temperature, but the time required is 16 to 24 hours.

‡ It may be necessary to interrupt the distillation to remove solid product from the condenser tube.

§ Maximum yields result when the tungsten(VI) chloride does not contact the reducing agent until the ether is saturated with carbon monoxide, when mixing is as thorough as possible, and when any tungsten(VI) oxychloride is absent. If the latter is present, addition of 5 ml. of iron pentacarbonyl to the initial reaction mixture will improve the yield.

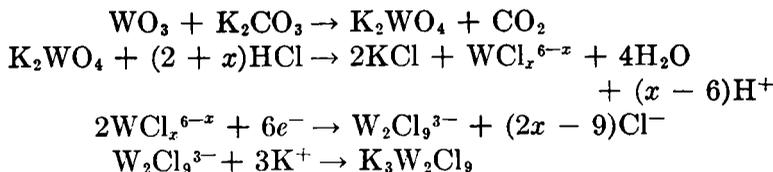
octahedrally around the tungsten atom.^{7,8} The W-C bond distance is 2.06 Å., and the C-O distance 1.13 Å. The compound sublimes *in vacuo* at 60 to 70°, decomposes slowly in sunlight, and decomposes rapidly at ca. 150° to tungsten and carbon monoxide.^{9,10} This decomposition is useful for plating tungsten on other metals and ceramic bodies.¹⁰ Unlike the carbonyls of iron, cobalt, and nickel, tungsten hexacarbonyl is almost inert chemically and nontoxic.^{11,12}

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TRIPOTASSIUM ENNEACHLORODITUNGSTATE(III) 139

38. TRIPOTASSIUM ENNEACHLORODITUNGSTATE(III)



SUBMITTED BY HANS B. JONASSEN,* A. R. TARSEY,* STANLEY CANTOR,*
AND G. F. HELFRICH*

CHECKED BY J. C. BRANTLEY† AND HARRIE M. HUMPHREYS†

Although the structure,¹ properties,² and reactions of tripotassium enneachloroditungstate(III), $\text{K}_3\text{W}_2\text{Cl}_9$, are well known, satisfactory methods for its preparation have not been developed. The preparation has been accomplished by reduction of tungsten(VI) with tin³⁻⁵ or by electrochemical methods.⁶ The electrolytic method described here has been found to be satisfactory with respect to yields and purity even though the actual time of reduction is somewhat long.

One of the difficulties of the reduction lies in the insolubility of tungsten(VI) oxide in acidic solution. Two ways of overcoming this difficulty have been suggested: (1) the reduction of the soluble $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot \text{H}_2\text{O}^{7,8}$ or (2) the use of a metastable solution of tungsten(VI) in very concentrated hydrochloric acid.⁹ The latter solution has been prepared by the rapid addition of potassium tungstate to hot concentrated hydrochloric acid. This is unsatisfactory, however, because too much insoluble yellow tungstic acid is formed. More complete solubility can be attained by adding the potassium tungstate to a very large volume of ice-cold hydrochloric acid as described below.

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Procedure

The apparatus is set up as shown in Fig. 14. The electrolysis is carried out in a 3-l. three-necked flask *A*, the center neck of which is blown large enough to allow the introduction of a porous cup *B* of 150 ml. capacity (Coors No. 700, cup size -5A). One side neck is fitted with a rubber stopper containing the rod-shaped lead cathode *C* (25 cm. long by 1 cm. diameter). The other is fitted with a two-hole rubber stopper containing a short piece of glass tubing *D* to serve as a vent to a hood and a piece of glass tubing *E* drawn to a capillary and extending to the bottom of the flask.

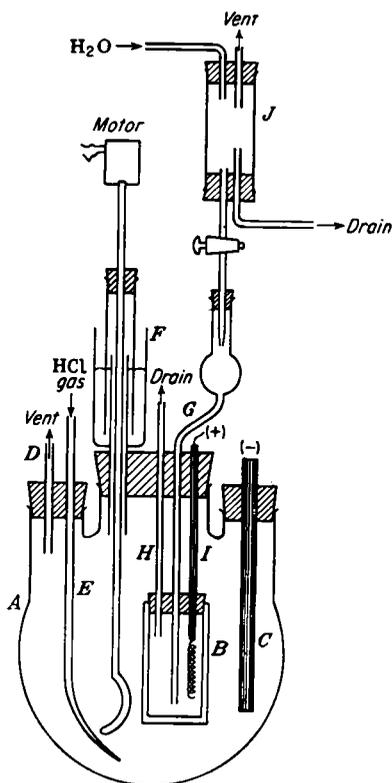


FIG. 14. Apparatus for the preparation of tripotassium enneachloroditungstate(III).

sealed. A spiral of 16-gage platinum wire serves as the anode.

To prepare the tungsten solution, 50 g. of tungsten(VI) oxide (0.22 mol) is mixed with 60 g. of potassium carbonate (0.43 mol) and 50 ml. of water. The mixture is stirred until a completely white slurry is formed. The slurry is

introduced of a porous cup *B* of 150 ml. capacity (Coors No. 700, cup size -5A). One side neck is fitted with a rubber stopper containing the rod-shaped lead cathode *C* (25 cm. long by 1 cm. diameter). The other is fitted with a two-hole rubber stopper containing a short piece of glass tubing *D* to serve as a vent to a hood and a piece of glass tubing *E* drawn to a capillary and extending to the bottom of the flask. The center neck is fitted with a mercury-seal stirring assembly *F* and three pieces of glass tubing that extend into the porous cup. Two of the tubes act as inlet *G* and overflow *H* for the constant-level water system *J* and the third *I* is the tube in which the anode is

then cooled to 0° in an ice bath. Twelve hundred milliliters of 12 *M* hydrochloric acid is introduced into the 3-l. flask, and the porous cup is filled with 2 *N* hydrochloric acid. The apparatus is assembled as shown in Fig. 14, leaving the side necks unstoppered. After the flask has been cooled in an ice bath, the cold slurry of potassium tungstate is slowly added to the ice-cold hydrochloric acid through one of the side necks. The fumes resulting from this operation are pulled off in a hood. Final assembly of the apparatus is then made. The inlet capillary tube is inserted in one neck, and the lead cathode is inserted in the other neck so that it dips into the solution to a depth of 6 to 6.5 cm.

A slow flow of anhydrous hydrogen chloride gas is now introduced through the capillary tube *E*. This hydrogen chloride addition should continue throughout the electrolysis to maintain a saturated solution. A trickle of water is allowed to drip into the porous cup. The rate of water addition determines the voltage requirement of the electrolytic cell. Thus, changes in the rate may be required during the electrolysis, but a convenient initial rate of addition is about 4 l./24 hr.

The electrolysis is now started, keeping the solution at 0°. The current is maintained at 10 amp. (for the electrode and cup arrangement specified here) or a current density of 0.35 to 0.5 amp./sq. cm.* The required current should be maintained with as low a voltage as possible.† The solution turns light blue within 10 minutes and grows progressively dark blue. After about 6 to 8 hours, the

* A high current density must be maintained throughout the electrolysis.

† In the apparatus used by the authors, the required potential was 30 to 35 volts, whereas the checkers found 12 to 14 volts sufficient with their apparatus. It should be pointed out that too high a voltage results in a fast rate of diffusion of water from the porous cup into the reaction flask. Should the current decline during the course of the preparation, the trickle of water is slowed down or stopped until a sufficiently high concentration of acid has diffused into the cup to raise the current. It is apparent that the electrolysis should be carried out with the minimum addition of water to the cup.

solution begins to turn red around the cathode, and the bath is allowed to warm to 45°, ice being added to the bath as necessary to hold the temperature at 45°. During the warm-up period special attention is paid to the gaseous hydrogen chloride flow to ensure complete saturation of the solution. After an additional 7 to 10 hours, the solution is completely wine-red, and a brown-green precipitate forms on further electrolysis. A total of 30 hours is usually sufficient to complete the electrolysis, no further change being noted after this time.

A sample of the suspension is then withdrawn and dissolved in water. A dark green aqueous solution that gives a green precipitate upon the addition of 95% ethanol is a positive test for the $W_2Cl_9^{3-}$ ion. If a red solution results from the test, the electrolysis must be continued. If the test is positive, the current is stopped and the water bath cooled to 0° for about 1 hour while the stream of gaseous hydrogen chloride is continued. After this, the precipitate can be removed by filtration. The filtered material is recrystallized by dissolving in a minimum of water, filtering, and immediately adding 95% ethanol to the filtrate to precipitate the product. Speed in these steps minimizes any oxidation of the product. The light green precipitate is finally removed by filtration, washed with ethyl ether, and kept in a desiccator over calcium chloride. The yield is about 35 g. (about 40%).

It is faster and less troublesome to remove the precipitate from the electrolysis solution by centrifugation. After the supernatant liquid of the electrolysis solution is decanted, small amounts of water are successively added to the solid to dissolve the product. The remaining solids are filtered off and the product reprecipitated from the filtrate by immediate addition of 95% ethanol.

Properties

Tripotassium enneachloroditungstate(III) is obtained as yellowish-green hexagonal crystals, the $W_2Cl_9^{3-}$ ion

consisting of two octahedra sharing the three chloride ions of one face.¹ The compound decomposes slowly in air. It is soluble in water but only very slightly soluble in 12 *M* hydrochloric acid or ethanol. Its dark green aqueous solutions (absorption maxima at 462 and 625 $m\mu$) oxidize on contact with air.

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39. URANIUM(IV) CHLORIDE



SUBMITTED BY JOHN A. HERMANN* AND JOHN F. SUTTLE*

CHECKED BY HENRY R. HOEKSTRA†

Methods of preparing uranium(IV) chloride and a complete survey of the literature pertaining to it have been given by Katz and Rabinowitch.¹ Although the compound results from the direct reaction of chlorine with the metal, its preparation from uranium oxides by reactions with various chlorinating agents is more convenient and important. Such chlorinating agents can be inorganic or organic. Inorganic reagents such as thionyl chloride, phosphorus(V) chloride, and ammonium chloride give low yields and products that are difficult to purify. Organic reagents such as carbon tetrachloride, phosgene, and hexachloropropene give better yields of more nearly pure product.

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Some of these reactions take place in the vapor phase at elevated temperatures; others are run in the liquid phase. The procedure involving hexachloropropene outlined here is typical. Although many such reactions yield some contaminating uranium(V) chloride, this contamination is minimized by differences in solubility relationships and by the thermal instability of uranium(V) chloride.

Procedure

One hundred seven and four-tenths grams of uranium(VI) oxide 2-hydrate (0.33 mol) and 470 ml. of hexachloropropene (3.33 mols) are added to a 3-l. two-necked flask equipped with a reflux condenser and placed in a hood.* The flask is heated slowly. Above 60° a highly exothermic reaction begins, and the flask is cooled, if necessary, to keep the temperature from rising above ca. 100°. After this reaction has subsided, the flask is heated continuously to reflux the trichloroacryloyl chloride (b.p. 158°) formed in the reaction. The solution is colored red by dissolved uranium(V) chloride. Refluxing is continued for 6 hours, during which time red uranium(V) chloride is gradually converted to insoluble green uranium(IV) chloride. The condenser is then rearranged and the trichloroacryloyl chloride removed by distillation. The contents of the flask are filtered by suction, using a dry fritted-glass funnel. Carbon tetrachloride, dried with calcium hydride, is continually added to the funnel to prevent exposure of the solid to moisture in the air. After hexachloropropene and other impurities are removed, the uranium(IV) chloride, wet with carbon tetrachloride, is quickly transferred to a dry Abderhalden drying pistol. Carbon tetrachloride is removed *in vacuo*, and the uranium(IV) chloride is heated *in vacuo* for 6 hours over boiling bromobenzene (156°). The green solid is transferred in a dry

* The mol ratio of hexachloropropene to uranium(VI) oxide must be at least 5:1 to assure complete reaction of the hydrated uranium(VI) oxide. The equation given is an idealized one which does not account for the formation of other products such as hydrogen chloride and phosgene.

box to a suitable container, which is then sealed. The yield is about 125 g. (about 98.7%). *Anal.* Calcd. for UCl_4 : U, 62.67; Cl, 37.33. Found: U, 62.66; Cl, 37.19.

Properties¹

Uranium(IV) chloride forms dark green octahedral crystals of tetragonal symmetry (m.p. 590°). The vapor pressure of the solid (350 to 505°) is given by the expression

$$\log p_{\text{mm.}} = \frac{-10,427}{T} + 13.2995$$

The vapor pressure of the liquid (590 to 790°) is expressed as

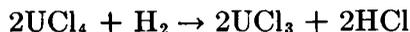
$$\log p_{\text{mm.}} = \frac{-7205}{T} + 9.65$$

The liquid boils at 792° (1 atm.). The heat of formation of the solid is 250.9 ± 0.6 kcal./mol at 0°. Uranium(IV) chloride dissolves readily in water and in polar organic solvents but is insoluble in nonpolar solvents such as hydrocarbons and ethyl ether. Its solutions have a number of characteristic and sharply defined light-absorption bands. The compound oxidizes in air and decomposes in aqueous solution. It is best preserved in a sealed container in a dry, inert atmosphere.

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40. URANIUM(III) CHLORIDE



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CHECKED BY HENRY R. HOEKSTRA†

Uranium(III) chloride has been prepared by treating uranium hydride or uranium metal with hydrogen chloride

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† Argonne National Laboratory, Lemont, Ill.

at 250 to 300° and by reducing uranium(IV) chloride with hydrogen iodide at 300 to 350°, with hydrogen at 500 to 575°, or with a metal such as zinc.¹ Detailed information on these procedures is summarized by Katz and Rabinowitch.¹ Hydrogen reduction is convenient and yields a pure product.

Procedure

A gastight system is arranged to include a hydrogen-purification train² containing Oxsorbent, Drierite, barium oxide, and sodium hydride; a tube furnace adapted to vertical operation; and a removable hydrogenator (Fig. 15). The hydrogenator consists of a 100-mm. length of 48-mm.-o.d. pyrex tubing *A* fitted with a 45/50 standard-taper ground-glass joint *B* and containing a 15-mm.-o.d. center tube *C*, to which a 35-mm.-o.d. tube *D* bearing a coarse-porosity fritted-glass disk *E* is sealed. Fitted to the upper end is a cap *F* of 48-mm.-o.d. tubing bearing a thermocouple well *G* of 10-

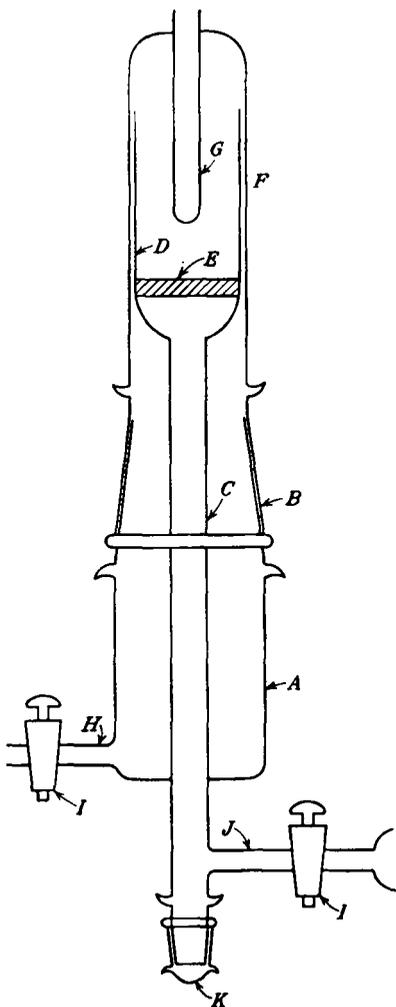


Fig. 15. Apparatus for the preparation of uranium(III) chloride.

mm.-o.d. tubing and so arranged that disk *E* is 150 mm. from the 45/50 joint. Tube *A* has a side arm *H* of 7-mm.-o.d. tubing containing a 2-mm. pressure stopcock *I* and ending

in an 18/9 socket joint. A second side-arm *J* of 7-mm. tubing with 2-mm. pressure stopcock *I* and 18/9 socket joint is attached to *C*. Tube *C* ends in a 14/35 standard-taper cap *K*.

Hydrogen is freed of oxygen and water vapor and passed through the hydrogenator for 2 hours while the latter is maintained at 500°. The hydrogenator is allowed to cool, and 40 g. of uranium(IV) chloride (0.105 mol, synthesis 39) is quickly placed on the fritted disk *E*. The hydrogenator is immediately returned to the gastight system. Hydrogen is passed through the apparatus through tube *J* for 1 hour. The temperature is then raised to 500° and maintained at this value for 6 hours. It is then raised to, and held at, 540° for 16 hours. Finally, the temperature is maintained at 580° for 1 hour, after which the furnace is allowed to cool.* When the system reaches room temperature, the hydrogen flow is stopped, the stopcocks are closed, the hydrogenator is removed, and the uranium(III) chloride is transferred in a dry box to ampoules, which can be stored in a dry atmosphere. The yield is essentially quantitative. *Anal.* Calcd. for UCl_3 : U, 69.08; Cl, 30.92. Found: U, 69.40; Cl, 30.82.

Properties¹

Uranium(III) chloride, as obtained by this procedure, is a dark purple, crystalline compound. Other procedures may yield products with varying colors. Uranium(III) chloride has a hexagonal lattice and is isomorphous with cerium(III) chloride and lanthanum bromide. The compound melts at 842° and has a density of 5.51. The vapor pressure (600 to 1000°) is given by the expression

$$\log p_{\text{mm.}} = \frac{-12,000}{T} + 10.00$$

* Initial reduction is carried out at lower temperatures to prevent liquefaction of uranium(IV) chloride. After sintering can no longer occur, a higher temperature increases the reaction rate. A sintered product may contain unreacted and occluded uranium(IV) chloride.

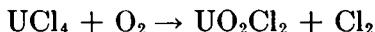
The heat of formation is 212.0 kcal./mol at 25°. Uranium(III) chloride is hygroscopic but less so than uranium(IV) chloride. It dissolves readily in water to give a purple solution, which evolves hydrogen and immediately turns green because of oxidation to uranium(IV). The compound is less soluble in polar organic solvents than uranium(IV) chloride and is insoluble in nonpolar solvents. In many of its physical and chemical properties, uranium(III) chloride resembles the lanthanon(III) chlorides.

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41. URANYL CHLORIDE

[Uranium(VI) Dioxydichloride]



SUBMITTED BY JOSEPH A. LEARY* AND JOHN F. SUTTLE*
CHECKED BY HENRY R. HOEKSTRA†

Uranyl chloride is usually prepared by a vapor-phase reaction in the absence of water. Among the procedures described¹ are reaction of chlorine with uranium(IV) oxide at 500°; reaction of carbon tetrachloride with uranium(VI) oxide at 290°; reaction of hydrogen chloride with partially hydrated uranium(VI) oxide to give the 1-hydrate, followed by removal of this water in dry hydrogen chloride at 300°; and reaction of oxygen with uranium(IV) chloride at 300 to 350°. The last reaction gives a pure product in high yield and is convenient to use.

* University of New Mexico, Albuquerque, N. Mex. Support was received from the Los Alamos Scientific Laboratory, Los Alamos, N. Mex.

† Argonne National Laboratory, Lemont, Ill.

Procedure

A gastight system of the general type described by Hummers, Tyree, and Yolles,² but containing a removable pyrex tube (20 mm. o.d.) equipped with standard-taper joints and surrounded by a tube furnace, is set up. The furnace is raised to 300 to 350°, and the system is flushed for 1 hour with dry oxygen. The reaction tube is allowed to cool and is removed. Then 9.7 g. of uranium(IV) chloride (0.025 mol, synthesis 39) is placed either directly in the tube or in a boat in the tube, and the latter is immediately returned to the system. The temperature is raised to 300 to 350° and maintained in this range for 7 hours while dry oxygen is passing over the uranium(IV) chloride. If no boat is used, the reaction tube is rotated occasionally to prevent sintering of the product. The tube is then allowed to cool to room temperature before the oxygen stream is stopped. The reaction tube is removed quickly to a dry box, and the product is transferred to a container, which is sealed. The conversion is quantitative, but adherence of the product to the reaction tube reduces the yield slightly. *Anal.* Calcd. for UO_2Cl_2 : U, 69.79; Cl, 20.82. Found: U, 69.70; Cl, 20.87.

Properties¹

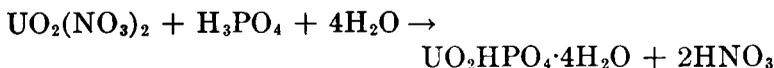
Uranyl chloride is a bright yellow substance which crystallizes in the orthorhombic system. The compound is only slightly volatile in oxygen or chlorine below 500°, and volatility is appreciable only above 775°. It decomposes *in vacuo* above 450° to give chlorine and the oxides UO_2 and U_3O_8 . Uranyl chloride is very hygroscopic and dissolves extensively in water. The compound is soluble in polar organic solvents such as acetone and the alcohols but does not dissolve in less polar solvents such as benzene. Its aqueous solutions are both thermally and photochemically unstable. A number of hydrates and addition compounds with halides and amines have been described.

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42. URANYL HYDROGEN ORTHO- PHOSPHATE 4-HYDRATE

[Uranium(VI) Hydrogen Dioxorthophosphate 4-Hydrate]



SUBMITTED BY JAMES M. SCHREYER*

CHECKED BY E. PHILIP HORWITZ† AND WARD B. SCHAAP‡

The preparation of uranyl hydrogen orthophosphate 4-hydrate has been described,^{1,2} but a detailed procedure giving a pure product has not been recorded. The directions given here represent a modification of those mentioned in the earlier reports.³

Procedure

Two hundred fifty milliliters of 1.1 *M* orthophosphoric acid is added with vigorous stirring to 250 ml. of 1 *M* uranyl nitrate or perchlorate solution. The solution is seeded with a few crystals§ of the product to promote immediate precipitation. The suspension is then stirred for 12 hours and the mother liquor removed by centrifuging or filtering. The precipitate is slurried in 250 ml. of ca. 0.01 *M* perchloric acid for 12 hours, and the suspension is filtered. The solid is then slurried twice in 125-ml. portions of acetone to remove solution and sorbed perchlorate and separated from each wash solution by filtration. The sample is dried in a vacuum desiccator, using continuous

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§ Prepared by a small-scale version of the same procedure.

suction, and is exposed to air for 12 hours. The yield is about 90 g. (about 82%).

Analysis

Uranium. A sample containing ca. 2 millimols of uranium is fumed down with sulfuric acid in a 150-ml. beaker to remove nitrate. Then 20 ml. of 18 *M* sulfuric acid and 20 ml. of 85% phosphoric acid are added, and the solution is diluted with water to 75 to 80 ml. and cooled.* This solution is passed over amalgamated zinc in a reductor at a rate of 30 ml./min. The reductor is washed successively with one 20-ml. portion of 3 *M* sulfuric acid, three 40-ml. portions of 7.5% sulfuric acid, and one 40-ml. portion of water, the washings being added to the reduced solution. The resulting light bluish-green uranium(IV) solution is treated with 30 ml. of iron(III) chloride solution (100 g. of the 6-hydrate per liter) and allowed to stand for 5 to 10 min. or until it becomes distinctly yellow. Fifteen milliliters of 85% phosphoric acid and 8 drops of diphenylaminesulfonic acid indicator are added, and the solution is titrated immediately with 0.1 *N* potassium dichromate to a sharp purple end point.

Phosphate. Because of interference by uranium in the usual magnesium ammonium orthophosphate procedure,⁵ uranium is first removed by a cation-exchange procedure. A column (2.5 by 36 cm.) of 50 to 75 cc. of Dowex-50 resin is washed with 200 ml. of 3 *N* hydrochloric acid and then 200 ml. of water at flow rates of 2 to 3 ml./min. An acidic solution of the product, containing 100 to 150 mg. of orthophosphate, is passed through the column at a rate of 1 ml./min. The column is washed with water until the washings are neutral to litmus, and phosphate is determined in the combined eluate and washings by the usual gravimetric procedure.⁵ Uranium can be eluted from the

* Precipitation of uranium(IV) orthophosphate in the reduced solution* is avoided by the high acidity.

column with 3 *N* hydrochloric acid at a flow rate of ca. 3 ml./min.

Anal. Calcd. for $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$: UO_2^{++} , 61.63; PO_4^{3-} , 21.68. Found: UO_2^{++} , 61.6, 61.9, 61.73; PO_4^{3-} , 21.6, 21.6.

Properties

Uranyl hydrogen orthophosphate 4-hydrate is a bright yellow compound, the crystals of which appear as tabular four-sided plates or truncated squares⁶ and belong to the tetragonal system.⁷ The calculated density is 3.41⁷ and the observed density 3.399.⁶ The compound dissolves readily in dilute acids. At 110° it is converted to the 2-hydrate.

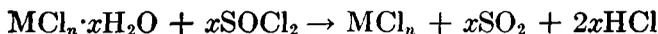
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CHAPTER VIIA

- See also: Dichloro(di-2-pyridyl-amine)copper(II) and bis(di-2-pyridyl-amine)copper(II) chloride, synthesis 4
- Bis(ethylenediamine)-copper(II) diiodocuprate(I), synthesis 5
- Disilver fluoride, synthesis 6
- Beryllium chloride, synthesis 7
- Boron halide-amine coordination compounds, synthesis 8
- Extraction of titanium(IV) oxide from ilmenite, synthesis 22
- 1,1,1-Trisubstituted hydrazonium chlorides, synthesis 25
- Phosphorus(III) fluoride, synthesis 26
- Selenium(IV) chloride, synthesis 33
- Chromium(III) iodide, synthesis 34
- Aquopentamine- and acidopentaminechromium(III) salts, synthesis 36
- Tripotassium enneachloroditungstate(III), synthesis 38
- Uranium(IV) chloride, synthesis 39
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- Dichloro(di-2-pyridylamine)-cobalt(II), synthesis 50
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- Sodium and potassium nickel(IV) paraperiodates, synthesis 58
- Ammonium hexabromoosmate(IV), synthesis 59
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- Platinum(II) chloride, synthesis 61
- Tetrachloro(diethylene)diplatinum(II), synthesis 62

43. ANHYDROUS METAL CHLORIDES



SUBMITTED BY ALFRED R. PRAY*

CHECKED BY RICHARD F. HEITMILLER,† STANLEY STRYCKER,† VICTOR D. AFTANDILIAN,† T. MUNIYAPPAN,† D. CHOUDHURY,† AND MILTON TAMRES†

General methods for the preparation of anhydrous chlorides have been described by Tyree.¹ Of the methods

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listed for dehydrating metal chlorides, that involving treatment with thionyl chloride² has the advantages of convenience and simplicity and requires no special apparatus. This method is generally useful regardless of the periodic group in which the metal appears.

Procedure

Twenty grams of the finely ground metal chloride hydrate is put into a round-bottomed flask, and 50 ml. of freshly distilled* thionyl chloride (ca. 0.64 mol) is added at room temperature. Evolution of sulfur dioxide and hydrogen chloride begins at once. After bubbling stops, the flask is equipped with a reflux condenser, and the slurry is refluxed for 1 to 2 hours. The condenser is then arranged for distillation, and the excess thionyl chloride is removed *in vacuo* using a dry nitrogen bleed. The flask containing the product is transferred immediately to a vacuum desiccator containing potassium hydroxide and stored for at least 12 hours to remove remaining thionyl chloride.

Chloride†	Starting material	Analyses			
		Metal		Chlorine	
		Calcd.	Found	Calcd.	Found
LiCl	LiCl + 20% H ₂ O	16.37	16.3	83.63	83.5
CuCl ₂	CuCl ₂ ·2H ₂ O	47.27	47.3	52.73	52.7
ZnCl ₂	ZnCl ₂ + 10% H ₂ O	47.97	47.5	52.03	51.5
CdCl ₂	CdCl ₂ ·2½H ₂ O	61.32	61.3	38.68	38.7
ThCl ₄ ‡	ThCl ₄ ·8H ₂ O	62.05	62.13	37.92	
CrCl ₃	CrCl ₃ ·6H ₂ O	32.84	31.5	67.16	64.5
FeCl ₃	FeCl ₃ ·6H ₂ O	34.43	34.3	65.57	65.3
CoCl ₂	CoCl ₂ ·6H ₂ O	45.39	45.3	54.61	54.4
NiCl ₂	NiCl ₂ ·6H ₂ O	45.29	44.3	54.71	53.5

† The method has also been applied to magnesium and neodymium chlorides by the checkers, but the products were not analyzed.

‡ Data obtained by checker T. Muniyappan (master's dissertation, University of Illinois, 1955).

* The reagent must be freshly distilled.

The product is then transferred in a dry box to a suitable container which can be sealed. Except for mechanical losses, the yield is quantitative. Results for a series of typical chlorides are as shown in the table.

Properties

Lithium chloride is a colorless, crystalline, hygroscopic, and deliquescent salt; its melting point is 613° and its boiling point is 1360° . Its specific gravity is 2.068. The compound is somewhat hydrolyzed in aqueous solution and is soluble in a number of organic liquids.

Copper(II) chloride is a brown solid, melting at 498° with some decomposition to copper(I) chloride. The compound is hygroscopic and deliquescent. It dissolves in water and the alcohols but is insoluble in many organic liquids.

Zinc chloride is a white, crystalline, deliquescent solid, melting point ca. 290° and boiling point 730° . It dissolves readily in water to give solutions which are extensively hydrolyzed. It is also soluble in alcohols, in acetone, and in ethyl ether.

Cadmium chloride is a hygroscopic, translucent, white, crystalline solid, melting at 568° and boiling at 960° . It is somewhat less soluble than zinc chloride in water and the alcohols and is insoluble in ethyl ether.

Thorium(IV) chloride is a white, hygroscopic solid, which dissolves readily in water, in the lower alcohols, and in ethylenediamine.³

The properties of chromium(III) chloride have been summarized by Heisig, Fawkes, and Hedin.⁴ The compound apparently exists in two forms. The hygroscopic, soluble form results in this synthesis. This form has a peach-blossom color.

The properties of iron(III) chloride have been described by Tarr.⁵

Cobalt(II) chloride is a blue, crystalline solid, which gives the red 6-hydrate upon exposure to moist air. The

compound melts at 724° and boils at 1049°. It dissolves readily in water, methanol, and ethanol but is sparingly soluble in most organic liquids.

Nickel(II) chloride is a yellow, crystalline, scalelike solid, which absorbs water from moist air to give the green 6-hydrate. The boiling point is 973°. The salt dissolves readily in water and the alcohols but is insoluble in acetone and the esters.

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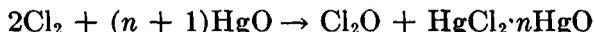
44. CHLORINE(I) COMPOUNDS

SUBMITTED BY GEORGE H. CADY*

CHECKED BY JAMES M. NAUGHTON† AND THEODORE H. DEXTER†

A. CHLORINE(I) OXIDE

(Chlorine Monoxide)



Chlorine(I) oxide was first prepared by Gay-Lussac¹ by the reaction of chlorine with dry yellow mercury(II) oxide, protected on the surface by a layer of sand. The procedure given here is one of the many reported variations.²

Procedure

Caution. Adequate safety shields and only small quantities of material should be used as precautions against explosions. Air containing mercury(II) oxide dust should not be inhaled. Contact of the hands with yellow mer-

* University of Washington, Seattle, Wash. Much of this work was completed in the research laboratory of the Columbia Chemical Division of the Pittsburgh Plate Glass Co.

† Olin Mathieson Chemical Corporation, Niagara Falls, N.Y.

cury(II) oxide should be avoided, for the compound causes the skin to crack.

A 500-g. quantity of *yellow* mercury(II) oxide (2.3 mols) is dried in an oven at 120° and mixed with an equal weight of chips* made by crushing glass tubing. This gives a porous bed of solid through which gas can pass readily. The mixture is poured into a vertical reaction vessel constructed from a 1-m. length of 35-mm.-i.d. glass tubing and provided with a glass-wool layer and a chlorine inlet at the bottom. A second layer of glass wool is placed on top of the bed of mercury(II) oxide. Care is taken to avoid tapping the tube and settling the bed. The tube is capped with a cover prepared from a ground-glass joint and provided with an outlet tube. The latter is connected through a ground-glass joint to a glass trap cooled with Dry Ice in acetone.† Streams of chlorine (ca. 5 l./hr.) and air (ca. 10 l./hr.) are dried by bubbling through 18 *M* sulfuric acid and are mixed and passed up through the reaction tube. Chlorine(I) oxide, containing some chlorine and traces of oxygen and nitrogen, is condensed in the cold trap. Under the conditions described, the yield approaches 50 g., about 92% of the chlorine passing through being converted to product. Nearly quantitative conversion of the chlorine results if the yield is limited to 25 g.

The basic mercury(II) chlorides produced are suspended in water at 15° and treated with excess sodium hydroxide solution. The yellow precipitate is washed and dried at 120°.

Properties

Chlorine(I) oxide resembles bromine in appearance. It boils at 2° and freezes at -120.6°. It is very soluble

* Maximum dimension 1 cm., with 10-mesh or smaller fines removed by screening.

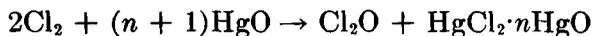
† No rubber or ordinary stopcock lubricant should contact chlorine(I) oxide. Concentrated sulfuric acid or, better, a waxy mixture of polymers of trifluorochloroethylene (supplied by M. W. Kellogg Co., Jersey City, N.J.) can be used.

in carbon tetrachloride and combines with water to form hypochlorous acid. A saturated aqueous solution at -9.4° contains 143.5 g. of chlorine(I) oxide in 100 g. of water. The compound can be caused to explode by a spark, by heating, or by contact with rubber, cork, or other form of organic matter. It can be stored for a long time at -78° , but it decomposes at a moderate rate at room temperature.

B. CHLORINE(I) OXIDE IN CARBON TETRACHLORIDE SOLUTION

A solution of chlorine(I) oxide in carbon tetrachloride is easier to obtain and safer to handle than the pure compound. The first³ of the two procedures given is better for laboratory syntheses; the second resembles an industrial method of producing chlorine(I) oxide.⁴ On a large scale, the second is the more economical and avoids the use of toxic mercury compounds. As a laboratory procedure, it has the disadvantages of being difficult to control and of converting only about half of the chlorine dissolved in the carbon tetrachloride into chlorine(I) oxide.

Procedure A

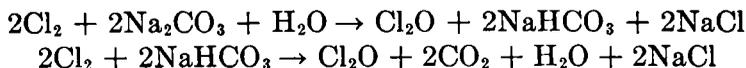


A dry 1-l. three-necked flask is equipped with a sealed stirrer, an inlet tube extending nearly to the bottom of the flask, and an exit tube leading to a hood. Four hundred fifty milliliters of dry carbon tetrachloride is placed in the flask and cooled with an ice bath. The stirrer is started, and chlorine is passed into the liquid. From time to time, a 1-ml. sample of the resulting solution is titrated iodometrically to determine its chlorine content. When a concentration of at least 50 g. of chlorine per liter is reached, the flow of chlorine is stopped. The flask is warmed to 25° , and at least 3.36 g. of dry *yellow* mercury(II) oxide per gram of chlorine (1.1 mol/mol of chlorine) is added. Stirring is continued for 45 minutes, after which interval

nearly all of the dissolved chlorine will have been consumed. The solution is separated from the solid by filtration through a coarse fluted paper or a coarse sintered-glass funnel in a hood. The solution is stable if kept cold and in the dark. The initial yield is about 97%, but losses upon filtration reduce the final yield to about 75%.

Mercury(II) oxide is recovered as outlined above. The same precautions regarding contact with the skin should be observed.

Procedure B



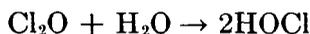
To 25 g. of dry sodium carbonate (0.24 mol),* 2.75 ml. of water is added drop by drop with stirring of the solid. The mixture is placed in a stoppered bottle and stored overnight. A solution of 53 to 80 g. of chlorine per liter in 450 ml. of carbon tetrachloride is prepared as described in procedure A. This solution is warmed to 25° and maintained at that temperature by means of a water bath. The solution is stirred vigorously with a glass rod while the prepared sodium carbonate is added. Stirring is continued for 4 minutes. The stirring rod is promptly removed, and the mixture is filtered rapidly (maximum period 1 minute) with suction, using a large coarse sintered-glass filter.† The vacuum is broken as soon as filtration is complete. The yield of chlorine(I) oxide is about 6.2 g. (about 41%)

* Commercial "light" soda ash from a freshly opened container is desirable, but a laboratory grade of anhydrous sodium carbonate can be used if it is first heated at 150 to 200° for at least 1 hour. "Light" soda ash is preferred to the "dense" material because of its small particle size. The completely dry solid reacts slowly, but an optimum reaction rate results when ca. 10% by weight of water is present.

† It is necessary to separate the solid from the liquid as soon as the maximum concentration of chlorine(I) oxide has been reached to minimize side reactions. If the separation is not made, the concentration of chlorine(I) oxide then decreases as the quantities of sodium hypochlorite and chlorate increase in the solid.

for a solution containing 25 g. of chlorine. Losses on filtration approximate 10%.

C. HYPOCHLOROUS ACID



Maximum concentrations of hypochlorous acid are obtained by treating pure liquid chlorine(I) oxide with water at 0°. Lower concentrations result from use of the gaseous oxide under reduced pressure or from use of solutions of the oxide in carbon tetrachloride. The last procedure is convenient for acid concentrations up to 5 *M*. The reaction is nearly quantitative, the equilibrium concentrations of hypochlorous acid and chlorine(I) oxide in the two phases at 0° being calculated from the data of Yost and Felt⁵ and of Secoy and Cady⁶ as

Concentration of HOCl in water, mol/l.....	1	2	3	4	5
Concentration of Cl ₂ O in carbon tetrachloride, g./l.....	0.46	1.84	4.15	7.40	11.6

The concentration of chlorine(I) oxide in carbon tetrachloride and the volume of the solution are first determined. Then the quantity of water that must be added to give a solution of hypochlorous acid of the desired concentration is calculated from the expression

$$\text{Liters of water} = \frac{2}{86.9} \times \frac{(\text{liters of CCl}_4 \text{ solution}) \times [(\text{g. of Cl}_2\text{O}/\text{l. of CCl}_4) - 0.46C^2]}{C}$$

where *C* is the molarity of the hypochlorous acid solution.

Procedure

Both the carbon tetrachloride solution of chlorine(I) oxide and the water are cooled nearly to 0°. The liquids are then added to a separatory funnel of suitable size*

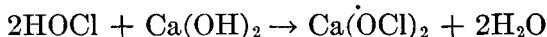
* The funnel must be thoroughly cleaned to remove all stopcock grease.

and shaken together very vigorously for 3 minutes. The carbon tetrachloride phase is withdrawn. The aqueous solution of hypochlorous acid is essentially free from chlorine, but its concentration is usually somewhat lower than that calculated because of thermal decomposition or mechanical losses.

Properties

Hypochlorous acid solutions undergo decomposition to chlorine, oxygen, and some chloric acid. The reaction rate is dependent upon hydrogen-ion concentration, reaching a maximum at pH 6.7 and a minimum at pH 13.1.⁷ The decomposition of the acid is very slow at -20° . At Dry Ice temperatures, no liquid is present, and the solid phases are ice and the compound $\text{HOCl}\cdot 2\text{H}_2\text{O}$. Hypochlorous acid solutions should be stored in the dark and at low temperatures to minimize decomposition.

D. CALCIUM HYPOCHLORITE



Pure calcium hypochlorite has not been prepared. The procedure here described gives a solid containing 90 to 94% calcium hypochlorite, the impurities present being calcium chlorate, calcium chloride, calcium carbonate, calcium hydroxide, and water.

Procedure

About 65 ml. of approximately 3 *M* hypochlorous acid is prepared as described above.* A 9.5-g. quantity of c.p. calcium hydroxide (0.13 mol) is placed in a beaker, and 23 ml. of water is added. The beaker is placed in a hood and equipped with a mechanical stirrer with a bent-glass-rod paddle. The stirrer is started, and 23 g. of finely chopped ice is added. The cold, freshly prepared hypo-

* Treatment of 450 ml. of a carbon tetrachloride solution containing 50 g./l. of chlorine with 76 g. of yellow mercury(II) oxide yields the desired volume of 3 *M* hypochlorous acid solution.

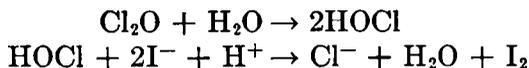
chlorous acid solution is added at once from a separatory funnel at a rate of 5 to 10 ml./min. If all the ice melts during the neutralization, more is added. As soon as all the acid solution has drained from the funnel, the remaining ice is removed from the beaker with a porcelain spoon.

The solution is then filtered through a medium-porosity sintered-glass funnel, and the solid is washed in the funnel with 5 ml. of water. The clear filtrate (with washings) is poured into an empty vacuum desiccator of at least 1 l. capacity and evaporated *in vacuo* and in the dark at room temperature.* After 6 days, the desiccator is opened, and the dry salt is removed. The yield of nearly white solid containing 90 to 94% calcium hypochlorite is 13 g. (93%, based on a pure product).

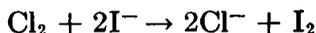
The salt, which is more stable than either chlorine(I) oxide or hypochlorous acid, is stored in a stoppered glass bottle in a refrigerator.

Analyses

A. Chlorine and Chlorine(I) Oxide in Carbon Tetrachloride.⁸ This procedure is based upon the fact that liberation of iodine by the reaction between either chlorine(I) oxide or hypochlorous acid and a solution of potassium iodide is accompanied by the consumption of hydrogen ion in the proportions shown by the equations



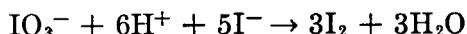
On the other hand, chlorine reacts without consuming or producing hydrogen ion, as



Procedure. About 2.5 g. of potassium iodide (0.015 mol) is dissolved in 75 ml. of water in an iodine flask. Sufficient

* An oil pump protected from water by a cold trap or a large tube containing calcium chloride and from chlorine or chlorine oxides by soda lime is satisfactory.

carefully standardized 0.1 *N* hydrochloric acid solution (ca. 15 to 25 ml.) is added to take care of the needs of the chlorine(I) oxide which is to react. A 2-ml. sample of the carbon tetrachloride solution of chlorine(I) oxide and chlorine is added below the surface of the water solution. The liberated iodine is titrated with 0.1 *N* sodium thio-sulfate until the last drop of the solution removes all of the yellow color of iodine from both liquid phases. No starch is used in the titration. To determine the quantity of hydrogen ion remaining in the solution, an excess (0.2 to 0.5 g.) of solid potassium iodate is added, and the iodine liberated according to the equation



is then titrated with the standard thiosulfate solution. Each gram-equivalent of iodine corresponds to 1 g.-equiv. of hydrogen ion present.

The sodium thiosulfate solution is standardized against a weighed sample of iodine. The hydrochloric acid solution is then standardized against the thiosulfate solution as follows. A measured volume (ca. 25 ml.) is added to a neutral solution containing excess potassium iodide in an iodine flask. About 0.2 g. of solid potassium iodate is added, and the liberated iodine is titrated with the thio-sulfate solution. The concentration of the acid is calculated as

$$N \text{ of HCl} = N \text{ of Na}_2\text{S}_2\text{O}_3 \times \frac{\text{ml. of Na}_2\text{S}_2\text{O}_3}{\text{ml. of HCl}}$$

Final calculations are made as follows:

$$\begin{aligned} \text{g. of Cl}_2/\text{l. of CCl}_4 &= 21.73[(a \times N \text{ of HCl}) \\ &\quad - (c \times N \text{ of Na}_2\text{S}_2\text{O}_3)] \\ \text{g. of Cl}_2/\text{l. of CCl}_4 &= 17.73[(b + 2c) \times N \text{ of Na}_2\text{S}_2\text{O}_3 \\ &\quad - 2a \times N \text{ of HCl}] \end{aligned}$$

where *a* represents the milliliters of standard hydrochloric acid solution, *b* represents the milliliters of standard sodium thiosulfate solution at the first end point, and *c* represents

the milliliters of standard sodium thiosulfate after addition of iodate.

B. Chlorine, Hypochlorous Acid, and Chloric Acid. The dissolved chlorine plus the small amount hydrolyzed to hypochlorous acid are reported as chlorine. The remainder (and nearly all) of the hypochlorous acid is reported as such. The method is like that given above except that an additional titration for chloric acid is included. The volume of hypochlorous acid sample used is related to the concentration of acid as follows:

ml.	50	25	10	5	2	1	0.5
<i>M</i> of HOCl	0.01-0.04	0.03-0.09	0.05-0.2	0.2-0.4	0.4-1	1-2	2-4

Procedure. The procedure outlined above is followed except that the indicated volume of hypochlorous acid solution is added in place of the carbon tetrachloride solution. The same end points are determined, but correction is made for hydrogen ion supplied by the chloric acid present to eliminate reported hypochlorous acid contents which are too low and chlorine contents which are too high. It is assumed that no iodine is liberated by chloric acid.

To determine the chloric acid content, a sample of hypochlorous acid solution of the same volume used above is added to an iodine flask containing about 0.5 g. of potassium bromide. Sufficient 12 *N* hydrochloric acid is added to give a final concentration of 15 ml. of this acid per 100 ml. of solution. This is followed by 50 ml. of standardized 0.1 *N* arsenious acid. The solution is boiled for 2 minutes and then removed from the flame. The excess arsenious acid is titrated with standardized 0.1 *N* potassium bromate, 6 to 8 drops of methyl orange solution being added as indicator. The color is bleached at the end point.

Calculations are made as follows:

$$\text{mols of HClO}_3/\text{l.} = \frac{(50 \times N \text{ of H}_3\text{AsO}_3) - (d \times N \text{ of KBrO}_3) - (b \times N \text{ of Na}_2\text{S}_2\text{O}_3)}{6 \times \text{ml. of HOCl sample}}$$

$$\begin{aligned} \text{mols of HOCl/l.} &= \\ \frac{(a \times N \text{ of HCl}) - (c \times N \text{ of Na}_2\text{S}_2\text{O}_3)}{\text{ml. of HOCl sample}} &+ \text{mols of HClO}_3/\text{l.} \\ \text{mols of Cl}_2/\text{l.} &= \\ \frac{b \times N \text{ of Na}_2\text{S}_2\text{O}_3}{2 \times \text{ml. of HOCl sample}} &- \text{mols of HOCl/l.} \end{aligned}$$

where a , b , and c have the same significances as in the previous determination, and d represents the milliliters of standard potassium bromate solution.

C. Calcium Hypochlorite. The impure calcium hypochlorite samples prepared by the procedure above are analyzed by determining the "available-chlorine" content and then calculating the calcium hypochlorite content.

Procedure. A weighed sample (close to 0.1 g.) is added to an iodine flask containing 40 ml. of a solution prepared by dissolving 2 g. of potassium iodide in dilute (not over 2 N) hydrochloric acid. The resulting solution is titrated immediately with standardized 0.1 N sodium thiosulfate until the yellow color of the iodine just vanishes. Any yellow color which may then develop on standing as a result of oxidation of iodide ion by chlorate ion is ignored.

Calculations are made as follows:

$$\begin{aligned} \% \text{ "available chlorine"} & \\ &= \frac{35.457 \times (\text{ml. of Na}_2\text{S}_2\text{O}_3) \times (N \text{ of Na}_2\text{S}_2\text{O}_3)}{10 \times \text{g. of sample}} \\ \% \text{ Ca(OCl)}_2 & \\ &= 1.008 \times \% \text{ "available chlorine"} \end{aligned}$$

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45. PURIFICATION OF "CARRIER-FREE" IODINE-131 ACTIVITY

SUBMITTED BY MILTON KAHN,* ARTHUR J. FREEDMANN,* AND C. G. SCHULTZ*

CHECKED BY JAMES E. SATTIZAHN†

The carrier-free iodine-131 solutions available from the U.S. Atomic Energy Commission usually contain on the order of 5 mg. of total solids per milliliter of solution. In terms of the procedure described below, approximately 90% of the activity in a solution of carrier-free iodine-131 can be distilled and collected in pure water. This procedure is based upon studies of the rate of distillation of carrier-free iodine-131 from various aqueous solutions.¹ Various species of iodine of high specific activity, for use in different radiochemical studies, can be prepared from the water solution obtained. Because of the peculiar behavior of iodine at low concentrations,² the chemical nature of the final product should be ascertained in each case.

Procedure

Two milliliters of carrier-free iodine-131 solution, as obtained from the Atomic Energy Commission (in general, the original iodine-131 solution is diluted with water in order to avoid working with high levels of radioactivity), is added to 200 ml. of 8 *M* sulfuric acid containing 1.06 g. of anhydrous cerium(IV) hydrogen sulfate. The resulting solution is stirred magnetically and refluxed for 30 minutes in a 500-ml. flask. The flask is then cooled to room temperature by replacing the heating mantle with a beaker of cold water,‡ and 0.65 g. of iron(II) sulfate 7-hydrate is added (10% excess). The reflux condenser is replaced by a condenser with an 8-mm. tube sealed to the receiving end. This tube is immersed in 5 ml. of water contained in a 25-ml.

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‡ Cooling is essential because addition of iron(II) sulfate to the hot solution will result in volatilization of some of the iodine-131.

graduated cylinder. The magnetically stirred solution is distilled until about 20 ml. of distillate has been collected. This volume of distillate contains approximately 90% of the initial iodine-131 activity. It is to be noted that about 90% of the iodine-131 distilled comes over with the first 10 ml. of distillate. All-glass apparatus is employed, with water as lubricant on all ground-glass joints.

This procedure is rather sensitive to the concentrations of cerium(IV) hydrogen sulfate and sulfuric acid. A lowering of the cerium(IV) concentration from 0.01 to 0.005 *M* results in a 10% decrease in the amount of activity distilled. Only 39% of the activity is recovered when iodine-131 is refluxed in 4 *M* sulfuric acid and 0.01 *M* cerium(IV) hydrogen sulfate. Large variations in the time of reflux, above 30 minutes, do not influence the yield. Variations in the amount of excess iron(II) sulfate from 40 to 120% have a negligible effect, but reducing the excess to about 10% increases the yield somewhat. When the iodide concentration in the solution before reflux is increased to 10^{-6} *F* or greater by the addition of carrier iodide, an appreciable loss of activity occurs owing to volatilization during reflux. Potassium dichromate, potassium permanganate, and potassium peroxydisulfate as oxidizing agents give considerably lower yields (52 to 80%).

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46. POLYHALOGEN COMPLEX SALTS

BY ALEXANDER I. POPOV* AND ROBERT E. BUCKLES*

Polyhalogen complex salts can be defined as the addition products of halides with one or more molecules of a halogen or of an interhalogen compound. They contain, therefore,

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complex polyhalogen anions, and they can exist either as metal salts or as alkyl-substituted "onium" salts.

The list of existing polyhalogen anions is rather impressive since, except for fluorine, nearly every combination of halogens is possible. Fluorine does not readily form polyhalogen complexes, and when it does, both the methods of preparation and the properties of the resulting complexes lie somewhat apart from the other polyhalides. This discussion is limited primarily to the complexes of chlorine, bromine, and iodine.

Since the polyhalide ions are formed by the addition of diatomic halogen molecules or of interhalogen molecules to a halide ion, the total number of halogen atoms in such a complex is always odd.* The most common case is that of the trihalides. Some penta-, hepta-, and enneahalides are likewise known. The highest known polyhalogen complex is $\text{PCl}_3\text{Br}_{13}$;¹ the structure of this has not been determined, but by analogy to other similar complexes it can probably be expressed as $[\text{PCl}_3\text{Br}]^+[\text{Br}_{17}]^-$. Table I lists the known polyhalide ions.

Not all metals are capable of forming polyhalide salts. Although considerable research remains to be done in this field, it seems at the present time that in order to form a polyhalide salt the cation must have a large radius and a small charge. The best known and the most stable of the metal polyhalogen salts are those of cesium and rubidium. The potassium salts are more difficult to form and are somewhat more unstable in the solid state. The sodium and lithium polyhalides have not been prepared in anhydrous form. Polyvalent cations apparently do not yield salts with the trihalides.† However, salts of magnesium, zinc,

* Distribution experiments on iodine-iodide systems between water and carbon tetrachloride [M. Davies and E. Gwynne, *J. Am. Chem. Soc.*, **74**, 2748 (1952)] seem to indicate possible existence of I_6^- ions. The interpretation of these data is somewhat controversial.

† Spectrophotometric evidence indicates formation of $\text{Al}(\text{ICl}_2)_3$ in acetonitrile solutions [(A. I. Popov and F. B. Stute, *J. Am. Chem. Soc.*, **78**, 5737 (1956)].

cobalt, nickel, and beryllium with the tetrachloroiodate(III) ion are known, although, again, very little work has been done on these compounds. Large complex cations,

TABLE I. KNOWN POLYHALIDE IONS IN CRYSTALLINE SOLIDS

X_3^-	X_5^-	X_7^-	X_9^-	Others
Cl_3^- (?)	I_5^-	I_7^-	I_9^-	Br_{11}^- (?)
Br_3^-	Br_5^-	I_6Br^-		Br_{13}^- (?)
I_3^-	ICl_4^-			Br_{17}^- (?)
I_2Cl^-				
ICl_2^-				
I_2Br^-				
IBr_2^-				
$BrCl_2^-$				
Br_2Cl^-				
$IBrCl^-$				

such as the dichlorobis(ethylenediamine)cobalt(III) ion, have likewise been reported to form polyhalide salts.

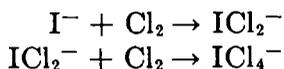
The conditions of large cationic radius and low charge are admirably fulfilled in the organic substituted "onium" salts, of which the tetraalkylammonium salts have been used most extensively in actual preparations.

Preparation

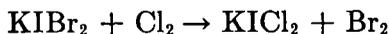
In general, the methods of preparation can be divided into two classes: reactions between solid halides or polyhalides and gaseous halogens or interhalogens, and reactions of the same type in an appropriate solvent. The conditions of the gas-solid reactions have been thoroughly investigated by Cremer and Duncan.² Their conclusions can be summarized as follows.

The gaseous halogens or interhalogens can add directly to a solid halide to form a corresponding complex salt provided that the temperature of the reaction is below the decomposition temperature of the polyhalide. The reaction usually yields a trihalide, but in the case of the addition

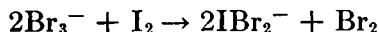
of chlorine to an iodide, it proceeds further and gives the tetrachloroiodate(III),



In the reaction of halogen or interhalogen with a solid polyhalide, the reaction product is usually the most stable of the possible polyhalide ions. For example, chlorine will react with the dibromoiodate(I) ion to give dichloroiodate(I) ion,



but it will not yield the highly unstable trichloride ion. The reaction is independent of whether the replacing halogen is more electropositive or more electronegative than the one replaced. Thus, iodine will replace bromine from a fairly unstable tribromide ion to form dibromoiodate(I) ion,



Preparative methods based upon the gas-solid reaction are usually quite cumbersome and result in fairly low yields, except for a few specific cases mentioned below. In general, the formation reaction occurs much more satisfactorily when it is carried out in solution.

One of the most comprehensive studies on the preparation of polyhalogen complexes in solutions has been made by Chattaway and Hoyle.³ These authors have prepared principally the tetraalkylammonium salts of the polyhalide ions.

The choice of an appropriate solvent as the reaction medium is of primary importance and usually involves a compromise among various unfavorable factors. Because of the high chemical reactivity of the halogens and of the polyhalides, solvents which are easily susceptible to halogenation or which effect solvolysis reactions are to be avoided. This, of course, precludes the use of aqueous solutions for many syntheses, with the exception of those of some polyiodides since iodine is fairly unreactive with water.

The most inert solvents, such as halogenated hydrocarbons, likewise are not suitable since they cannot dissolve halide salts. The best possibility seems to be either methanol or glacial acetic acid. It must be noted, however, that the entire problem of polyhalide-solvent interaction is still obscure.

The methods of preparation amount to the addition of a slight excess of a halogen or an interhalogen to a solution of an appropriate halide salt. On standing, the polyhalide crystallizes out, usually in a fair degree of purity, and can be purified further by recrystallization. Difficulties arise when the complex anion is of higher order than the trihalide or when it is prone to disproportionate in solution. For example, the addition of iodine to a soluble chloride in order to form the iodochloroiodate(I) ion, I_2Cl^- , is complicated by the formation of the ions ClI_4^- and I_5^- . Such tendencies very often necessitate rather rigid conditions for the preparation and the subsequent purification. It is relatively simple to prepare the polyhalides of high stability, such as the species I_3^- , ICl_2^- , and IBr_2^- , but the difficulties of preparation naturally increase with the decreasing stability of the ion. No satisfactory method has, as yet, been devised for the preparation of a trichloride salt, which has a high dissociation pressure at room temperature. Another important factor, as was mentioned above, is the reactivity of the halogens with the solvent. All polyhalides dissociate to some extent in solution into the halide ion and the corresponding halogen. Although such dissociations are normally rather small, if the liberated halogen is chlorine or bromine, they may proceed completely because of the removal of the halogen by the solvent. The dissociation constants of many polyhalide ions in acetonitrile have been found to be of the order of magnitude of 10^{-7} .^{4,5} The dissociation constants determined in aqueous solutions by Korenman⁶ are not reliable since the author neglected to take into account the hydrolysis reactions of the halogens. He also calculated the concentrations of

TABLE II. METHODS OF PREPARATION

Compound	Preparation ^a	Recrystallization solvent	Melting point	Appearance	Yield	Reference
Me ₄ Ni ^b	2.0 g. Me ₄ Ni + 3.3 g. I ₂ in 30 ml. MeOH	117-117.2°	Purple needles	77-80 %	3
Pr ₄ Ni ₃	3.0 g. Pr ₄ Ni + 2.5 g. I ₂ in 30 ml. EtOH	97°	Dark red needles	90 %	3
Bu ₄ Ni ^c	3.7 g. Bu ₄ Ni + 2.5 g. I ₂ in 25 ml. MeOH (hot)	95% EtOH	70.0-70.5°	Purple crystals	87 %	15
CsI ₄	2.6 g. CsI + 3.0 g. I ₂ in 30 ml. H ₂ O (hot)	Decomposes	Purple needles	70 %	5
Me ₄ Ni ^d	2.0 g. Me ₄ Ni + 5.0 g. I ₂ in 60 ml. MeOH	HC ₂ H ₃ O ₂	129-130°	Green plates	96 %	3
Pr ₄ Ni ₃	2.1 g. Pr ₄ Ni + 5.0 g. I ₂ in 100 ml. EtOH (hot)	EtOH	81.5-82°	Green plates	60 %	3
Pr ₄ Ni ₃ ^e	3.1 g. Pr ₄ Ni + 7.6 g. I ₂ in 100 ml. EtOH (hot)	EtOH satd. with I ₂	85°	Green powder	85 %	3
Me ₄ Ni ₅	2.0 g. Me ₄ Ni + 10.0 g. I ₂ in 120 ml. MeOH (hot)	110°	Dark purple crystals	75 %	3
Me ₄ NBr ₃ ^f	2.7 g. Me ₄ NBr + 3.2 g. Br ₂ in 100 ml. HC ₂ H ₃ O ₂	118.0-118.5°	Red-orange crystals	93 %	3
Et ₄ NiCl ₃ ^g	3.1 g. Et ₄ NCl + 3.2 g. ICl in 30 ml. HC ₂ H ₃ O ₂	102.5°	Yellow crystals	60 %	3
Pr ₄ NiCl ₃ ^h	4.4 g. Pr ₄ Ni + Cl ₄ (g) in excess in 40 ml. HC ₂ H ₃ O ₂	EtOH	145°	Yellow crystals	65 %	3
Bu ₄ NiCl ₃ ⁱ	5.6 g. Bu ₄ NCl + 3.2 g. ICl in 30 ml. HC ₂ H ₃ O ₂	EtOH	68°	Yellow crystals	95 %	4
Me ₃ SiCl ₃ ^j	2.0 g. Me ₃ Si + Cl ₄ (g) in excess	103-104°	Yellow crystals	60 %	16
RbCl ₄ ^k	2.4 g. RbCl + 2.5 g. I ₂ + Cl ₄ (g) in excess in 30 ml. H ₂ O (hot)	212-213°	Yellow crystals	90 %	5
CsCl ₃	3.4 g. CsCl + 2.5 g. I ₂ in 30 ml. H ₂ O (hot)	Dilute HCl	Decomposes	Yellow crystals	95 %	5
Me ₄ NiCl ₄	20.0 g. Me ₄ NiCl ₃ + Cl ₄ (g) in excess in 80 ml. HC ₂ H ₃ O ₂ + 20 ml. 6 N HCl	287-289°	Yellow crystals	98-100 %	17
Me ₃ SiCl ₄ ^l	2.0 g. Me ₃ Si + Cl ₄ (g) in excess in 200 ml. HC ₂ H ₃ O ₂ containing 8% CCl ₄	180°	Yellow crystals	50 %	16
Me ₄ NiBr ₃	3.6 g. Me ₄ Ni + 3.2 g. Br ₂ in 30 ml. EtOH (warm)	EtOH	192°	Dark orange crystals	90 %	3
Pr ₄ NiBr ₃	5.0 g. Pr ₄ Ni + 3.2 g. Br ₂ in 30 ml. EtOH (warm)	EtOH	139-140°	Dark orange crystals	75 %	3
CsIBr ₃	4.8 g. CsI + 3.2 g. Br ₂ in 10 ml. 50% EtOH (hot)	Decomposes	Dark orange crystals	90 %	5
Me ₄ Ni ₄ Cl ^m	2.2 g. Me ₄ NCl + 5.3 g. I ₂ in 45 ml. isopropyl alc. (warm)	102°	Bronze-red crystals	18
Me ₄ Ni ₃ Br	2.8 g. Me ₄ NBr + 4.6 g. I ₂ in 40 ml. EtOH (hot)	143°	Dark red crystals	3
Me ₄ NBrCl ₃	2.0 g. Me ₄ NBr + Cl ₄ (g) in excess, in least possible quantity of HC ₂ H ₃ O ₂	160-163°	Yellow crystals	3
Me ₄ NiBrCl	8.0 g. Me ₄ NBr + 6.6 g. ICl in 30 ml. HC ₂ H ₃ O ₂	HC ₂ H ₃ O ₂ + 3% ICl	205-206°	Orange crystals	3
Me ₄ Ni ₄ Cl ⁿ	2.0 g. Me ₄ Ni + 2.5 g. I ₂ + 1.9 g. ICl in 50 ml. EtOH + 50 ml. H ₂ O	95% EtOH	107-108°	Green plates	3

TABLE II. METHODS OF PREPARATION (*Continued*)

- The quantities of reagents specified are those found to be effective by the submitters and are not necessarily those listed in the cited references.
- Disproportionates to tetramethylammonium iodide and the compound Me_4NI_2 upon recrystallization.
- Oily liquid forms in methanol solution. This crystallizes on cooling.
- Recrystallization usually unnecessary.
- About 98% pure by iodometric titration. Decomposes on standing.
- Add 20 ml. of carbon tetrachloride to hot acetic acid solution of tetramethylammonium bromide and bromine, cool, filter, and wash crystals with carbon tetrachloride containing small amounts of bromine.
- Add 10 ml. of ethyl ether to acetic acid solution of tetraethylammonium chloride and iodine monochloride. Cool.
- Boil product for a few minutes in ethanol to decompose tetrachloroiodate(III) ion.
- Chlorine passed slowly over dry trimethylsulfonium iodide with flask immersed in ice water.
- Cool to 0°. Literature lists m.p. 180 to 200°.
- Crystals appear on cooling to 0°.
- Mixture of the compounds $\text{Me}_4\text{NI}_2\text{Cl}$ and Me_4NI_2 separates on cooling. Filtrate then yields pure $\text{Me}_4\text{NI}_2\text{Cl}$ on standing.
- Dissolve iodine and iodine monochloride in hot ethanol and add to hot solution of tetramethylammonium iodide.

ionic species in alkali halide solutions on the basis of the Arrhenius equation $\alpha = \Lambda/\Lambda_0$.

Stability

The stability of the solid polyhalide depends on numerous factors, among them the size of the cation, the size and the nature of the polyhalide ion, and the chemical resistance of the compound to atmospheric moisture. The most stable salts are formed when the ionic sizes of the cation and the anion are similar. In the alkali metal series the stability of the polyhalides decreases in the order $\text{Cs} > \text{Rb} > \text{NH}_4 > \text{K} > \text{Na}$, which corresponds to the order of decrease in cationic size. Not enough work has, as yet, been done on the substituted "onium" polyhalides to allow any convincing generalizations.

With salts of the same cation or in polar solvents, where the polyhalides behave as strong electrolytes,⁷ the stability of the trihalides seems to depend upon the nature of the central ion. Ions containing iodine are usually the most stable, and the stability seems to decrease as the iodine is progressively replaced by the lighter halogens, provided the ion remains symmetrical. Inasmuch as the heaviest halogen is invariably found to be the central atom of a linear (or nearly linear) trihalide ion, the species IX_2^- ($\text{X} = \text{Cl}$ or Br) is more stable than the species I_2X^- , which would have the structure I-I-X . Polyhalogen complexes do not exhibit any isomerism, and, as was recently shown by Scott,⁸ any structure that would involve a lighter halogen as the central atom would be thermodynamically unstable. Ephraim has determined the dissociation pressures of cesium and rubidium polyhalides⁹ and places these compounds in the order of decreasing stability as $\text{CsI}_3 > \text{CsICl}_2 > \text{CsI}_2\text{Br} > \text{CsBr}_3 > \text{CsBrCl}_2 > \text{CsBr}_2\text{Cl}$.

Analysis

One of the most convenient analytical techniques for the determination of purity of a polyhalide is the iodometric titration of the total reducible halogen. When the complex

salts are easily soluble in water, the technique is very simple. Difficulties arise mainly with some of the substituted "onium" salts, where the alkyl groups may have more than one carbon atom. Such compounds can be dissolved easily in many polar organic solvents, such as methanol, ethanol, acetonitrile, and acetone, which are miscible with water, but in most cases the iodine-starch reaction is rather faint. The best results are obtained by dissolving the complex in a small amount of warm glacial acetic acid, diluting with water, and then titrating according to conventional procedures. The presence of acetic acid does not seem to influence the starch-iodine reaction.

Methods of Preparation

Typical procedures involving (1) reaction of dissolved halide salt with dissolved halogen, (2) reaction of dissolved halide salt with gaseous halogen, and (3) reaction of solid halide salt with gaseous halogen are illustrated in synthesis 47. Table II gives details for the syntheses of other polyhalogen complexes by these three methods.

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47. TYPICAL POLYHALOGEN COMPLEX SALTS

SUBMITTED BY ALEXANDER I. POPOV* AND ROBERT E. BUCKLES*
CHECKED BY WALTER C. SCHUMB† AND JOHN W. GEORGE‡

A. TETRAMETHYLAMMONIUM DICHLOROIODATE(I)

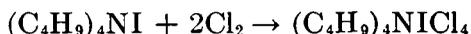
(Tetramethylammonium Iododichloride)



To a solution of 21.9 g. of tetramethylammonium chloride (0.20 mol) in 400 ml. of glacial acetic acid is added 32.5 g. of iodine(I) chloride¹⁰ (0.20 mol). The yellow crystals which precipitate are removed by filtration and washed with carbon tetrachloride. The yield is 51.0 to 53.0 g. (94 to 97%). The product (m.p. 237 to 238°) can be recrystallized from isopropyl alcohol containing a small quantity of iodine(I) chloride. The final melting point is the reported¹¹ value of 226 to 230°.‡ *Anal.* Calcd. for $(\text{CH}_3)_4\text{NICl}_2$: C, 17.66; H, 4.42; N, 5.15; iodometric equivalent, 59.3. Found: C, 17.71; H, 4.38; N, 5.38; iodometric equivalent, 59.0.

B. TETRABUTYLAMMONIUM TETRACHLOROIODATE(III)

(Tetrabutylammonium Tetrachloriodide)



A 3-l. Erlenmeyer flask is fitted with an inlet tube reaching nearly to the bottom of the flask and an exit tube and is placed in a hood. A solution of 200 g. of tetrabutylammonium iodide^{5,12} (0.54 mol) in 1500 ml. of chloroform is placed in the flask. The solution is cooled in an ice-water bath, and tank chlorine which has been passed through a 500-ml. gas-washing bottle containing 250 ml. of 18 M sulfuric acid and a similar empty-bottle spray trap is passed into the solution through the inlet tube. The color

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‡ The decrease in melting point is due to decomposition on recrystallization. The compound is best used without recrystallization.

changes to yellow, to orange, and finally to deep red. A rapid change to yellow-orange then occurs, and yellow crystals begin to precipitate. When precipitation is complete, the flow of chlorine is stopped. The suspension is heated on a steam bath for 10 minutes (*Hood!*) to remove excess chlorine and is then cooled in an ice bath. The yellow crystals are removed by filtration and dried in air or a desiccator in the absence of light. The yield is 262 to 272 g. (95 to 99%). The product has the reported¹⁷ melting point of 137 to 139°. *Anal.* Calcd. for $(C_4H_9)_4NiCl_4$: C, 37.60; H, 7.10; N, 2.74; iodometric equivalent, 45.6. Found: C, 37.2; H, 7.15; N, 2.78; iodometric equivalent, 44.9. The product must be stored in the dark.

C. TETRABUTYLAMMONIUM DIBROMOBROMATE(I)

(Tetrabutylammonium Tribromide)



Fifty grams of tetrabutylammonium bromide¹³ (0.155 mol) is placed in a crystallizing dish in a desiccator which contains at least 10 ml. of liquid bromine (0.195 mol). The desiccator is closed and allowed to stand for 24 hours. The viscous liquid or semisolid mass in the crystallizing dish is transferred to a 500-ml. suction flask and mixed with 150 ml. of carbon tetrachloride. A one-hole stopper fitted with a capillary inlet drawn from 6-mm. glass tubing is inserted into the neck of the flask. The capillary is adjusted to extend below the surface of the liquid in the flask. The side arm of the flask is connected to a water pump, and air is drawn in through the capillary. As the solvent and excess bromine evaporate, crystals of the product are formed. When the oily liquid has disappeared and the solution has become light orange, the crystals are removed by filtration and washed with carbon tetrachloride.* A yield of 47 to 55 g. (63 to 75%) of light orange

* The checkers prefer to remove remaining bromine by a vacuum operation.

crystals (m.p. 71 to 73°) is obtained. The recorded melting point¹⁴ is 72.5 to 74°. *Anal.* Calcd. for $(C_4H_9)_4NBr_3$: C, 39.83; H, 7.47; Br, 49.8; iodometric equivalent, 241. Found: C, 39.70; H, 7.71; Br, 49.3; iodometric equivalent, 240.

References

References cited are the same as those listed for synthesis 46 (p. 175).

CHAPTER VIII

See also: Preparation of metal derivatives of 1,3-diketones, synthesis 29
Anhydrous metal chlorides, synthesis 43

48. IRON(II) CHLORIDE 2-HYDRATE

SUBMITTED BY KARL H. GAYER* AND LEO WOONTNER†

CHECKED BY RUSSELL S. DRAGO‡ AND THOMAS SHEPHERD‡

Hydrated iron(II) chlorides are usually prepared by dissolving pure iron in hydrochloric acid solution and crystallizing.^{1,2} The hydrate formed depends upon the temperature of crystallization,^{1,2} the 6-hydrate forming below 12.3°, the 4-hydrate above 12.3°, and the 2-hydrate above 72.6°. Contamination by iron(III) is difficult to avoid in the majority of these procedures. Samples of the 2-hydrate free from iron(III) can be obtained conveniently from the commercially available 4-hydrate by recrystallization in the presence of pure iron in an inert atmosphere.

Procedure

The apparatus used (Fig. 16) consists of two 500-ml.

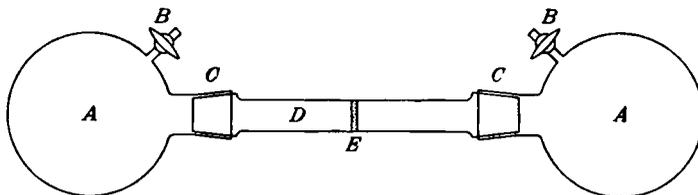


FIG. 16. Apparatus for the preparation of iron(II) chloride 2-hydrate.

round-bottomed pyrex flasks *A*, each provided with a stopcock *B* and a ground-glass joint *C*. A 20-cm. length of

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† Parker Rust Proof Company, Detroit, Mich.

‡ University of Illinois, Urbana, Ill.

20-mm. glass tube *D*, fitted at each end with a ground-glass joint and having sealed at the center a medium-porosity sintered-glass disk *E*, connects the two flasks.

Two hundred forty grams of reagent-quality iron(II) chloride 4-hydrate (1.21 mols), 65 ml. of conductivity water, 10 ml. of 38% hydrochloric acid, and 8 to 10 g. of pure electrolytic iron are placed in one of the flasks. The apparatus is assembled (long axis vertical), and a current of oxygen-free nitrogen is passed through the assembly, escaping gas being passed through a mercury trap. The suspension in the flask is warmed to dissolve the salt and then heated for 30 minutes to effect complete reduction of any iron(III). The apparatus is then inverted and the solution freed from unreacted iron by filtration through disk *E*, a slight pressure of nitrogen being maintained in the upper flask to aid filtration. The clear solution in the second flask is cooled to room temperature. After crystallization is complete, the unit is inverted again, and the crystals are filtered free from mother liquor by applying nitrogen pressure to the top flask and applying suction to the bottom flask. The relatively dry product is a mixture of hydrates. The stopcock in the top flask is then closed, and evacuation is continued while the assembly is heated in a water bath at 80°. Vigorous effervescence yields iron(II) chloride 2-hydrate as a whitish powder. The product is stored in the reaction vessel under nitrogen or transferred to a 100-ml. round-bottomed flask equipped with a three-way stopcock cap. The flask is then alternately evacuated and filled with dry oxygen-free nitrogen. The yield is about 134 g. (about 68%). *Anal.* Calcd. for $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$: Fe, 34.30; Cl, 43.6. Found: Fe, 34.34; Cl, 43.5, 43.8.

Properties

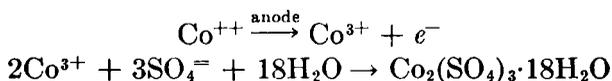
Iron(II) chloride 2-hydrate, so prepared, is white with a very pale green tint. The crystal form is monoclinic. The compound is slowly oxidized in air, but its freshly

prepared aqueous solutions give no color with thiocyanate ion. At 120° the 2-hydrate decomposes to the 1-hydrate.

References

1. J. N. FRIEND (ED.): "A Textbook of Inorganic Chemistry," Vol. IX, Part II, p. 92, Charles Griffin & Co., Ltd., London, 1925
2. J. W. MELLOR: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XIV, pp. 12-13, Longmans, Green & Co., Ltd., London, 1935.

49. COBALT(III) SULFATE 18-HYDRATE



SUBMITTED BY SHERLOCK SWANN, JR.,* THEODORE S. XANTHAKOS,* AND RICHARD STREHLOW*

CHECKED BY MARVIN D. RAUSCH† AND JACOB KLEINBERG‡

Cobalt(III) sulfate has been prepared from cobalt(II) sulfate by electrolytic oxidation¹ and by treatment with ozone² or fluorine.³ The electrolytic oxidation of a saturated solution of cobalt(II) sulfate in 10 *N* sulfuric acid at 5 to 10°¹ gives cobalt(III) sulfate 18-hydrate. Under these conditions, this compound is insoluble and does not decompose rapidly.

Procedure

An anode is prepared by sealing a platinum wire into the end of a 7-cm. length of 6- to 8-mm. glass tubing in such a manner that electrical contact can be made. A 4- by 10-cm. piece of platinum foil is welded to the wire by placing the wire on the foil, heating to redness with a Bunsen burner, and striking the wire sharply with a hammer.‡ The tubing is then inserted into a one-hole rubber stopper so that it can be mounted in a clamp. Mercury is added to the tube to a depth of 1 to 2 cm., and electrical contact is established through a copper wire inserted into the mercury. A cathode is formed from a

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† University of Kansas, Lawrence, Kans.

‡ A stronger seal weld is obtained if the wire is first bent into a small loop.

4- by 10-cm. sheet of thin copper and is bent to fit snugly into a 1-l. tall-form beaker.

A 500-ml. porous porcelain cup* is filled with 10 *N* sulfuric acid and allowed to stand overnight. A sample of acid from the cup is then tested for iron(III) with ammonium thiocyanate. If iron is found, the cup is soaked repeatedly in new portions of the 10 *N* acid until no test for iron(III) results. The cup, containing acid in its pores, is then ready for use. The catholyte is prepared by adding 150 ml. of concentrated sulfuric acid (sp. gr. 1.84) slowly and with stirring to 310 ml. of water. It is cooled to 5° before being used. The anolyte is prepared by dissolving 84 g. of cobalt(II) sulfate 7-hydrate† (0.3 mol) in 275 ml. of water at room temperature in a 1-l. beaker. The solution is cooled in an ice-salt bath, and 150 ml. of concentrated sulfuric acid (sp. gr. 1.84) is added slowly with stirring. The solution is then cooled to 5° before being used.

• The porous cup is placed in the 1-l. tall-form beaker. Sufficient anolyte solution is decanted from any precipitated cobalt(II) sulfate into the porous cup to fill the latter to 2 cm. below the rim of the beaker. Sufficient catholyte solution is added to the beaker to make the two liquid levels the same. The anode is lowered into the anolyte until the foil is completely submerged. The entire cell is placed in a 3-l. beaker, which is then packed with an ice-salt mixture.‡ A direct current of 4 amp.§ from a

* The yield is reduced if the pores are too large. If the cup leaks distilled water at a rate greater than 10 ml./hr., it should be soaked in 20% sodium silicate (water glass) for 1 hour and then treated with 20% sulfuric acid for 1 hour before soaking in the 10 *N* acid.

† Both crystals and solution should be deep red in color. Pink samples do not dissolve well in water.

‡ The temperature of the anolyte should be about 6° and should not be permitted to rise above 10° during the electrolysis. If necessary, brine may be siphoned out of the 3-l. beaker and replaced with ice-salt mixture.

§ The optimum current density is 0.05 amp./sq. cm. If the current exceeds 1 amp. for each 100 ml. of anolyte, the low temperature cannot be maintained.

suitable source is allowed to flow through the cell for 4 hours. Lustrous gray-blue crystals of cobalt(III) sulfate 18-hydrate are formed in suspension in the anode compartment in 90 to 95% material yield, based on the initial quantity of cobalt(II) sulfate 7-hydrate.* The suspension can be used directly for oxidation of many organic compounds.¹ The crystalline product is recovered by filtration through asbestos or sintered glass, but the mother liquor is difficult to remove completely.

Analysis

One-milliliter samples of the suspension are pipetted into measured excess volumes of standard oxalic acid solution. Each sample is diluted to 100 ml., and the unoxidized oxalic acid is then titrated with 0.1 *N* potassium permanganate solution which has been standardized against oxalic acid. Since the concentration of crystals in the anolyte is not absolutely uniform, the material yield calculated from the quantity of oxidizing agent present depends upon the region from which the sample is taken. Larger samples are analyzed electrometrically because of the indefiniteness of the visual end point.¹

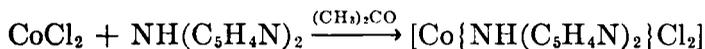
Properties

Crystals of cobalt(III) sulfate 18-hydrate decompose at room temperature within a few hours, but they can be stored in a refrigerator for 3 to 4 days without decomposing noticeably. Aqueous solutions of the compound evolve oxygen, the reaction occurring instantaneously in warm water and rapidly even in cold water. Suspensions in cold 10 *N* sulfuric acid decompose very slowly. Cobalt(III) sulfate oxidizes many organic compounds very vigorously.¹

References

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* Since ozone is also an anode product, electrochemical yields are lower than chemical yields.

50. DICHLORO(DI-2-PYRIDYLAMINE)COBALT(II)

SUBMITTED BY JOHN C. BAILAR, JR.,* AND STANLEY KIRSCHNER*

CHECKED BY HENRY F. HOLTZCLAW, JR.†

Cobalt(II) ion, like copper(II) ion (synthesis 4), coordinates readily with di-2-pyridylamine. A mono(dipyridylamine) derivative results by direct precipitation in acetone solution. Subsequent reaction with excess amine to give a tris(dipyridylamine) complex is evidence for the bidentate character of the complexing agent.

Procedure

Anhydrous cobalt(II) chloride is prepared by heating the 6-hydrate at 120° for several hours. A solution consisting of 7.5 g. of the anhydrous cobalt(II) chloride (0.058 mol) dissolved in 300 ml. of reagent-quality acetone is filtered to remove any undissolved material. To the filtrate is added, with vigorous stirring, a solution containing 10.0 g. of di-2-pyridylamine‡ (0.058 mol) dissolved in 50 ml. of reagent-quality acetone. A blue precipitate, consisting of small, needle-shaped crystals, is formed immediately. It is freed from mother liquor by filtration (without suction) and is washed with four successive 50-ml. portions of acetone. The product is dried for 12 hours at 110°. The yield is 15.7 g. (90%). *Anal.* Calcd. for $[\text{Co}\{\text{NH}(\text{C}_5\text{H}_4\text{N})_2\}\text{Cl}_2]$: C, 39.9; H, 3.01; N, 13.99; Cl, 23.55. Found: C, 39.8; H, 2.87; N, 13.80; Cl, 23.69.

Properties

The material crystallizes from acetone as minute needles, has a royal-blue color, and is stable in air up to its decomposition temperature of 400°. It is only very slightly

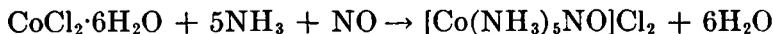
* University of Illinois, Urbana, Ill.

† University of Nebraska, Lincoln, Nebr.

‡ Supplied by Reilly Tar and Chemical Corp., Indianapolis, Ind.

soluble in solvents such as acetone, ethyl ether, benzene, carbon tetrachloride, and absolute ethanol. However, it reacts with water to give an orange solution, which, when evaporated at room temperature or on a steam bath, yields the original blue compound. This behavior is probably due to a hydration reaction (with the subsequent ionization of the chlorides) followed by a dehydration reaction (with the recoordination of the chlorides).

51. NITROSYLPENTAMMINECOBALT(II) CHLORIDE, BLACK, AND NITROSYLPENTAMMINECOBALT(III) CHLORIDE, PINK (CORRECTION)¹



SUBMITTED BY THERALD MOELLER* AND GLENDALL L. KING*
CHECKED BY FRED BASOLO†

Messrs. James V. Quagliano,‡ Raphael Penland,‡ and Ernest P. Bertin, S.J.,‡ have called attention to the incorrectness of the statement "This may be converted to the pink chloride by treatment with concentrated hydrochloric acid" (synthesis 55, p. 168 of Volume IV).¹ They report on the basis of both analytical and infrared data that the compound so obtained is actually chloropentamminecobalt(III) chloride rather than a nitrosyl complex. This is in agreement with Milward, Wardlaw, and Way's report² that treatment of cobalt(II) nitrate solution with ammonia and nitrogen(II) oxide yields pink nitrosylpentamminecobalt(III) nitrate, which in turn is converted to chloropentamminecobalt(III) chloride by cold concentrated hydrochloric acid. Preparations of pink nitrosylpentamminecobalt(III) nitrate and sulfate are apparently well established,³⁻⁵ but the existence of a corresponding chloride is doubtful.

* University of Illinois, Urbana, Ill.

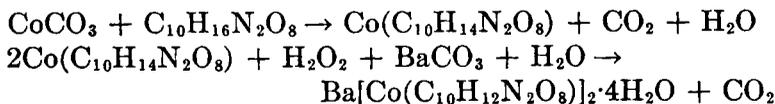
† Northwestern University, Evanston, Ill.

‡ University of Notre Dame, Notre Dame, Ind.

References

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**52. BARIUM (ETHYLENEDIAMINETETRAACETATO)-
COBALTATE(III) 4-HYDRATE**



SUBMITTED BY STANLEY KIRSCHNER*

CHECKED BY ELEONORA C. GYARFAS†

Barium (ethylenediaminetetraacetato)cobaltate(III) 4-hydrate has been obtained by treating cobalt(II) chloride with barium acetate and ethylenediaminetetraacetic acid in glacial acetic acid, oxidizing the resulting cobalt(II) complex with bromine¹ or hydrogen peroxide,² and removing coordinated bromide ion or hydroxyl ion from the cobalt(III) complexes formed with silver(I) ion¹ or perchloric acid.² Ease of manipulation and yield are both improved materially by the variation of the hydrogen peroxide procedure² given here. The sodium or potassium salt of the complex anion is readily obtained by treating a solution of the barium salt with the corresponding sulfate and removing precipitated barium sulfate. Alkali metal salts are also obtained by bromine,^{1,3} chlorite,⁴ or hydrogen peroxide⁵ oxidation of the appropriate cobalt(II) complexes.

Procedure

A slurry of 4.76 g. of cobalt(II) carbonate (0.04 mol), 11.69 g. of ethylenediaminetetraacetic† acid (0.04 mol), and 50 ml. of water in a 250-ml. beaker is warmed slowly

* Wayne State University, Detroit, Mich.

† University of Illinois, Urbana, Ill.

‡ A pure sample of acid is necessary because impurities will accumulate in the product.

with vigorous stirring to 75°. Stirring is continued until evolution of carbon dioxide ceases, after which 10 ml. of 30% hydrogen peroxide is added with stirring to the slurry.* Then 3.95 g. of powdered barium carbonate (0.02 mol) is added slowly with vigorous stirring. Stirring is continued until evolution of carbon dioxide ceases. The mixture is then filtered through a clean, *dry*† sintered-glass funnel, and the beaker is rinsed with 5 ml. of water, which is also poured through the funnel. The combined filtrate and washings are poured very slowly and with very vigorous stirring into 1700 ml. of absolute ethanol.‡ The resulting precipitate is removed by filtration, washed with two 25-ml. portions of absolute ethanol, and dried in an oven at 50° for at least 24 hours. The yield is 16.8 to 17.1 g. (93 to 94.7%). *Anal.* Calcd. for $\text{Ba}[\text{Co}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)]_2 \cdot 4\text{H}_2\text{O}$: C, 26.58; H, 3.57; N, 6.20. Found: C, 26.60; H, 3.62; N, 6.25.§ The product can be recrystallized from water at -5° but with no improvement in analysis.

Properties

The compound precipitates from ethanol as minute, violet crystals. Larger, darker-colored crystals are obtained by recrystallization from water. The salt is very soluble in water but is only slightly soluble in methanol, ethanol, carbon tetrachloride, chloroform, acetone, ethyl ether, or benzene. The anion is asymmetric,^{2,5} the salt thus existing as a racemic mixture of dextro and levo forms.

References

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2. S. KIRSCHNER: doctoral dissertation, University of Illinois, 1954.

* A precipitate of cobalt(II) dihydrogen ethylenediaminetetraacetate forms.

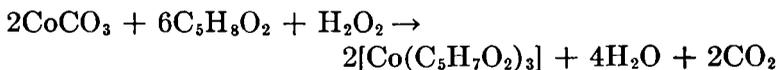
† Excessive dilution increases the ethanol requirement and reduces the yield.

‡ The checker reports some improvement in crystal size and ease of filtration by adding the ethanol to the aqueous solution.

§ Analyses by the checker suggest the retention of very small quantities of water beyond the 4-hydrate even after drying for as long as 4 days.

3. D. H. BUSCH and J. C. BAILAR, JR.: *J. Am. Chem. Soc.*, **75**, 4574 (1953).
4. H. BRINTZINGER, H. THIELE, and U. MÜLLER: *Z. anorg. u. allgem. Chem.*, **251**, 285 (1943).
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53. COBALT(III) ACETYLACETONATE [Tris(2,4-pentanediono)cobalt(III)]



SUBMITTED BY BURL E. BRYANT* AND W. CONARD FERNELIUS*

CHECKED BY DARYLE H. BUSCH,† R. CARL STOUFER,† AND WILMER STRATTON†

Cobalt(III) acetylacetonate has been prepared by the reaction of an aqueous suspension of cobalt(III) oxide with acetylacetone and by the oxidation of an aqueous solution of a cobalt(II) salt with hypochlorite ion in the presence of acetylacetone.¹⁻³ The present synthesis may be considered a modification of these in that it involves oxidation of a cobalt(II) compound in the presence of acetylacetone.

Procedure

A mixture of 5 g. of cobalt(II) carbonate (0.042 mol) and 40 ml. of acetylacetone (ca. 0.4 mol) in a 125-ml. Erlenmeyer flask is heated to 90 to 100°. Then the mixture is stirred rapidly (preferably with a magnetic stirrer to avoid splashing) while 60 ml. of 10% hydrogen peroxide is added dropwise. Care must be taken during the initial minutes of the reaction not to add the hydrogen peroxide too rapidly, since considerable heat is evolved and rapid gas evolution causes frothing. The addition requires about 45 minutes. At the end of the reaction the liquid layer is an intense green color, and a quantity of green solid has been deposited. The mixture is chilled in an ice-salt bath and filtered. The crystals are dried at 110° and dis-

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† The Ohio State University, Columbus, Ohio.

solved in 50 ml. of boiling benzene. About 300 ml. of heptane or petroleum ether is added to the warm benzene solution, and the mixture is cooled in an ice-salt bath. The product is removed by filtration and air-dried. The yield is 10 to 12 g. (67 to 80%) of dark green crystals (m.p. 213°). *Anal.* Calcd. for $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$: C, 50.57; H, 5.94. Found:* C, 50.46; H, 6.14.

Properties

Cobalt(III) acetylacetonate forms dark green crystals (d 1.43),⁴ which are soluble in most organic solvents (except ligroin) but are insoluble in water. The compound is isomorphous with the corresponding aluminum, chromium(III), and manganese(III) compounds,⁴ all of which are monoclinic, belong to the space group C_{2h} ⁵, and have four molecules to the unit cell. The electric polarization³ of the compound and its rotatory dispersion⁵ have been measured. The dipole moment is 1.35×10^{-18} e.s.u.⁵ The compound is monomolecular in the vapor state² and in benzene solution.¹ Previously reported melting points of 240 to 241°¹⁻³ may suggest the possible existence of more than one crystalline form.

References

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* Values supplied by the checkers.

54. DICOBALT OCTACARBONYL

SUBMITTED BY IRVING WENDER,* HEINZ W. STERNBERG,* SOL METLIN,*
AND MILTON ORCHIN*

CHECKED BY M. A. LYNCH, JR.,† AND W. J. SESNY†

Dicobalt octacarbonyl has been prepared by the thermal decomposition of cobalt tetracarbonyl hydride¹ and by the reaction of suspensions of cobalt(II) compounds such as the carbonate in inert organic liquids with carbon monoxide under superatmospheric pressure.^{2,3} The procedure described here may be regarded as a modification of the second approach. It is superior to the first in giving a higher yield.

Procedure

Caution. Some cobalt tetracarbonyl hydride results in this reaction. Because of its toxicity, previously outlined precautions¹ must be observed.

In a 500-ml. stainless-steel autoclave‡ are placed 150 ml. of petroleum ether (boiling range 32 to 63°) and 15 g. of cobalt(II) carbonate (0.126 mol).§ The autoclave is flushed three times with carbon monoxide and is then filled with an approximately equimolar mixture of carbon monoxide and hydrogen to a pressure of 3500 p.s.i. The autoclave is heated with agitation to 150 to 160° and maintained in this temperature range for 3 hours. A maximum

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† Tonawanda Research Laboratory, Linde Air Products Company, Tonawanda, N.Y.

‡ The commercial rocking autoclave available from the American Instrument Co., Superpressure Division, Silver Spring, Md., is satisfactory. Consistently high yields are obtained after the autoclave has been used several times. Addition of small portions of preformed carbonyl also increases the yield.

§ Commercial cobalt(II) carbonates vary in cobalt content because of hydration and of the presence of basic compounds. The submitters state that preparations containing 46% cobalt are satisfactory.

pressure (ca. 4300 p.s.i.) is reached at 120°, but at the end of the reaction the pressure (at 155°) is about 3900 p.s.i. The autoclave is cooled to room temperature, the gases are vented carefully, and the autoclave is opened in a well-ventilated hood.

The clear, dark solution of dicobalt octacarbonyl is pipetted from the autoclave with a syringe and filtered through filter paper into an Erlenmeyer flask.* The flask is stored overnight in the freezing compartment of a refrigerator, whereupon large, well-formed crystals of the product are deposited.† The solvent is decanted, and the crystals are dried by passing a stream of dry carbon monoxide through the flask for several minutes. The dry crystals melt with decomposition at 51 to 52°. The yield is 15.6 to 16.8 g. (73 to 78%). The product is stored in a sealed tube containing carbon monoxide.

Properties

Several of the properties of dicobalt octacarbonyl have been summarized previously.¹ Ultraviolet and infrared spectra of the compound⁴⁻⁶ indicate a structure containing two bridging C=O groups, which amounts to two trigonal pyramids sharing an edge. The compound can be determined quantitatively by its reaction with iodine to give cobalt(II) iodide and carbon monoxide.⁷

References

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2. C. H. McKEEVER: U.S. patent 2,476,263 (July 12, 1949); *cf. C. A.*, **43**, 9397 (1949).
3. C. H. McKEEVER: U.S. patent 2,477,553 (July 26, 1949); *cf. C. A.*, **43**, 8107 (1949).

* If difficulty with filtration of the last few milliliters is encountered, this small amount of liquid should be discarded.

† Rapid cooling to very low temperature (-15 to -25°) causes the octacarbonyl to precipitate as a finely divided, orange powder. In this form, the compound decomposes in air to pyrophoric tetracobalt dodecacarbonyl, [Co(CO)₃]₄. Slow crystallization and storage under petroleum ether until the product is needed are recommended.

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55. COBALT TETRACARBONYL HYDRIDE

(Cobalt Hydrocarbonyl)

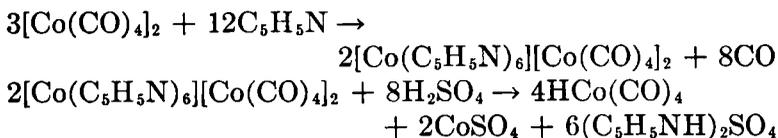
SUBMITTED BY HEINZ W. STERNBERG,* IRVING WENDER,* AND MILTON ORCHIN*

CHECKED BY M. A. LYNCH, JR.,† AND W. J. SESNY†

Cobalt tetracarbonyl hydride is prepared by the reaction of acids with salts containing the cobalt tetracarbonyl anion, $[\text{Co}(\text{CO})_4]^-$.¹⁻⁵ Alkali metal salts, obtained by treating alkaline cobalt(II) cyanide suspensions with carbon monoxide,^{1,4,6,7} can be employed,¹⁻³ but either the hexapyridinecobalt(II) salt or the pyridinium salt gives higher yields.⁵

Procedure A

Preparation from the Hexapyridinecobalt(II) Salt



Caution. In this and the following procedure, previously outlined⁴ precautions must be observed. A well-ventilated hood is essential.

A 500-ml. three-necked flask is provided with a separatory funnel, an outlet tube, and an inlet tube which is constricted at the tip to about 2 mm. and is inserted nearly to the bottom of the flask. The top of the separatory funnel and the inlet tube are connected through a T-tube

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arrangement. To the outlet tube is attached a 35- by 110-mm. drying tube containing an intimate mixture of phosphorus(V) oxide and glass beads.* This is attached in turn to a cold trap (30 by 280 mm.) immersed in liquid nitrogen. The outlet tube from the cold trap is connected to a tube dipping into 20 ml. of a solution of tris(1,10-phenanthroline)nickel(II) chloride.†

Three grams of dicobalt octacarbonyl (ca. 0.009 mol, synthesis 54) is placed in a 300-ml. Erlenmeyer flask equipped with a ground-glass connection. Twenty milliliters of c.p. pyridine (0.248 mol) is added, and the flask is fitted with a male ground-glass joint, to which is sealed a U-tube containing just enough mercury to prevent entry of air but permit escape of liberated carbon monoxide. Evolution of carbon monoxide is complete in a few minutes. The solution in the flask is decanted into the separatory funnel.‡ A solution of 25 ml. of 18 *M* sulfuric acid and 75 ml. of water is cooled to 0 to 5° and placed in the 500-ml. flask, and the flask is immersed in an ice bath. The apparatus is assembled and purged with carbon monoxide at a flow rate of about 300 ml./min. The pyridine solution is then added dropwise to the acidic solution in the flask, the rate of addition being so controlled that droplets of oily cobalt tetracarbonyl hydride forming on the surface of the aqueous solution disappear before more pyridine solution is added.§ About 45 to 60 minutes is required for complete addition. The flask is then swept with

* Desiccants such as calcium chloride, Drierite, or sulfuric acid give lower yields. Two drying tubes in series are advantageous if the synthesis is to be repeated several times.

† This solution prevents access by air to the cold trap and indicates the presence of any untrapped tetracarbonyl hydride by formation of a voluminous precipitate of composition $[\text{Ni}(o\text{-phen})_3][\text{Co}(\text{CO})_4]_2$ (*o*-phen represents 1,10-phenanthroline).

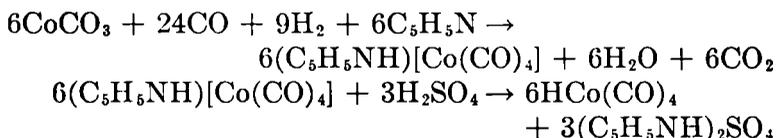
‡ The solution cannot be stored in contact with air, but the short exposure to air during transfer is not detrimental.

§ More rapid addition causes losses due to decomposition in the flask. Flow rates of carbon monoxide in excess of that recommended result in incomplete condensation of the product.

carbon monoxide for another 15 minutes. The yield of product condensed in the cold trap is 1.61 to 1.91 g. (80 to 95%).

Procedure B

Preparation from the Pyridinium Salt



Twenty grams of cobalt(II) carbonate (0.168 mol)* and 150 ml. of c.p. pyridine (1.86 mols) are placed in a 500-ml. stainless-steel autoclave (synthesis 54). The autoclave is flushed three times with carbon monoxide at a pressure of 200 p.s.i. An equimolar mixture of carbon monoxide and hydrogen is admitted to a pressure of 3500 p.s.i. The rocking mechanism is started, and the temperature is raised to 155 to 160° and maintained in this range for 2 hours.† The vessel is then allowed to cool to room temperature, and the gases are vented. The solution in the bomb contains about 2.5 g. of the pyridinium salt of the cobalt tetracarbonyl anion per 10 ml. (yield about 90%).‡

This solution is so diluted with pyridine that each 20 ml. contains 2.9 g. of the salt. The carbonyl hydride is then prepared as outlined in procedure A. The over-all yield is 20 to 23 g. (69 to 80%).

Properties

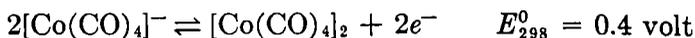
Certain of the properties of cobalt tetracarbonyl hydride have been summarized previously.⁴ The pure compound decomposes thermally by a second-order process⁵ to hydrogen and dicobalt octacarbonyl.⁸ The compound is strongly

* Based on a material containing 46% cobalt.

† Maximum pressure attained is about 4000 p.s.i. The pressure then falls and becomes constant at about 3100 p.s.i. at 155°.

‡ The checkers note that the addition of preformed dicobalt octacarbonyl improves the yield and emphasize that a yield of 70 to 80% would be more likely for an occasional synthesis of the compound.

acidic in aqueous solution.^{5,9} The tetracarbonyl anion is mildly reducing in character¹⁰

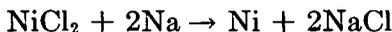


but the salts are much more stable than the parent acid. Structurally, the central cobalt atom is surrounded tetrahedrally by four C≡O groups,⁵ with the hydrogen in the hydride lying in one face of the tetrahedron and being bonded to three C≡O groups.¹¹⁻¹³ Precipitation of the cobalt tetracarbonyl anion as the tris(1,10-phenanthroline)-nickel(II) salt is the basis of a method of determining the species.¹⁴

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56. NICKEL POWDER



SUBMITTED BY T. P. WHALEY*

CHECKED BY C. C. CHAPPELOW, JR.†

Nickel powder can be prepared by reducing the oxide with hydrogen at 150 to 250°,^{1,2} by reducing a suspension of the chloride in ethyl ether with a Grignard reagent,³ by heating the formate or oxalate in the absence of oxygen at 250°,⁴ or by dissolving the aluminum from an aluminum-

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† Midwest Research Institute, Kansas City, Mo.

nickel alloy in alkaline solutions.⁵ A convenient laboratory procedure involves reduction of the anhydrous chloride with a sodium dispersion.⁶

Procedure

The apparatus employed for the preparation of sodium dispersions (Fig. 2, synthesis 2) is used without modification, except that a 500-ml. creased flask is more convenient than a 1-l. flask. To 100 ml. of *white* mineral oil (b.p. above 280°)* in the creased flask are added 24 g. of anhydrous nickel(II) chloride (0.185 mol)† and 16 g. of clean, freshly cut sodium (ca. 0.7 mol, synthesis 2). A slow nitrogen purge (about 0.2 l./min.) is started and is maintained throughout all subsequent operations. The contents of the flask are heated to about 105° and agitated vigorously with the stirrer operating at maximum speed; this will codisperse the sodium and nickel(II) chloride in the mineral oil. Heating and agitation are continued until a sudden temperature rise indicates that the threshold temperature has been reached and reaction has occurred. The temperature rise is accompanied by a color change from gray to black and takes place at about 250 to 270°. The heating current is turned off, and moderate agitation is continued until the temperature has dropped to approximately 50°. At this point, the stirring speed is reduced, and the excess unreacted sodium is destroyed by the slow addition of a solution of 20 ml. of isopropyl alcohol in 50 ml. of kerosine to the reaction mass.

The reaction mass is centrifuged‡ and the supernatant liquid decanted from the solids. The solid reaction mass—sodium chloride, sodium isopropoxide, and nickel powder—

* Carnation oil, supplied by L. Sonneborn Sons, Inc., New York, N.Y., was employed by both submitter and checker.

† Anhydrous nickel(II) chloride is prepared from the 6-hydrate by heating for 2 hours at 350° in a stream of dry hydrogen chloride. This operation is carried out conveniently in the reduction flask in order to eliminate subsequent handling.

‡ A large centrifuge is necessary for the quantities of liquid involved in this synthesis.

is washed* once with kerosine to remove the last traces of mineral oil and three times with isopropyl alcohol to remove the last traces of kerosine. The soluble sodium salts are then leached from the reaction mass with deaerated distilled water. Aqueous leaching is repeated until a silver nitrate test on the wash water shows no chloride ion present. The nickel powder is then washed successively with ethanol and ethyl ether and dried under vacuum. The product should be stored in an airtight container under a nitrogen or argon atmosphere and should be handled with the care required for a potentially pyrophoric material. The yield is quantitative.

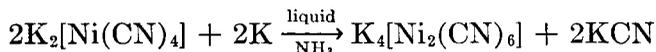
Properties

Nickel powder is light gray in color and may be pyrophoric in air if the particle size is sufficiently small. Nickel powder is useful as a catalyst for many organic chemical reactions or as a starting material for the synthesis of nickel compounds.

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57. POTASSIUM HEXACYANODINICKELATE(I)



SUBMITTED BY WAYLAND M. BURGESS† AND JOHN W. EASTES†

CHECKED BY WILLIAM E. PARKER‡ AND JACOB KLEINBERG‡

Reduction of aqueous solutions of potassium tetracyanonickelate(II), *e.g.*, by hydroxylamine, potassium amalgam, or tin and sodium hydroxide, yields a red solu-

* All washing operations are followed by centrifugation because the nickel powder is so finely divided that it remains suspended in the wash liquid.

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‡ University of Kansas, Lawrence, Kans.

tion from which a deep red solid can be precipitated by means of ethanol.^{1,2} This red substance contains unipositive nickel and has a composition corresponding to $K_2[Ni(CN)_3]$.^{1,2} The same substance can be prepared by reduction of a liquid ammonia solution of the nickel(II) complex with metallic potassium.² It has been shown that the anion in the complex is dimeric,^{3,4} and the compound is therefore formulated as $K_4[Ni_2(CN)_6]$.

The following directions describe the preparation of the nickel(I) compound in liquid ammonia solution.²

Procedure

An apparatus is constructed as indicated in Fig. 17. Individual sections of the apparatus are connected by

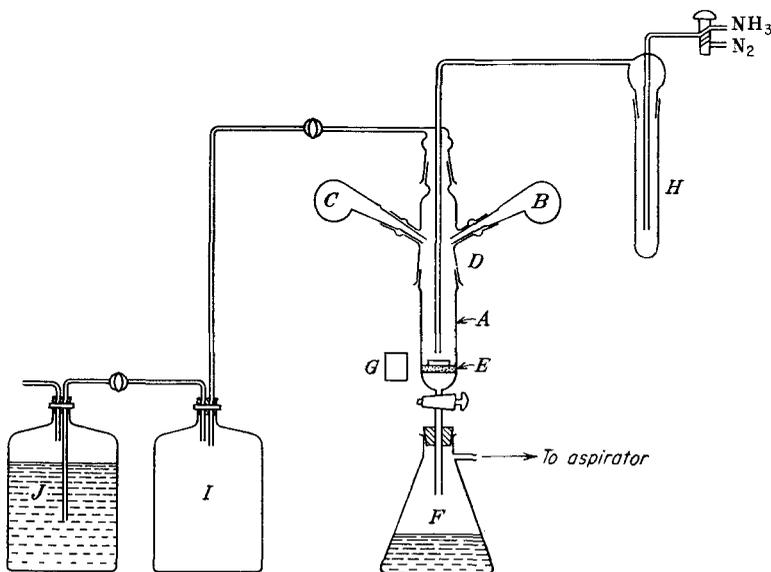


Fig. 17. Apparatus for the preparation of potassium hexacyanodnickelate(I).

means of flexible Tygon tubing. The reaction chamber *A* is about 3.5 cm. in diameter and 25 cm. high. Duplicate sampling bulbs *B* and *C* are inserted in the reaction chamber through ground-glass joints. A large standard-taper joint *D* permits the removal of the lower part of the reaction

chamber. The fritted-glass disk *E* sealed into the bottom of the chamber serves, after removal of the solvent into the filter trap *F* by means of an aspirator, to hold the insoluble nickel(I) complex formed in the reduction reaction. A magnetic stirrer *G* is arranged for agitation just above the fritted disk. A drying vessel *H*, equipped with a two-way stopcock for the admission of either nitrogen or ammonia, a 20-l. safety vessel *I*, and a 20-l. waste bottle *J* containing water complete the apparatus.

All pieces of the reaction vessel are first cleaned and then dried in an oven at 110°. The apparatus is then completely assembled except for the sampling bulbs *B* and *C*. The openings for the bulbs are stoppered with standard-taper plugs, and the system is swept out with dry nitrogen for at least 1 hour. One of the sampling bulbs is charged with about 0.8 g. of potassium tetracyanonickelate(II)⁵ (0.003 mol) previously dried to remove all water of crystallization, and to the other is added 0.06 g. of potassium metal (0.0015 mol) which has been cut and weighed under toluene.* Ammonia which has been dried by condensation on metallic sodium in drying vessel *H* with the use of a Dry Ice–Cellosolve bath is permitted to pass through the system, and the sampling bulbs are quickly inserted into the reaction chamber, a positive internal pressure of ammonia preventing air from entering the system during the insertion of the bulbs.

Between 60 and 70 ml. of dry ammonia is then condensed in the reaction chamber by cooling the latter with a Dry Ice–Cellosolve bath. The potassium tetracyanonickelate(II) is added by rotation of the appropriate sampling bulb, and the magnetic stirrer is started. The salt dissolves readily to form a yellow solution. The metallic potassium is then added. A bright red precipitate

* An excess of potassium tetracyanonickelate(II) is necessary to prevent reduction to potassium tetracyanonickelate(0). The desired nickel(I) complex is the only reduction product if at least a twofold excess of the nickel(II) complex is present.

forms immediately and settles out readily. After all the potassium has reacted, the liquid ammonia is removed with an aspirator, and the red product is washed several times with dry ammonia condensed in the reaction chamber. With a thin layer of ammonia standing over the product, the lower part of the reaction chamber is removed, plugged with a one-hole rubber stopper, and transferred to a dry box which has been flushed with gaseous ammonia for a period of hours. After evaporation of the cover of ammonia, the sample is transferred to a weighing bottle for analysis. The yield is approximately 0.33 g. (95%, based on the weight of potassium used).

Analysis

For analysis, the red product is dissolved in water. The resulting red solution is decolorized with oxygen and made slightly acidic with nitric acid. Aliquot portions of the solution are analyzed for potassium by precipitation of potassium hexanitrocobaltate(III), for cyanide by precipitation of silver cyanide, and for nickel by precipitation of the dimethylglyoxime derivative. *Anal.* Calcd. for $K_4[Ni_2(CN)_6]$: K, 36.3; Ni, 27.3; CN, 36.4. Found: K, 36.0; Ni, 27.1; CN, 35.8.

Properties

Potassium hexacyanodnickelate(I) is a bright red compound which reacts slowly in air to form a yellow solid. It is insoluble in ethanol and liquid ammonia but dissolves readily in water, giving a blood-red solution with strong reducing properties. In the presence of excess cyanide ion the unipositive nickel is rapidly oxidized by water to the dipositive condition. It has been reported¹ that acidification of aqueous solutions of the complex results in the precipitation of nickel(I) cyanide and that the latter dissolves in aqueous potassium cyanide with the formation of the original complex. Solutions of the unipositive nickel complex rapidly absorb carbon monoxide

to give the compound $K_2[Ni(CN)_3CO]$.⁶ X-ray measurements have suggested that a planar structure involving C=N bridging groups between the nickel(I) ions characterizes the anion.³ Infrared data favor an arrangement with C≡N bridging groups held to each nickel(I) ion by a half bond and a spin coupling of the two odd electrons on the two nickel(I) ions.⁴ The compound is diamagnetic.⁷

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58. SODIUM AND POTASSIUM NICKEL(IV) PARAPERIODATES

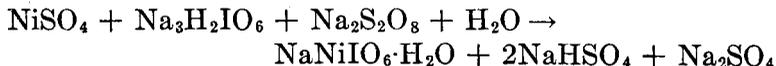
SUBMITTED BY P. RÂY*

CHECKED BY HAROLD M. STATE†

Compounds in which nickel is present in a higher oxidation state than 2+ are uncommon and often relatively unstable. Exceptions are found in sodium and potassium nickel(IV) paraperiodates, which have been described by Rây and Sarma¹ and which correspond to the formulation $Na(K)NiIO_6 \cdot xH_2O$. These compounds are readily prepared by peroxydisulfate oxidation of nickel(II) in the presence of periodate.

Procedure

A. SODIUM NICKEL(IV) PARAPERIODATE 1-HYDRATE



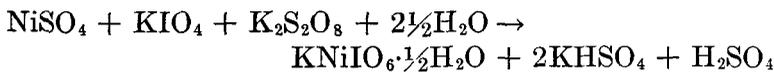
Five grams of trisodium dihydrogen paraperiodate (0.017 mol)² is suspended in 100 ml. of water. The sus-

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† Allegheny College, Meadville, Pa.

pension is warmed on a water bath, and 6 *N* sulfuric acid is added drop by drop until the solid dissolves completely. This solution is diluted to 250 to 300 ml. and heated to boiling. A solution of 2 g. of nickel(II) sulfate 7-hydrate (0.007 mol) in 15 ml. of water is added. The resulting solution is maintained at the boiling temperature while 8 g. of sodium peroxydisulfate (0.034 mol) is added in 0.4-g. increments with constant stirring over a period of 1 hour. As oxidation proceeds, the green color of the solution changes to red, and dark purple, almost black, metallic-appearing crystals of the product form.* These crystals are removed by filtration through a sintered-glass funnel and are washed eight to ten times with 10-ml. volumes of hot 1% sodium peroxydisulfate. Peroxydisulfate is then removed by washing them once or twice with hot water,† and the product is air-dried for 24 hours. The yield is 1.05 g. (46%, based on the nickel used). A small additional quantity of product can be obtained by heating the filtrate with a 2-g. portion of the peroxydisulfate. *Anal.* Calcd. for $\text{NaNiIO}_6 \cdot \text{H}_2\text{O}$: Na, 7.13; Ni, 18.19; I, 39.36; total active O, 24.79. Found: Na, 6.99, 7.3;‡ Ni, 18.20, 18.26;‡ I, 38.86, 40.64;‡ total active O, 24.35, 25.14.‡

B. POTASSIUM NICKEL(IV) PARAPERIODATE $\frac{1}{2}$ -HYDRATE



To a solution of 3 g. of potassium metaperiodate (0.013 mol) in 400 to 500 ml. of boiling water is added, with stirring, a solution of 2 g. of nickel(II) sulfate 7-hydrate (0.007 mol). The boiling solution is stirred vigorously and treated over a period of 25 to 30 minutes with 4 g. of

* The crystals adhere to the walls of the beaker and may form a bright mirror on that surface.

† Washing with water may cause some peptization of the product and consequent loss on filtration. Addition of a few drops of nitric acid to the wash water prevents peptization.

‡ Values reported by the checker.

potassium peroxydisulfate (0.015 mol) added in 0.40-g. increments.* Boiling is continued for 5 to 10 minutes after all the peroxydisulfate has been added. The dark red, almost black, crystals that form are allowed to settle† and are then washed several times by decantation, 100 ml. of 1% hot potassium peroxydisulfate solution being used for each wash. The product is transferred to a sintered-glass funnel‡ and washed repeatedly with boiling water to remove adsorbed periodate. All moisture is removed by suction, and final drying is effected at room temperature over anhydrous calcium chloride. The yield is under 1.4 g. (61.3%). An additional small quantity of product is obtained by treating the boiling filtrate with 4 g. of potassium peroxydisulfate according to the same procedure. *Anal.* Calcd. for $\text{KNiIO}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$: K, 11.84; Ni, 17.78; I, 38.48; total active O, 24.24. Found: K, 12.16, 12.5;§ Ni, 17.80, 18.09;§ I, 38.80, 39.21;§ total active O, 23.77, 24.71.§

Analysis

Nickel is determined by the gravimetric dimethylglyoxime procedure after reduction of the compound with sulfur dioxide and hydrochloric acid. Iodine is determined as silver iodide after reduction with sulfur dioxide in sulfuric acid medium. Total active oxygen is calculated by measuring the quantity of iodine liberated from potassium iodide in acidic solution. Alkali metals are determined as sulfates in the filtrates from the nickel determinations.

Properties

Sodium and potassium nickel(IV) paraperiodates are almost completely insoluble in cold water. They decom-

* The vigor of the reaction may necessitate removal of the flame from the bottom of the beaker during addition of the peroxydisulfate.

† The crystals tend to adhere to the walls of the beaker.

‡ The product undergoes reduction in contact with filter paper.

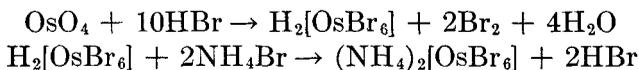
§ Values reported by the checker.

pose readily when heated and emit an odor of ozone in contact with the air. The existence of nickel in the tetrapositive state is suggested by the active oxygen contents of the compounds. A crystal lattice involving both NiO_6 and IO_6 octahedra is not unreasonable.^{1,3}

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59. AMMONIUM HEXABROMOOSMATE(IV)



SUBMITTED BY F. P. DWYER* AND J. W. HOGARTH*
CHECKED BY RICHARD N. RHODA†

Potassium and ammonium hexahaloosmates(IV) are commonly used as starting materials for the preparation of various other osmium compounds. Osmium(VIII) oxide is the most convenient source of osmium for the preparation of these hexahalo complexes.

Ammonium hexabromoosmate(IV) has been prepared by allowing sodium tetrasulfitodioxoosmate(VI) [obtained from osmium(VIII) oxide and sodium sulfite] to react with hydrobromic acid and then ammonium bromide;¹ by treating ammonium tetranitrodioxoosmate(VI) with hydrobromic acid;² and by refluxing osmium(VIII) oxide with constant-boiling hydrobromic acid containing a small quantity of ethanol, evaporating, and ultimately precipitating the product with ammonium bromide.³ The second procedure is somewhat less involved than the first but results in considerable loss of osmium material. The procedure given here is essentially a modification of the third approach. It gives the product with a minimum of laboratory manipulation and in quantitative yield. An important characteristic of the procedure is the limitation

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† The International Nickel Company, Inc., Bayonne, N.J.

of the quantity of water present, as dictated by the observation that hydroxylated products which are extremely resistant to reconversion to hexabromoosmate(IV) ion result in dilute hydrobromic acid solutions.⁴

Procedure

Caution. Osmium(VIII) oxide is extremely toxic. The yellow solid melts at 31° and has an appreciable vapor pressure even at room temperature. The compound is often liberated when solutions of osmium compounds are treated with oxidizing agents. Ample precautions to protect eyes, nose, and mouth are essential.

A 1-g. ampoule of osmium(VIII) oxide (ca. 0.004 mol)* is broken into a 100-ml. Erlenmeyer flask, and 36 ml. of 47% hydrobromic acid is added immediately. The mixture is boiled under reflux for 2 hours. The solution is decanted from the portions of broken glass into a 125-ml. beaker, and the flask is rinsed with an additional 7 ml. of the hydrobromic acid solution. To the hot solution in the beaker, 3 g. of ammonium bromide (0.03 mol) is added. After the solid has dissolved completely, the mixture is cooled to room temperature, and 50 ml. of absolute ethanol is added with stirring. The dense black solid which forms is allowed to settle† and is then washed by decantation with absolute ethanol until the washings are nearly free from bromide ion. The residue is transferred to a sintered-glass filter and washed on the filter with absolute ethanol until the filtrate gives no turbidity with ethanolic silver nitrate solution.‡ The product is then dried at 140°.

* Commercially available ampoules contain 0.96 to 1.008 g. of osmium(VIII) oxide. The ampoule should be opened carefully at its center and dropped immediately into the flask.

† If the precipitate settles slowly, it is more satisfactory to transfer it immediately to a sintered-glass filter and wash there. The washing is less efficient, however, and should be more thorough.

‡ Traces of water may cause some of the product to dissolve, giving washings with a yellowish tint. Ethanolic silver nitrate then gives a bluish color [colloidal silver hexabromoosmate(IV)], but the sensitivity of the test for bromide ion is not impaired.

The yield is 2.7 g. (ca. 96%). *Anal.* Calcd. for $(\text{NH}_4)_2\text{[OsBr}_6\text:]$: Os, 26.9; Br, 67.9. Found: Os, 26.9; Br, 68.0.

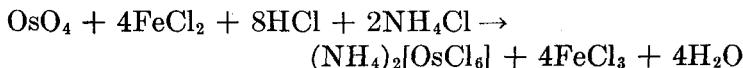
Properties

Ammonium hexabromoosmate(IV) crystallizes as minute black cubes and octahedra. The compound dissolves sparingly in cold water to give a red solution. Hot aqueous solutions deposit black osmium(IV) oxide. The compound is soluble in warm glycerol or ethylene glycol but is insoluble in ethanol or methanol.

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60. AMMONIUM HEXACHLOROOSMATE(IV)



SUBMITTED BY F. P. DWYER* AND J. W. HOGARTH*
CHECKED BY RICHARD N. RHODA†

Ammonium hexachloroosmate(IV) was originally prepared by heating a mixture of osmium and potassium chloride with chlorine, leaching the residue, and adding ammonium chloride.^{1,2} Wintrebert³ obtained the compound by allowing potassium tetranitrodioxoosmate(VI) to react with boiling hydrochloric acid and then adding ammonium chloride. Direct reduction of osmium(VIII) oxide with hydrochloric acid (analogous to synthesis 59) is inefficient because of similarities of oxidation potentials for the couples osmium(IV)-osmium(VIII) and chlorine(-I)-chlorine(0). Ethanol can be added as an auxiliary reducing agent,⁴ but better results are obtained with iron(II) chloride. The resulting hexachloroosmic(IV) acid

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† The International Nickel Company, Inc., Bayonne, N.J.

solution is then treated with ammonium chloride to give the product.

Procedure

Caution. The same precautions mentioned in synthesis 59 should be observed.

A 1-g. ampoule of osmium(VIII) oxide (0.004 mol) is broken into a 100-ml. Erlenmeyer flask (synthesis 59). Thirty milliliters of 12 *M* hydrochloric acid (0.36 mol) and 10 g. of either iron(II) chloride 6-hydrate (0.043 mol) or iron(II) chloride 4-hydrate (0.050 mol) are added. The flask is stoppered loosely and heated on a water bath with occasional shaking for 2 hours, whereupon the deep green color of the solution changes to orange-red. The solution is decanted from the broken glass into a 125-ml. beaker, and the flask is rinsed with 10 ml. of 12 *M* hydrochloric acid. Ten milliliters of 20% ammonium chloride solution (0.04 mol) is added, and the mixture is cooled with ice. The solid which forms is washed by decantation with 80% ethanol, transferred to a sintered-glass filter, and washed on the filter with absolute ethanol until free from chloride ion. It is then dried at 120°. The yield is 1.57 to 1.63 g. (91 to 94%). *Anal.* Calcd. for $(\text{NH}_4)_2[\text{OsCl}_6]$: Os, 43.35. Found: Os, 43.4.

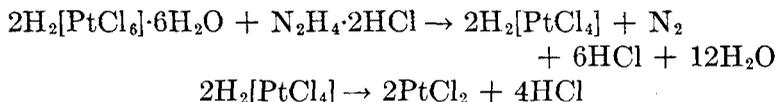
Properties

Ammonium hexachloroosmate(IV) crystallizes as deep red cubes and octahedra. It dissolves sparingly in cold water to give a greenish-yellow solution.

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61. PLATINUM(II) CHLORIDE



SUBMITTED BY WILLIAM E. COOLEY* AND DARYLE H. BUSCH*

CHECKED BY L. C. DRAKE† AND P. G. WALDO‡

The methods previously reported for the preparation of tetrachloroplatinic(II) acid¹ and platinum(II) chloride are laborious and difficult to control. Platinum(II) chloride has been prepared by the thermal decomposition of ammonium hexachloroplatinate(IV)² or of anhydrous platinum(IV) chloride.³ According to a recent report,⁴ hydrazine sulfate is an effective reducing agent for the preparation of tetrachloroplatinate(II) salts from the corresponding hexachloroplatinate(IV) salts. This procedure has been extended to the preparation of aqueous tetrachloroplatinic(II) acid and solid platinum(II) chloride.

Procedure

Ten and six-tenths grams‡ of pure hexachloroplatinic(IV) acid 6-hydrate (0.0205 mol) is dissolved in 50 ml. of water in a 150-ml. beaker. One and seven-hundredths grams of solid hydrazine dihydrochloride (0.0103 mol) is added in small portions to the solution. Each addition is followed by effervescence, which soon subsides. The total time of addition is about 5 minutes. The resulting cherry-red solution is placed on a steam bath and warmed until bubbling stops. Any traces of finely divided platinum (platinum black) which are present are then removed by filtration.§ The red solution is evaporated to dryness on a steam bath with the aid of a stream of air. The

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‡ This corresponds to three vials of the commercial product.

§ The solution should be examined very carefully for platinum black to avoid contamination of the product.

chocolate-brown residue, containing hydrochloric acid, tetrachloroplatinic(II) acid, and unreduced platinum(IV) chloride, is dried for 12 hours at 112° and then pulverized as completely as possible with a spatula. It is subsequently dried for 4 hours at 150°. These operations remove the hydrogen chloride. Unreduced platinum(IV) chloride and remaining traces of tetrachloroplatinic(II) acid are removed by warming the solid on a steam bath with 10 ml. of water and decanting through a filter. This extraction is repeated three to four times, and the product is poured on the filter with the last extract. It is then washed with a few milliliters of cold water and dried at 110° for 2 hours. The yield is 4.4 to 4.9 g. (81 to 90%).

Analysis

The platinum content is determined by igniting a 1-g. sample in a weighed crucible.* For determination of chloride, 0.5 g. of the sample is placed in a 100-ml. beaker with 35 ml. of water and 10 ml. of 15 *N* aqueous ammonia. About 0.5 ml. of 16 *N* nitric acid is added, and the mixture is heated with occasional stirring until solution is complete. The solution is treated with 1 g. of silver nitrate dissolved in 5 ml. of water and with sufficient 16 *N* nitric acid to render it definitely acidic. The suspension is warmed to coagulate the precipitated silver chloride and filtered. The residue is dried at 110° and weighed. *Anal.* Calcd. for PtCl₂: Pt, 73.35; Cl, 26.65. Found: Pt, 72.65, 73.19, † 72.85, † 73.40; † Cl, 26.89, 26.63, † 26.88, † 26.80. †

Properties

Platinum(II) chloride, prepared in this manner, is a chocolate-brown solid. It is insoluble in water but soluble in hydrochloric acid and aqueous ammonia, in which

* The checkers note that the tendency of platinum(II) chloride to creep up the sides of the crucible during heating can be overcome by reducing the compound with a few drops of hydrazine hydrate prior to heating.

† Values reported by the checkers.

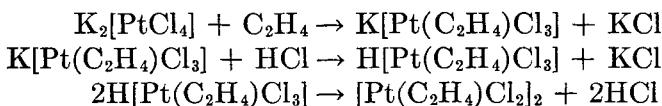
media it forms tetrachloroplatinic(II) acid and tetraammineplatinum(II) chloride, respectively. Unlike platinum(II) chloride prepared by thermal decomposition of platinum(IV) chloride,³ the product obtained in this procedure dissolves without leaving a residue of metallic platinum.

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62. TETRACHLORO(DIETHYLENE)DIPLATINUM(II)

[Dichloro(ethylene)platinum(II) Dimer]



SUBMITTED BY J. CHATT* AND M. L. SEARLE*

CHECKED BY C. F. LIU† AND C. ELMER WYMORE†

It is probable that tetrachloro(diethylene)diplatinum(II) was first prepared by Zeise by decomposition of trichloro(ethylene)platinic(II) acid.¹ Boiling hexachloroplatinic(IV) acid with chloroform also gave the compound.² However, it was first obtained in sufficient quantity for investigation by Anderson,³ who boiled an ethanolic solution of sodium hexachloroplatinate(IV) 6-hydrate until reduction to platinum(II) was complete. This procedure is tedious, and the yields are affected markedly by impurities in the platinum salt and by the presence of other platinum metals.⁴ Optimum yields of 75% are obtained only after much experience. The general method of Kharasch and Ashford,⁵ involving adding an olefin to a suspension of platinum(IV) chloride in warm benzene or glacial acetic

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acid, is not suitable for preparation of tetrachloro(diethylene)diplatinum(II). The method described here is reliable and gives excellent yields of pure material.⁶ The starting material, Zeise's salt or potassium trichloro(ethylene)platinate(II), is obtained by a modification of the method of Chernyaev and Hel'man.⁷

Procedure

A 250-ml. distilling flask *A*, with the side arm bent as shown in Fig. 18, is clamped in a vibratory shaker. Two

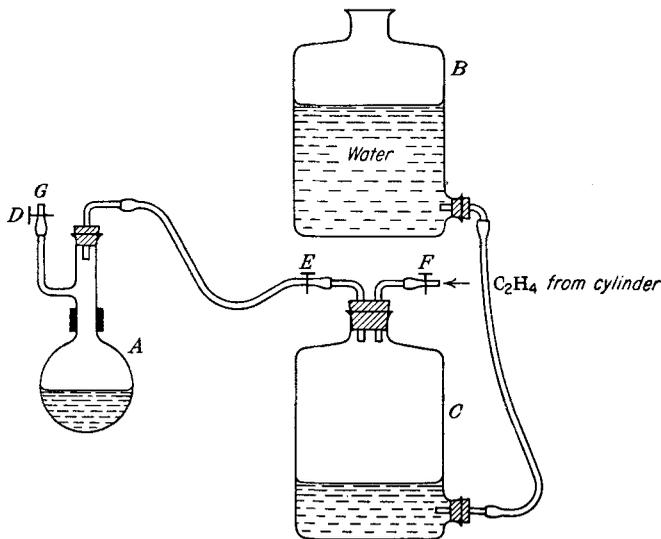


FIG. 18. Apparatus for the reaction of potassium tetrachloroplatinate(II) with ethylene.

2-l. aspirator bottles *B* and *C* are arranged as shown. Bottle *C* is a reservoir for ethylene, which is maintained under slight pressure by water in bottle *B*. All parts of the apparatus are connected by thick-walled rubber tubing provided with screw clamps (or stopcocks) *D*, *E*, and *F*.

Twenty grams of potassium tetrachloroplatinate(II) (0.048 mol) is placed in flask *A*, and a solution of 10 ml. of hydrochloric acid (sp. gr. 1.18) in 90 ml. of water is

added.* Vessel *C* is filled completely with water, and with clamp *E* closed sufficient ethylene is introduced through *F* to fill *C* and force water into *B*. Clamp *F* is then closed. The flask *A* is attached to a water pump at *G* and evacuated as completely as possible with clamp *D* open and *E* closed. Screw clamp *D* is closed and *E* opened slowly to fill the flask with ethylene. The process is repeated twice to remove air completely. Bottle *C* is then refilled with ethylene, and with clamp *E* open flask *A* is shaken for about 240 hours† at ca. 20°. During this time, the solution changes from dark red to golden-yellow in color. The solution is then poured into an evaporating dish and covered with a watch glass to prevent loss by spattering. It is evaporated to dryness in a vacuum desiccator containing some 18 *M* sulfuric acid and a dish of potassium hydroxide pellets. The resulting residue is a mixture of yellow crystals of potassium trichloro(ethylene)platinate(II) with small quantities of potassium chloride and traces of dark red unreacted potassium tetrachloroplatinate(II). The material is crushed and extracted with 200 ml. of ethanol containing 8 ml. of hydrochloric acid (sp. gr. 1.18).‡ The suspension is filtered through a Büchner funnel to remove potassium chloride. The yellow filtrate is evaporated to dryness under reduced pressure (12 mm. Hg) in a 500-ml. round-bottomed flask *A* (Fig. 19), which is equipped with a splash head *B* and a capillary air leak *C*, and is placed on a water bath. The capillary is connected to a calcium chloride drying tube. The temperature of the solution is maintained at about

* The submitters report that substitution of an ethanolic solution of sodium tetrachloroplatinate(II) reduces the time necessary for ethylene absorption to 1 day.

† The checkers, using one-fourth the recommended quantities, find that 120 hours is sufficient to produce the desired color change. Even with the quantities recommended, the yield is only slightly decreased by saturation for 120 hours.

‡ This is about 100% in excess of the theoretical quantity required for precipitating all of the potassium in potassium trichloro(ethylene)platinate(II) acid as the chloride.

20° until the color deepens to a yellow-orange. The temperature is then raised slowly to 60°, and the flask is shaken to assist solidification. The viscous orange liquid crystallizes suddenly. Crystals of tetrachloro(diethylene)-diplatinum(II) so formed are transferred immediately to a small bottle and stored in a desiccator. The yield is 13.0 to 13.5 g. [90 to 95%, based on potassium tetrachloroplatinate(II)].

The product (decomp. 160 to 165°) is purified as follows:* Five grams of the crude material is added to 80 ml. of toluene at the boiling temperature of the latter. About 30 mg. of dry animal charcoal is added to remove colloidal platinum. The suspension is boiled under reflux for about

2 minutes† and then filtered rapidly through a fluted paper in a heated funnel. The filtrate is cooled in an ice bath and stirred vigorously. The resulting solid, consisting of long, pale orange needles and larger, darker orange granular crystals, is removed by filtration, washed with toluene, and dried in a vacuum desiccator over sulfuric acid. The yield is 2.7 g. (54%). The mother liquor is used to dissolve an additional 2.7 g. of the crude product and then yield about 2.1 g. of the pure material. The process is then repeated with another 2.7 g. of crude product. The

* All operations must be carried out rapidly to prevent decomposition to dark-colored products. Recrystallization of a small quantity each time causes the least loss of product.

† A small quantity of material may remain undissolved, but losses by decomposition in the time necessary for complete solution more than offset any gains in dissolved product.

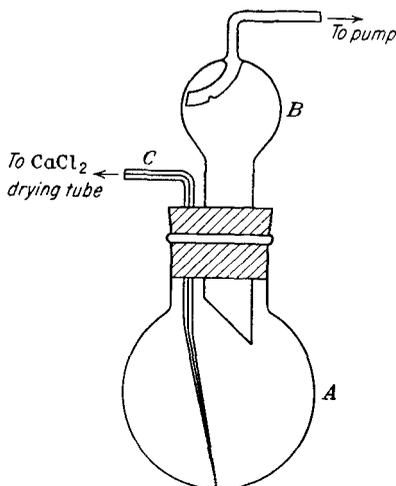


FIG. 19. Apparatus for the crystallization of tetrachloro(diethylene)diplatinum(II).

pure material so obtained is sensitive to moisture and darkens after exposure to the air for a few hours. It darkens also when heated to 190° and decomposes rapidly at 210°.

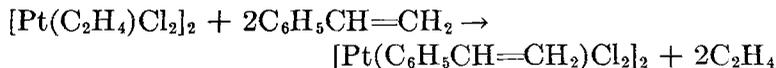
Potassium trichloro(ethylene)platinate(II) 1-hydrate can be isolated in about a 7-g. quantity by cooling to 0° the yellow aqueous solution obtained from flask A (Fig. 18) after absorption of ethylene is complete. Tetrachloro-(dipropylene)diplatinum(II) can be prepared by the same procedure used for the ethylene compound except that twice the time of shaking is needed for propylene absorption and that final evaporations must be carried out below 40°. ⁶

Properties

The needle and granular crystals are dimorphic forms of tetrachloro(diethylene)diplatinum(II), the granular form being the more stable. The needle form is obtained upon rapid cooling of the saturated solution but changes into the granular form upon standing in contact with the mother liquor. Both forms undergo slow reduction to platinum in contact with the mother liquor. Tetrachloro-(diethylene)diplatinum(II) is only slightly soluble in most organic liquids, but it dissolves readily in acetone or ethanol. Its solution in ethanol darkens rapidly when warmed.

The more important chemical characteristics of tetrachloro(diethylene)diplatinum(II) can be summarized as follows:

1. Ethylene is readily displaced by less volatile olefins. This provides a convenient method for preparing complexes containing these hydrocarbons, ³ *e.g.*,

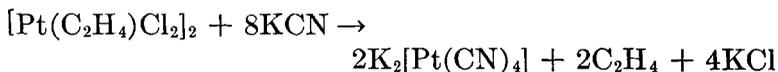


2. Trichloro(ethylene)platinate(II) ion is formed by reaction with aqueous chloride solutions³

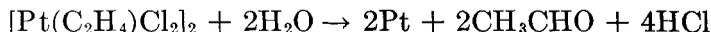


Fairly rapid decomposition occurs in neutral solutions, but the compound is stable almost indefinitely in 3% hydrochloric acid.⁷

3. Ethylene is liberated when cyanides or other substances that coordinate strongly with platinum(II) are added³



4. Platinum and acetaldehyde are formed with boiling water³



5. A yellow, crystalline, thermally unstable complex of composition $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{Cl}_2]$ (trans form?) is obtained by reaction with ethylene in acetone solution at -80° ⁸



6. A white, insoluble substance of composition $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{Cl}_2]$ (cis form?) is obtained by reaction with ethylene in acetone solution at room temperature.

General accounts of the properties and possible structures of these olefin complexes are available.^{6,9-11}

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SUBJECT INDEX

Names employed in the cumulative subject index for Volumes I to V are based upon those adopted in Volume II (Appendix, page 257) with a few changes that have been standardized and approved since publication of Volume II. Some of the general principles that have been followed in setting up the index are: (1) The Stock system, based on the use of Roman numerals to designate oxidation state, has been generally preferred; for example, *Iron(III) chloride*, rather than ferric chloride; *Potassium hexachlororhenate(IV)* rather than potassium chlororhenite. (2) In the case of heteropoly acids, the structure-determining element is named last, as for instance, *12-Tungstophosphoric acid* instead of phosphotungstic acid. (3) General headings such as *Chromium(III) complex compounds* and *Ammines* are employed for grouping coordination compounds of similar types. In addition, entries are made under the specific names for individual compounds. (Halogeno and cyano complexes, however, have been entered only under their specific names.) (4) Numerical prefixes and prefixes such as "ortho-" and "meta-" (but not "hypo-" and "per-") have been dropped at the beginning of many names to form general headings covering classes of compounds, such as *Silicon chlorides* and *Phosphoric acids*. (5) Formulas for specific compounds are used under general headings. The Formula Index should also prove particularly helpful in troublesome cases. (6) Because of changes in practice since the appearance of Volume I, it has been deemed advisable to make extra entries or cross references under names that have been changed and under many specific names for compounds entered also under general headings. (7) Two entries are made for compounds having two cations. (8) Unsatisfactory names that have been retained for want of better ones are placed in quotation marks.

Inverted names are used only for derivatives of silanes (as *Silane, dibromo-*; and *Disilane, hexachloro-*), germanes, phosphine, and the like, but not for the few organic compounds. For the nomenclature of some of these and other classes of compounds, see the heading *Nomenclature*.

Headings are alphabetized straight through, letter by letter, as in *Chemical Abstracts* indexes, not word by word. Roman numerals in Stock names are ignored in alphabetizing unless two or more names are otherwise the same.

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 of, with hafnium phosphate,
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FORMULA INDEX

The chief aim of this formula index, like that of other formula indexes, is to help in locating specific compounds, or even groups of compounds, that might not be easily found in the Subject Index. To this end, formulas have been used wherever it seemed best in their usual form (*i.e.*, as used in the text) for easy recognition: PbO_2 , EuSO_4 , Si_2Cl_6 , ThOBr_2 . However, for compounds containing the more uncommon elements and groupings and also for complexes, the significant or central atom has been placed first in the formula in order to throw together as many related compounds as possible. This procedure usually involves placing the cation last (often of relatively minor interest, especially in the case of alkali and alkaline earth metals): PtCl_4K_2 ; $[\text{Al}(\text{C}_2\text{O}_4)_3]\text{K}_3 \cdot 3\text{H}_2\text{O}$; $(\text{IO}_6)_2\text{Ba}_3\text{H}_4$. The guiding principle in these cases has been the chapter in the text in which the preparation of a compound is described. Where there is likely to be almost equal interest in two or more parts of a formula, two or more entries have been made: AgClO_3 and ClO_3Ag ; Al_2Se_3 and Se_3Al_2 ; SF_6 and F_6S (simple halides other than fluorides are entered only under the other elements in most cases); NaNH_2 and NH_2Na ; $\text{NH}_2\text{SO}_3\text{H}$ and $\text{SO}_3\text{H}\text{NH}_2$.

Formulas for organic compounds are structural or semistructural so far as possible: $\text{CH}_3\text{COCH}_2\text{COCH}_3$. Consideration has been given to probable interest for inorganic chemists, *i.e.*, any element other than carbon, hydrogen, or oxygen in an organic molecule is given priority in the formula if only one entry is made, or equal rating if more than one entry; $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4 \cdot 10\text{H}_2\text{O}$; $\text{NaC}\equiv\text{CH}$ and $\text{CH}\equiv\text{CNa}$.

The names used with the formulas are the preferred specific names.

The formulas are listed alphabetically by atoms or by groups (considered as units) and then according to the number of each in turn in the formula rather than by total number of atoms of each element. This system results in arrangements such as the following:

$\text{NH}_2\text{SO}_3\text{NH}_2$
 $(\text{NH}_2)_2\text{C}_2\text{H}_4$ (instead of $\text{N}_2\text{H}_4\text{C}_2\text{H}_4$, $\text{N}_2\text{H}_3\text{C}_2$, or $\text{C}_2\text{H}_3\text{N}_2$)
 NH_3

$\text{Si}(\text{CH}_3)\text{Cl}_3$
 $\text{Si}(\text{CH}_3)_3\text{Cl}$
 $\text{Si}(\text{CH}=\text{CH}_2)\text{Cl}_3$
 $\text{Si}(\text{C}_2\text{H}_4\text{Cl})\text{Cl}_3$

Cr(CN)₆K₃ (instead of CrC₆N₆K₃)
 Cr(C₂H₃O₂)₂ (instead of CrC₄H₆O₄)
 [Cr(C₂O₄)₃]K₃·3H₂O (instead of CrC₆O₁₂K₃·H₆O₃ or CrC₆O₁₅K₃H₆)
 [Cr(en)₂Cl₂]Cl·H₂O ("en" is retained for simplicity and is alphabetized as such rather than as C₂H₄(NH₂)₂ or (NH₂)₂C₂H₄)

A

- AgCl Silver chloride, 1:3
 AgClO₃ Silver chlorate, 2:4
 AgF Silver(I) fluoride, 4:136; 5:19, 20
 AgF₂ Silver(II) fluoride, 3:176
 AgI Silver iodide, 2:6
 AgO Silver(II) oxide, 4:12
 Ag₂CN₂ Silver cyanamide, 1:98
 Ag₂CO₃ Silver(I) carbonate, 5:19
 Ag₂F Disilver fluoride, 5:18, 19
 Ag₂PO₃F Silver monofluorophosphate, 3:109
 Ag₇O₈NO₃ Silver oxynitrate, 4:13
 AlBr₃ Aluminum bromide, 3:30, 33
 [Al(C₂O₄)₃]K₃·3H₂O Potassium trioxalatoaluminate, 1:36
 Al(C₅H₇O₂)₃ Aluminum acetylacetonate, 2:25
 [AlCl₄]⁻[SeCl₃]⁺ Aluminum chloride compound, with selenium(IV) chloride, 5:127
 AlCs(SO₄)₂·12H₂O Cesium alum, 4:8
 AlP Aluminum phosphide, 4:23
 Al₂I₆ Aluminum iodide, 4:117
 Al₂Se₃ Aluminum selenide, 2:183, 184
 AsF₃ Arsenic(III) fluoride, 4:137, 150
 AsI₃ Arsenic(III) iodide, 1:103
 AuBr₄K Potassium tetrabromoaurate(III), 4:14, 16
 AuCl₄H Tetrachloroauric(III) acid, 4:14, 15

B

- BBr₃ Boron bromide, 3:27, 29
 BCl₃ Boron chloride, 3:27, 28, 29

- BCl₃·(CH₃)₃N Boron chloride-trimethylamine, 5:27
 BF₃ Boron fluoride, 1:21, 23; compound with hexamethyldisilazane, 5:58
 BF₃·(CH₃)₃N Boron fluoride-trimethylamine, 5:26
 BF₄H Tetrafluoroboric acid, 1:25
 BF₄K Potassium tetrafluoroborate, 1:24
 BF₄NH₄ Ammonium tetrafluoroborate, 2:23
 B(O₂C₂H₅)₃ Ethyl orthoborate, 5:29
 B₂O₃ Boron oxide, 2:22
 Ba(BrO₃)₂·H₂O Barium bromate, 2:20
 Ba(SCN)₂ Barium thiocyanate, 3:24
 Be(C₅H₇O₂)₂ Beryllium acetylacetonate, 2:17
 Be(C₆H₉O₃)₂ Beryllium derivative of ethyl acetoacetate, 2:19
 Be(C₁₀H₉O₂)₂ Beryllium derivative of benzoylacetone, 2:19
 Be(C₁₅H₁₁O₂)₂ Beryllium derivative of dibenzoylmethane, 2:19
 BeCl₂ Beryllium chloride, 5:22
 (BeO)_x·(BeCO₃)_y Beryllium carbonate, 3:10
 Be₄O(CHO₂)₆ Beryllium formate, 3:7, 8
 Be₄O(C₂H₃O₂)₂(C₄H₇O₂)₄ Beryllium diacetate tetraisobutyrate, 3:7
 Be₄O(C₂H₃O₂)₃(C₃H₅O₂)₃ Beryllium triacetate tripropionate, 3:7, 8
 Be₄O(C₂H₃O₂)₆ Beryllium acetate, 3:4, 7, 8, 9

- $\text{Be}_4\text{O}(\text{C}_3\text{H}_5\text{O}_2)_6$ Beryllium propionate, **3:7**, 8, 9, 10
 $\text{Be}_4\text{O}(\text{C}_4\text{H}_7\text{O}_2)_6$ Beryllium butyrate, **3:7**, 8
 Beryllium isobutyrate, **3:7**, 8
 $\text{Be}_4\text{O}(\text{C}_5\text{H}_9\text{O}_2)_6$ Beryllium isovalerate, **3:7**
 Beryllium pivalate, **3:7**, 8
 $\text{Be}_4\text{O}(\text{C}_7\text{H}_4\text{ClO}_2)_6$ Beryllium *o*-chlorobenzoate, **3:7**
 $\text{Be}_4\text{O}(\text{C}_7\text{H}_5\text{O}_2)_6$ Beryllium benzoate, **3:7**
 BiI_3 Bismuth(III) iodide, **4:114**
 $2\text{Bi}(\text{NO}_3)_3 \cdot 3\text{Mg}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ Bismuth magnesium nitrate, **2:57**
 $\text{BrCl}_2\text{N}(\text{CH}_3)_4$ Tetramethylammonium dichlorobromate(I), **5:172**
 BrF Bromine(I) fluoride, **3:185**
 BrF_3 Bromine(III) fluoride, **3:184**
 BrF_5 Bromine(V) fluoride, **3:185**
 BrH Hydrobromic acid, **1:151**, 152, 155
 Hydrogen bromide, **1:39**, 114, 149, 150, 151, 152
 $(\text{BrO}_3)_2\text{Ba} \cdot \text{H}_2\text{O}$ Barium bromate, **2:20**
 Br_2NH Dibromamide, **1:62**, 64
 $\text{Br}_3\text{N}(\text{CH}_3)_4$ Tetramethylammonium dibromobromate(I), **5:172**
 $\text{Br}_3\text{N}(\text{C}_4\text{H}_9)_4$ Tetrabutylammonium dibromobromate(I), **5:177**
- C**
- CF_4 Carbon tetrafluoride, **1:34**; **3:178**
 $\text{CH}\equiv\text{CH}$ Acetylene, **2:76**
 $\text{CH}\equiv\text{CNa}$ Monosodium acetylide, **2:75**, 76, 79
 $\text{CH}_3\text{COCH}_2\text{COCH}_3$ Acetylacetone (2,4-pentanedione), **2:10**
 $\text{CH}_3\text{CO}_2\text{C}_3\text{H}_7$ Isopropyl acetate, **3:48**
 $\text{CH}_3\text{CO}_2\text{H}$ Acetic acid, **2:119**
 Cl_4 Carbon tetraiodide, **3:37**
 $(\text{CN})_2$ Cyanogen, **5:43**, 44
 $(\text{CN})_2$ Paracyanogen, **2:92n**.
 CNCl Cyanogen chloride, **2:90**, 93
 $(\text{CN})_2\text{Ni}$ Nickel cyanide, **2:228**
 $\text{C}(\equiv\text{NH})(\text{NH}_2)\text{NHCN}$ Dicyanodiamide, **3:43**
 $[\text{C}(\equiv\text{NH})(\text{NH}_2)_2\text{H}]\text{NO}_3$ Guanidinium nitrate, **1:94**, 96, 97
 $[\text{C}(\text{NH}_2)_2(\text{N}_2\text{H}_3)]\text{HCO}_3$ Aminoguanidonium hydrogen carbonate, **3:45**
 CN_2Ag_2 Silver cyanamide, **1:98**
 CN_2H_2 Cyanamide, **3:39**, 41
 $\text{CNa}\equiv\text{CNa}$ Disodium acetylide, **2:79**, 80
 CO Carbon monoxide, **2:81**
 $\text{CO}(\text{N}_3)_2$ Carbonyl azide, **4:35**
 CO_2 Carbon dioxide, **5:44n**.
 $\text{C}_2\text{N}_2\text{Cl}_3$ Cyanuric chloride, **2:94**
 $[\text{C}_6\text{H}_4(\text{OH})\text{CH}=\text{NCH}_2]_2$ *N,N'*-Disalicylaethylenediamine, **3:198**
 CaCO_3 Marble, **2:49**
 CaF_2 Calcium fluoride, **4:137**
 $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ Calcium dihydrogen orthophosphate 1-hydrate, **4:18**
 $\text{Ca}(\text{OCl})_2$ Calcium hypochlorite, **5:161**, 165
 CdCl_2 Cadmium chloride, **5:154**
 $\text{Ce}(\text{NO}_3)_3$ Cerium(III) nitrate, **2:51**
 $2\text{Ce}(\text{NO}_3)_3 \cdot 3\text{Mg}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ Cerium(III) magnesium nitrate, **2:57**
 ClH Hydrogen chloride, **1:147**; **2:72**; **3:14**, 131; **4:57**, 58; **5:25n**.
 ClNH_2 Chloramide, **1:59**, 62; **5:92**
 ClNO Nitrosyl chloride, **1:55**, 57; **4:48**
 ClNO_2 Nitryl chloride, **4:52**
 ClOH Hypochlorous acid, **5:160**, 164; 2-hydrate, **5:161**
 ClONa Sodium hypochlorite, **1:90**; **5:159n**.
 $(\text{ClO})_2\text{Ca}$ Calcium hypochlorite, **5:161**, 165
 ClO_2 Chlorine(IV) oxide, **4:152**; 8-hydrate, **4:158**
 ClO_2Na Sodium chlorite, **4:156**
 ClO_3Ag Silver chlorate, **2:4**
 ClO_3H Chloric acid, **5:161**, 164

- ClO_3Na Sodium chlorate, **5**:159*n*.
 ClO_4H Perchloric acid, **2**:28
 $(\text{ClO}_4)_3\text{Ga}\cdot 6(\text{and } 9\frac{1}{2})\text{H}_2\text{O}$ Gallium(III) perchlorate, **2**:26, 28
 $\text{ClSO}_3(\text{C}_2\text{H}_4\text{Cl})$ 2-Chloroethyl chlorosulfonate, **4**:85
 ClSO_3H Chlorosulfonic acid, **4**:52
 Cl_2O Chlorine(I) oxide, **5**:156, 158, 159, 162
 Cl_3N Nitrogen(III) chloride, **1**:65, 67
 Cl_6C_2 Hexachloroethane, **4**:124
 $\text{Co}(\text{CN})_6\text{K}_3$ Potassium hexacyanocobaltate(III), **2**:225
 $[\text{Co}(\text{CO})_3]_4$ Tetracobalt dodecacarbonyl, **2**:243; **5**:191*n*.
 $[\text{Co}(\text{CO})_4](\text{C}_5\text{H}_5\text{NH})$ Cobalt tetracarbonyl hydride, pyridinium salt, **5**:194
 $\text{Co}(\text{CO})_4\text{H}$ Cobalt tetracarbonyl hydride, **2**:238, 240; **5**:190, 192, 194
 $\text{Co}(\text{CO})_4\text{K}$ Cobalt tetracarbonyl hydride, potassium salt, **2**:238
 $[\text{Co}(\text{CO})_4]_2$ Dicobalt octacarbonyl, **2**:238, 242; **5**:190, 194
 $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{C}_5\text{H}_5\text{N})_6]$ Cobalt tetracarbonyl hydride, hexapyridinecobalt(II) salt, **5**:192
 $[\text{Co}(\text{CO})_4]_2[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_3]$ Cobalt tetracarbonyl hydride, tris-(1,10-phenanthroline)nickel(II) salt, **5**:193*n*, 195
 $[\text{Co}(\text{C}_2\text{O}_4)_3]\text{K}_3$ Potassium trioxalatocobaltate(III), **1**:37
 $[\text{Co}(\text{C}_5\text{H}_5\text{N})_6][\text{Co}(\text{CO})_4]_2$ Cobalt tetracarbonyl hydride, hexapyridinecobalt(II) salt, **5**:192
 $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$ Cobalt(III) acetylacetonate, **5**:188
 $\text{Co}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)\text{H}_2$ Cobalt ethylenediaminetetraacetate, **5**:187*n*.
 $[\text{Co}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)]\text{K}$ Potassium (ethylenediaminetetraacetato)cobaltate(III), **5**:186
 $[\text{Co}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)]\text{Na}$ Sodium (ethylenediaminetetraacetato)cobaltate(III), **5**:186
 $[\text{Co}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)]_2\text{Ba}\cdot 4\text{H}_2\text{O}$ Barium (ethylenediaminetetraacetato)cobaltate(III) 4-hydrate, **5**:186
 $\{[\text{Co}(\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2)]_2\text{H}_2\text{O}\}$ Bis-[*N,N'*-disalicylaethylenediamine- μ -aquadicobalt(II)], **3**:196, 198, 200
 CoCl_2 Cobalt(II) chloride, **5**:154
 $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ *cis*- and *trans*-Dichlorobis(ethylenediamine)cobalt(III) chloride, **2**:222, 223, 224
 $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{NO}_2$ *cis*-Dinitrobis(ethylenediamine)cobalt(III) nitrite, **4**:178
 $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{NO}_3$ *cis*- and *trans*-Dinitrobis(ethylenediamine)cobalt(III) nitrate, **4**:176, 177
 $[\text{Co}(\text{en})_3]\text{Cl}_3$ Tris(ethylenediamine)cobalt(III) chloride, **2**:221
 CoF_3 Cobalt(III) fluoride, **3**:175
 $[\text{Co}\{\text{NH}(\text{C}_5\text{H}_4\text{N})_2\}\text{Cl}_2]$ Dichloro-(di-2-pyridylamine)cobalt(II), **5**:184
 $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ Bromopentamminecobalt(III) bromide, **1**:186
 $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ Chloropentamminecobalt(III) chloride, **5**:185
 $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{NO}_3$ Carbonatopentamminecobalt(III) nitrate, **4**:171
 $[\text{Co}(\text{NH}_3)_5\text{C}_2\text{H}_3\text{O}_2](\text{NO}_3)_2$ Acetato-pentamminecobalt(III) nitrate, **4**:175
 $[\text{Co}(\text{NH}_3)_5\text{F}](\text{NO}_3)_2$ Fluoropentamminecobalt(III) nitrate, **4**:172
 $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Br}_3$ Aquopentamminecobalt(III) bromide, **1**:187, 188
 $[\text{Co}(\text{NH}_3)_5\text{I}](\text{NO}_3)_2$ Iodopentamminecobalt(III) nitrate, **4**:173
 $[\text{Co}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$ Nitrosylpentamminecobalt(II) chloride, **4**:168; (corr.), **5**:185
 Nitrosylpentamminecobalt(III) chloride, **4**:168; (corr.), **5**:185

- [Co(NH₃)₅NO₂](NO₃)₂ Nitropentamminecobalt(III) nitrate, **4**:174
- [Co(NH₃)₅NO₂](NO₃)₂ Nitratopentamminecobalt(III) nitrate, **4**:174
- [Co(NH₃)₆]Br₃ Hexamminecobalt(III) bromide, **2**:219
- [Co(NH₃)₆]Cl₃ Hexamminecobalt(III) chloride, **2**:127; 6-ammoniate, **2**:220
- [Co(NH₃)₆](NO₃)₂ Hexamminecobalt(III) nitrate, **2**:218
- [Co(NH₃)₆]₂(C₂O₄)₃·4H₂O Hexamminecobalt(III) oxalate, **2**:220
- CoNO(CO)₃ Cobalt nitrosyl tricarbonyl, **2**:238, 239
- Co₂(SO₄)₃·18H₂O Cobalt(III) sulfate 18-hydrate, **5**:181
- Cr(CN)₆K₃ Potassium hexacyanochromate(III), **2**:203
- Cr(CO)₆ Chromium hexacarbonyl, **3**:156
- Cr(C₂H₃O₂)₂ Chromium(II) acetate, **1**:122; **3**:148
- [Cr(C₂O₄)₃]K₃·3H₂O Potassium trioxalatochromate(III), **1**:37
- Cr(C₅H₇O₂)₃ Chromium(III) acetylacetonate, **5**:130
- CrCl₂ Chromium(II) chloride, **1**:124, 125; **3**:150
3- and 4-hydrates, **1**:126
- CrCl₃ Chromium(III) chloride, **2**:193; **5**:154
- [Cr(en)₂Cl₂]Cl·H₂O *cis*-Dichlorobis(ethylenediamine)chromium(III) chloride, **2**:200, 201
- [Cr(en)₂(SCN)₂](SCN)·H₂O *trans*-Bis(thiocyanato)bis(ethylenediamine)chromium(III) thiocyanate, **2**:200, 202
- [Cr(en)₃]Br₃·4H₂O Tris(ethylenediamine)chromium(III) bromide, **2**:199
- [Cr(en)₃]Cl₃·3½H₂O Tris(ethylenediamine)chromium(III) chloride, **2**:198
- [Cr(en)₃]I₃·H₂O Tris(ethylenediamine)chromium(III) iodide, **2**:199
- [Cr(en)₃](SCN)₃·H₂O Tris(ethylenediamine)chromium(III) thiocyanate, **2**:199
- [Cr(en)₃]₂(SO₄)₃ Tris(ethylenediamine)chromium(III) sulfate, **2**:198
- CrI₂ Chromium(II) iodide, **5**:130
- CrI₃ Chromium(III) iodide, **5**:128, 129
- [Cr(NH₃)₅Br]Br₂ Bromopentamminechromium(III) bromide, **5**:134
- [Cr(NH₃)₅Cl]Cl₂ Chloropentamminechromium(III) chloride, **2**:196
- [Cr(NH₃)₅(H₂O)]Br₃ Aquopentamminechromium(III) bromide, **5**:134
- [Cr(NH₃)₅(H₂O)](NO₃)₃ Aquopentamminechromium(III) nitrate, **5**:134
- [Cr(NH₃)₅(H₂O)](NO₃)₃·NH₄NO₃ Aquopentamminechromium(III) ammonium nitrate, **5**:132
- [Cr(NH₃)₅(NO₂)](NO₃)₂ Nitropentamminechromium(III) nitrate, **5**:133
- [Cr(NH₃)₅(NO₃)](NO₃)₂ Nitratopentamminechromium(III) nitrate, **5**:133
- [Cr(NH₃)₆]Cl₃ Hexamminechromium(III) chloride, **2**:196
- [Cr(NH₃)₆](NO₃)₃ Hexamminechromium(III) nitrate, **3**:153
- CrO₂Cl₂ Chromyl chloride, **2**:205
- CrO₂·2C₅H₅N Pyridine-chromium(VI) oxide, **4**:94
- CrO₂·2C₅H₇N 3 (and 4)-Picoline-chromium(VI) oxide, **4**:95
- CrO₃ClK Potassium monochlorochromate, **2**:208
- (CrO₄)₃Cr₂ Chromium(III) chromate, **2**:192
- Cr₂O₃ + xH₂O Chromium(III) oxide gel, **2**:190, 191

$\text{Cr}_2(\text{SO}_4)_3$ Chromium(III) sulfate, 2:197

$\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ Cesium alum, 4:8

$3\text{CsCl} \cdot 2\text{SbCl}_3$ Cesium antimony-(III) chloride, 4:6

CsNO_3 Cesium nitrate, 4:6; 1-hydrogen nitrate, 4:7

CsN_3 Cesium azide, 1:79

CuBr Copper(I) bromide, 2:3

CuCl Copper(I) chloride, 2:1

$[\text{CuCl} \cdot \text{CO}] \cdot 2\text{H}_2\text{O}$ Copper carbonyl chloride, 2:4

CuCl_2 Copper(II) chloride, 5:154

$[\text{CuI}_2][\text{Cu}(\text{en})_2]$ Bis(ethylenediamine)copper(II) diiodocuprate(I), 5:16, 17

$[\text{Cu}(\text{en})_2][\text{CuI}_2]$ Bis(ethylenediamine)copper(II) diiodocuprate(I), 5:16, 17

$[\text{Cu}(\text{en})_2]\text{I}_2$ Bis(ethylenediamine)copper(II) iodide, 5:18

$[\text{Cu}\{\text{NH}(\text{C}_5\text{H}_4\text{N})_2\}\text{Cl}_2]$ Dichloro-(di-2-pyridylamine)copper(II), 5:14

$[\text{Cu}\{\text{NH}(\text{C}_5\text{H}_4\text{N})_2\}_2]\text{Cl}_2$ Bis(di-2-pyridylamine)copper(II) chloride, 5:14, 15

E

EuCO_3 Europium(II) carbonate, 2:69, 71

$\text{Eu}(\text{C}_2\text{H}_3\text{O}_2)_2$ Europium(II) acetate, 2:68

$\text{Eu}(\text{C}_2\text{H}_3\text{O}_2)_3$ Europium(III) acetate, 2:66

EuCl_2 Europium(II) chloride, 2:68, 69, 71

EuSO_4 Europium(II) sulfate, 2:69, 70

$\text{Eu}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ Europium(III) oxalate, 2:66

Eu_2O_3 Europium(III) oxide, 2:66

Eu_3Hg_2 Europium amalgam, 2:68n.

F

FAg Silver(I) fluoride, 4:136; 5:19, 20

FAg_2 Disilver fluoride, 5:18

FBr Bromine(I) fluoride, 3:185

FH Hydrogen fluoride, 1:134; 3:112; 4:136

FHg Mercury(I) fluoride, 4:136

$\text{FPOCl}(\text{CH}_3)$ Methyl chlorofluorophosphite, 4:141

FPO_3Ag_2 Silver monofluorophosphate, 3:109

FPO_3K_2 Potassium monofluorophosphate, 3:109

$\text{FPO}_3(\text{NH}_4)_2$ Ammonium monofluorophosphate, 2:155

FPO_3Na_2 Sodium monofluorophosphate, 3:106, 108

F_2Ag Silver(II) fluoride, 3:176

F_2Ca Calcium fluoride, 4:137

F_2Hg Mercury(II) fluoride, 4:136

F_2KH Potassium hydrogen fluoride, 1:140

F_2Ni Nickel(II) fluoride, 3:173

F_2O Oxygen fluoride, 1:109

$\text{F}_2\text{PO}(\text{CH}_3)$ Methyl difluorophosphite, 4:141

$\text{F}_2\text{PO}_2\text{NH}_4$ Ammonium difluorophosphate, 2:157

F_3As Arsenic(III) fluoride, 4:137, 150

F_3B Boron fluoride, 1:21, 23; compound with hexamethyldisilazane, 5:58

$\text{F}_3\text{B} \cdot (\text{CH}_3)_3\text{N}$ Boron fluoride-trimethylamine, 5:26

F_3Er Bromine(III) fluoride, 3:184

F_3Co Cobalt(III) fluoride, 3:175

F_3P Phosphorus(III) fluoride, 4:149; 5:95

F_3Sb Antimony(III) fluoride, 4:134

F_4C Carbon tetrafluoride, 1:34; 3:178

F_4Ge Germanium(IV) fluoride, 4:147

F_4Si Silicon tetrafluoride, 4:145

- F_5Br Bromine(V) fluoride, **3:185**
 F_5Nb Niobium(V) fluoride, **3:179**
 F_5Ta Tantalum(V) fluoride, **3:179**
 F_6GeBa Barium hexafluorogermanate(IV), **4:147**
 F_6PK Potassium hexafluorophosphate, **3:111, 115**
 F_6PNH_4 Ammonium hexafluorophosphate, **3:111, 114**
 F_6PNa Sodium hexafluorophosphate, **3:111, 115**
 F_6S Sulfur(VI) fluoride, **1:121; 3:119**
 F_6Se Selenium(VI) fluoride, **1:121**
 F_6SiBa Barium hexafluorosilicate, **4:145**
 F_6Te Tellurium(VI) fluoride, **1:121**
 F_6W Tungsten(VI) fluoride, **3:181**
 $FeBr_2 \cdot 6NH_3$ Iron(II) bromide, 6-ammoniate, **4:161**
 $Fe(CHO_2)_2 \cdot 2H_2O$ Iron(II) formate, **4:159**
 $Fe(CO)_4H_2$ Iron tetracarbonyl dihydride, **2:243**
 $Fe(CO)_4K_2$ Iron tetracarbonyl dihydride, potassium salt, **2:244**
 $[Fe(C_2O_4)_3]K_3 \cdot 3H_2O$ Potassium trioxalatoferrate(III), **1:36**
 $[Fe(C_5H_5N)_4]Cl_2$ Tetrapyrroline-iron(II) chloride, **1:184**
 $FeCl_2$ Iron(II) chloride, 1-hydrate, **5:181; 2-hydrate, 5:179**
 $FeCl_3$ Iron(III) chloride, **3:190; 4:124; 5:24n., 154**
 FeO_2H β -Iron(III) oxide hydrate, **2:215**
 FeO_4K_2 Potassium ferrate(VI), **4:164**
 Fe_2O_3 γ -Iron(III) oxide, **1:185**
 $Fe_2O_3 \cdot H_2O$ β -Iron(III) oxide hydrate, **2:215**
 γ -Iron(III) oxide hydrate, **1:185**

G

- $GaCl_2$ Gallium(II) chloride, **4:111**
 $GaCl_3$ Gallium(III) chloride, **1:26**
 $Ga(ClO_4)_3 \cdot 6(\text{and } 9\frac{1}{2})H_2O$ Gallium(III) perchlorate, **2:26, 28**

H

- $HfCl_4$ Hafnium chloride, **4:121**
 HgF Mercury(I) fluoride, **4:136**
 HgF_2 Mercury(II) fluoride, **4:136**

HgO Mercury(II) oxide, **5**:157,
159
HgS Mercury(II) sulfide, **1**:19
Hg₂Eu₃ Europium amalgam, **2**:
68*n*.

I

IBrClN(CH₃)₄ Tetramethylam-
monium bromochloroiodate(I),
5:172
IBr₂Cs Cesium dibromoiodate(I),
5:172
IBr₂N(CH₃)₄ Tetramethylammo-
nium dibromoiodate(I), **5**:172
IBr₂N(C₃H₇)₄ Tetrapropylam-
monium dibromoiodate(I), **5**:
172
ICl Iodine(I) chloride, **1**:165
ICl₂Cs Cesium dichloroiodate(I),
4:9; **5**:172
ICl₂N(CH₃)₄ Tetramethylammo-
nium dichloroiodate(I), **5**:176
ICl₂N(C₂H₅)₄ Tetraethylammo-
nium dichloroiodate(I), **5**:172
ICl₂N(C₃H₇)₄ Tetrapropylammo-
nium dichloroiodate(I), **5**:172
ICl₂N(C₄H₉)₄ Tetrabutylammo-
nium dichloroiodate(I), **5**:172
ICl₂Rb Rubidium dichloroiodate-
(I), **5**:172
ICl₂S(CH₃)₃ Trimethylsulfonium
dichloroiodate(I), **5**:172
ICl₃ Iodine(III) chloride, **1**:167
ICl₄N(CH₃)₄ Tetramethylammo-
nium tetrachloroiodate(III),
5:172
ICl₄N(C₄H₉)₄ Tetrabutylammo-
nium tetrachloroiodate(III),
5:176
ICl₄S(CH₃)₃ Trimethylsulfonium
tetrachloroiodate(III), **5**:172
IH Hydriodic acid, **1**:157, 158,
159, 162; **2**:210
Hydrogen iodide, **1**:159
IO₃Na Sodium iodate, **1**:168
IO₄K Potassium metaperiodate, **1**:
171

IO₄Na Sodium metaperiodate, **1**:
170
IO₆H₆ Paraperiodic acid, **1**:172,
173
IO₆KNi·½H₂O Potassium nickel-
(IV) paraperiodate ½-hydrate,
5:201, 202, 203
IO₆NaNi·H₂O Sodium nickel(IV)
paraperiodate 1-hydrate, **5**:201,
203
IO₆Na₃H₂ Sodium paraperiodate,
1:169, 170; **2**:212
(IO₆)₂Ba₃H₄ Barium paraperio-
date, **1**:171
I₂BrN(CH₃)₄ Tetramethylammo-
nium bromoiodoiodate(I), **5**:
172
I₂ClN(CH₃)₄ Tetramethylammo-
nium chloroiodoiodate(I), **5**:
172
I₃Cs Cesium diiodoiodate(I), **5**:172
I₃N(CH₃)₄ Tetramethylammo-
nium diiodoiodate(I), **5**:172
I₃N(C₃H₇)₄ Tetrapropylammo-
nium diiodoiodate(I), **5**:172
I₃N(C₄H₉)₄ Tetrabutylammonium
diiodoiodate(I), **5**:172
I₄ClN(CH₃)₄ Tetramethylammo-
nium chlorotriiodoiodate(III),
5:172
I₅N(CH₃)₄ Tetramethylammo-
nium tetraiodoiodate(III), **5**:
172
I₅N(C₃H₇)₄ Tetrapropylammo-
nium tetraiodoiodate(III), **5**:
172
I₇N(C₃H₇)₄ Tetrapropylammo-
nium heptaiodoiodate(V), **5**:172
I₉N(CH₃)₄ Tetramethylammo-
nium octaiodoiodate(VIII),
5:172

K

KI Potassium iodide, **1**:163
KNH₂ Potassium amide, **2**:135
KN₃ Potassium azide, **1**:79; **2**:139,
140

L

- LaCl₃ Lanthanum chloride, 1:32
 La(NO₃)₃ Lanthanum nitrate, 5:
 41
 LiCl Lithium chloride, 5:154
 LiN Lithium nitride, 4:1
 LiNH₂ Lithium amide, 2:135
 LiOH·H₂O Lithium hydroxide, 5:3
 LiO₂·H·H₂O Lithium hydroper-
 oxide 1-hydrate, 5:1, 2, 4
 Li₂CO₃ Lithium carbonate, 1:1;
 5:3
 Li₂O Lithium oxide, 5:1, 5
 Li₂O₂ Lithium peroxide, 5:1, 3, 4

M

- MgCl₂ Magnesium chloride, 1:29;
 5:154n.
 3Mg(NO₃)₂·2Bi(NO₃)₃·24H₂O
 Magnesium bismuth nitrate,
 2:57
 3Mg(NO₃)₂·2Ce(NO₃)₃·24H₂O
 Magnesium cerium(III) nitrate,
 2:57
 Mn(CN)₆K₃ Potassium hexacy-
 anomanganate(III), 2:213, 214
 Mn(CN)₆K₄ Potassium hexacy-
 anomanganate(II), 2:214
 MnCl₂ Manganese(II) chloride,
 1:29
 MnO₂ + xH₂O Pyrolusite, 2:168
 MnO₄K Potassium permanganate,
 2:60, 61
 MnPO₄ Manganese(III) ortho-
 phosphate, 2:213
 Mo(CN)₈K₄·2H₂O Potassium oc-
 tacyanomolybdate(IV) 2-hy-
 drate, 3:160
 MoCl₅ Molybdenum(V) chloride,
 3:165
 [MoCl₅H₂O]K₂ Potassium penta-
 chloroaquomolybdate(III), 4:
 97
 [MoCl₆]K₃ Potassium hexachloro-
 molybdate(III), 4:97, 99

N

- (—N=CHC₆H₅)₂ Benzalazine, 1:
 92, 93, 94
 N(CH₃)₂C₆H₅ Dimethylaniline, 2:
 174n.
 N(CH₃)₃ Trimethylamine, 2:
 159
 NC₅H₅ Pyridine, 2:173n.
 (NC₅H₄)₂NH Di-2-pyridylamine,
 5:14
 NCl₃ Nitrogen(III) chloride, 1:65,
 67
 NHBr₂ Dibromamide, 1:62, 64
 NH=C(NH₂)NHCN Dicyanodi-
 amide, 3:43
 [NH=C(NH₂)₂H]NO₃ Guanido-
 nium nitrate, 1:94, 96, 97
 [NH=C(NH₂)₂H]₆P₄O₁₃·H₂O
 Hexaguanidonium tetraphos-
 phate 1-hydrate, 5:97, 100
 NH(C₆H₅)SO₂[NC₅H₆] Pyridinium
N-phenylsulfamate, 2:175
 NHGe Germanium(II) imide, 2:
 108
 NH(SO₂NH₄)₂ Diammonium imi-
 dodisulfate, 2:180
 [NHSi(CH₃)₂]₃ Cyclotrisilazane,
 hexamethyl-, 5:61
 [NHSi(CH₂)₂]₄ Cyclotetrasilazane,
 octamethyl-, 5:61
 NH[Si(CH₃)₃]₂ Disilazane, hexa-
 methyl-, 5:56; compound with
 BF₃, 5:58
 [NHSi(C₂H₅)₂]₃ Cyclotrisilazane,
 hexaethyl-, 5:62
 [NHSi(C₂H₅)₂]₄ Cyclotetrasilaza-
 zane, octaethyl-, 5:62
 (NH)₂Ge Germanium(IV) imide,
 2:114
 NH₂CONHCON₂H₃ Allophanyl
 hydrazide, 5:48, 50; hydra-
 zones, 5:51; salts, 5:51
 NH₂CONHCON₃ Allophanyl
 azide, 5:51
 NH₂CONHCOOCH₃ Methyl al-
 lophanate, 5:48, 49, 52

- $\text{NH}_2\text{CONHCOOC}_2\text{H}_5$ Ethyl al-
lophanate, **5**:48, 49, 52
 $(\text{NH}_2\text{CONHNH})_2\text{CO}$ Carbohydra-
zide-*N,N*-dicarboxamide, **4**:38
 $\text{NH}_2\text{CONHNHCONH}_2$ Biurea,
4:26; **5**:53, 54
 NH_3CONH_2 Urea, **2**:89
 $\text{NH}_2\text{CO}_2\text{NH}_4$ Ammonium carbam-
ate, **2**:85
 $\text{NH}_2\text{CSNHNH}_2$ Thiosemicarba-
zide, **4**:39
 $\text{NH}_2\text{CS}_2\text{NH}_4$ Ammonium dithio-
carbamate, **3**:48
 NH_2Cl Chloramide, **1**:59, 62; **5**:92
 NH_2K Potassium amide, **2**:135
 NH_2Li Lithium amide, **2**:135
 $\text{NH}_2\text{N}(\text{CH}_3)_2(\text{C}_2\text{H}_4\text{OH})\text{Cl}$ 1,1-
Dimethyl-1-(2-hydroxyethyl)-
hydrazonium chloride, **5**:92
 $\text{NH}_2\text{N}(\text{CH}_3)_2(\text{C}_6\text{H}_4\text{CH}_3)\text{Cl}$ 1,1-
Dimethyl-1-(*p*-tolyl)hydra-
zonium chloride, **5**:92
 $\text{NH}_2\text{N}(\text{CH}_3)_2\text{C}_6\text{H}_5\text{Cl}$ 1,1-Di-
methyl-1-phenylhydrazonium
chloride, **5**:92
 $\text{NH}_2\text{N}(\text{CH}_3)_3\text{Cl}$ 1,1,1-Trimethyl-
hydrazonium chloride, **5**:92, 94
 $\text{NH}_2\text{N}(\text{C}_2\text{H}_5)_2(\text{C}_2\text{H}_4\text{OH})\text{Cl}$ 1,1-
Diethyl-1-(2-hydroxyethyl)-
hydrazonium chloride, **5**:92
 $\text{NH}_2\text{N}(\text{C}_2\text{H}_5)_2(\text{C}_3\text{H}_6\text{OH})\text{Cl}$ 1,1-
Diethyl-1-(3-hydroxypropyl)-
hydrazonium chloride, **5**:92
 $\text{NH}_2\text{N}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5\text{Cl}$ 1,1-Diethyl-
1-phenylhydrazonium chloride,
5:92
 $\text{NH}_2\text{N}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_{11}\text{Cl}$ 1-Cyclo-
hexyl-1,1-diethylhydrazonium
chloride, **5**:92
 $\text{NH}_2\text{N}(\text{C}_2\text{H}_5)_3\text{Cl}$ 1,1,1-Triethyl-
hydrazonium chloride, **5**:92, 94
 $\text{NH}_2\text{N}(\text{C}_3\text{H}_7)_3\text{Cl}$ 1,1,1-Triisopro-
pylhydrazonium chloride, **5**:92
 $\text{NH}_2\text{N}(\text{C}_7\text{H}_{15})_3\text{Cl}$ 1,1,1-Tri-*n*-
heptylhydrazonium chloride,
5:92
 $(\text{NH}_2\text{NH})_2\text{CO}$ Carbohydrazide, **4**:
32
- $\text{NH}_2\text{NHCONHNHCONH}_2$ Carbo-
hydrazide-*N*-carboxamide, **4**:36
 NH_2NH_2 Hydrazine, **1**:90, 92; **5**:
124
 $\text{NH}_2\text{NH}_2\cdot 2\text{HCl}$ Hydrazine dihy-
drochloride, **1**:92
 $\text{NH}_2\text{NH}_2\cdot \text{C}_2\text{H}_5\text{N}_3\text{O}_2$ Hydrazine
urazolate, **5**:53, 54
 $[\text{NH}_2\text{NH}_3]\text{HSO}_4$ Hydrazonium hy-
drogen sulfate, **1**:90, 92
 NH_2NO_2 Nitramide, **1**:68, 72
 NH_2Na Sodium amide, **1**:74, **2**:80,
128
 NH_2OH Hydroxylamine, **1**:87
 $\text{NH}_2\text{OSO}_3\text{H}$ Hydroxylamine-*O*-
sulfonic acid, **5**:122, 123
 $\text{NH}_2\text{SO}_3\text{H}$ Sulfamic acid, **2**:176,
177, 178
 $\text{NH}_2\text{SO}_3\text{NH}_4$ Ammonium sulfam-
ate, **2**:175, 180
 $[(\text{NH}_2)_2\text{C}(\text{N}_2\text{H}_3)]\text{HCO}_3$ Amino-
guanidonium hydrogen car-
bonate, **3**:45
 $(\text{NH}_2)_2\text{C}_2\text{H}_4$ Ethylenediamine, **2**:
197
 NH_3 Ammonia, **2**:76, 128; **3**:48
 $[\text{NH}_3\text{OH}]\text{Cl}$ Hydroxylammonium
chloride, **1**:89
 $[\text{NH}_3\text{OH}]_2\text{C}_2\text{O}_4$ Hydroxylammo-
nium oxalate, **3**:83
 $[\text{NH}_3\text{OH}]_3\text{AsO}_4$ Hydroxylammo-
nium arsenate, **3**:83
 $[\text{NH}_3\text{OH}]_3\text{PO}_4$ Hydroxylammo-
nium phosphate, **3**:82
 $\text{NH}_4\text{NO}_3\cdot[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{NO}_3)_2$
Ammonium aquopentammine-
chromium(III) nitrate, **5**:132
 NH_4N_3 Ammonium azide, **2**:136,
137
 NLi Lithium nitride, **4**:1
 $\text{NNH}_4(\text{SO}_3\text{NH}_4)_2\cdot \text{H}_2\text{O}$ Triammo-
nium imidodisulfate, **2**:179, 180
 NO Nitrogen(II) oxide, **2**:126; **5**:
118*n.*, 119
 NOCl Nitrosyl chloride, **1**:55, 57;
4:48
 NOHSO_4 Nitrosylsulfuric acid,
1:55

- NO_2 Nitrogen(IV) oxide, **5:90**
 $\text{NO}_2\text{C}_4\text{H}_9$ Butyl nitrite, **2:139**
 NO_2Cl Nitryl chloride, **4:52**
 $\text{NO}_2\text{NHCO}_2\text{C}_2\text{H}_5$ Nitrourethan, **1:69**
 NO_2NH_2 Nitramide, **1:68, 72**
 $\text{NO}_2\text{NKCO}_2\text{K}$ Potassium nitrocarbamate, potassium salt, **1:68, 70**
 $\text{NO}_2\text{N}(\text{NH}_4)\text{CO}_2\text{C}_2\text{H}_5$ Ammonium salt of nitrourethan, **1:69**
 NO_3H Nitric acid, **3:13; 4:52**
 $\text{N}(\text{SO}_3\text{K})_3$ Potassium nitridotrisulfate, **2:182**
 $\text{N}[\text{Si}(\text{CH}_3)_3]_2\text{CH}_2$ Disilazane, *N*-methylhexamethyl-, **5:58**
 $\text{N}_2\text{O}_2\cdot\text{K}_2\text{SO}_3$ Potassium *N*-nitrosohydroxylamine-*N*-sulfonate, **5:117, 120**
 $\text{N}_2\text{O}_2\cdot(\text{NH}_4)_2\text{SO}_3$ Ammonium *N*-nitrosohydroxylamine-*N*-sulfonate, **5:120**
 $\text{N}_2\text{O}_2\cdot\text{Na}_2\text{SO}_3$ Sodium *N*-nitrosohydroxylamine-*N*-sulfonate, **5:119**
 N_2O_4 Nitrogen(IV) oxide, **5:87**
 N_2O_5 Nitrogen(V) oxide, **3:78**
 $\text{N}_3\text{CS}_2\text{H}$ Azidodithiocarbonic acid, **1:81, 82**
 $\text{N}_3\text{CS}_2\text{Na}$ Sodium azidodithiocarbonate, **1:82**
 $\text{N}_3\text{C}_2\text{H}_3\text{O}_2(\text{NH}_2)$ Urazine (4-aminourazole), **4:29; salts, 4:31**
 $\text{N}_3\text{C}_2\text{H}_3\text{O}_2$ Urazole, **5:52-54; hydrazine salt, 5:53, 54**
 N_3Cs Cesium azide, **1:79**
 N_3H Hydrazoic acid, **1:77, 78**
 Hydrogen azide, **1:77, 78**
 N_3K Potassium azide, **1:79, 2:139, 140**
 N_3NH_4 Ammonium azide, **2:136**
 N_3Na Sodium azide, **1:79, 2:139**
 N_3Rb Rubidium azide, **1:79**
 $(\text{N}_3)_2\text{CO}$ Carbonyl azide, **4:35**
 $(\text{N}_3\text{SCS})_2$ "Azido-carbon disulfide," **1:81, 82**
 $\text{NaC}\equiv\text{CH}$ Monosodium acetylide, **2:75, 76, 79**
 $\text{NaC}\equiv\text{CNa}$ Disodium acetylide, **2:79, 80**
 $\text{NaGe}(\text{C}_6\text{H}_5)_3$ Sodium (triphenylgermyl)-, **5:72, 74**
 NaH Sodium hydride, **5:10, 13**
 NaNH_2 Sodium amide, **1:74; 2:80, 128**
 NaN_3 Sodium azide, **1:79; 2:139**
 NaOC_4H_9 Sodium butoxide, **1:88**
 NaO_2 Sodium superoxide, **4:82**
 Na_2CO_3 Sodium carbonate, **5:159**
 $\text{Na}_2\text{Ge}(\text{C}_6\text{H}_5)_2$ Sodium, (diphenylgermyl)di-, **5:72**
 $\text{Na}_2\text{O}_2\cdot 8\text{H}_2\text{O}$ Sodium peroxide, **3:1**
 NbF_5 Niobium(V) fluoride, **3:179**
 NdCl_3 Neodymium chloride, **1:32; 5:154n.**
 $\text{Nd}(\text{NO}_3)_3$ Neodymium nitrate, **5:41**
 $\text{Nd}_2(\text{C}_2\text{O}_4)_3\cdot 10\text{H}_2\text{O}$ Neodymium oxalate, **2:60**
 NiCN Nickel(I) cyanide, **5:200**
 $\text{Ni}(\text{CN})_2$ Nickel(II) cyanide, **2:228**
 $[\text{Ni}(\text{CN})_3\text{CO}]\text{K}_2$ Potassium tricyanocarbonylnickelate(I), **5:201**
 $\text{Ni}(\text{CN})_4\cdot\text{K}_2\cdot\text{H}_2\text{O}$ Potassium tetracyanonickelate(II), **2:227, 228**
 $\text{Ni}(\text{CO})_4$ Nickel tetracarbonyl, **2:234**
 NiCl_2 Nickel(II) chloride, **5:154, 196**
 NiF_2 Nickel(II) fluoride, **3:173**
 $\text{NiKIO}_6\cdot\frac{1}{2}\text{H}_2\text{O}$ Nickel(IV) potassium paraperiodate $\frac{1}{2}$ -hydrate, **5:201-203**
 $[\text{Ni}(\text{NH}_3)_6]\text{Br}_2$ Hexamminenickel(II) bromide, **3:194**
 $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ Hexamminenickel(II) iodide, **3:194**
 $\text{NiNaIO}_6\cdot\text{H}_2\text{O}$ Nickel(IV) sodium paraperiodate 1-hydrate, **5:201, 203**
 $[\text{Ni}_2(\text{CN})_6]\text{K}_4$ Potassium hexacyanodinitnickelate(I), **5:197, 200**

O

- (OCN)K Potassium cyanate, **2:87**
 (OCN)Na Sodium cyanate, **2:88**
 OF₂ Oxygen fluoride, **1:109**
 [OsBr₆](NH₄)₂ Ammonium hexabromoosmate(IV), **5:204**
 [OsCl₆](NH₄)₂ Ammonium hexachloroosmate(IV), **5:206**
 OsO₂ Osmium(IV) oxide, **5:206**
 OsO₄ Osmium(VIII) oxide, **5:205**

P

- PAI Aluminum phosphide, **4:23**
 PBr₃ Phosphorus(III) bromide, **2:147**
 PCl₃ Phosphorus(III) chloride, **2:145**
 PCl₅ Phosphorus(V) chloride, **1:99**
 PF₃ Phosphorus(III) fluoride, **4:149; 5:95**
 PF₆K Potassium hexafluorophosphate, **3:111, 115**
 PF₆Na Sodium hexafluorophosphate, **3:111, 115**
 PF₆NH₄ Ammonium hexafluorophosphate, **3:111, 114**
 PH₄I Phosphonium iodide, **2:141, 143**
 P(NHC₆H₅)₃ Phosphine, trianilino-, **5:61**
 P(=NH)OC₂H₅ Ethyl phosphenimidate, **4:65**
 POBr₃ Phosphorus(V) oxybromide, **2:151**
 POClF(CH₃) Methyl chlorofluorophosphite, **4:141**
 POCl₂(CH₃) Methyl dichlorophosphite, **4:63**
 POCl₂(C₂H₄Cl) 2-Chloroethyl dichlorophosphite, **4:66**
 POCl₂(C₂H₅) Ethyl dichlorophosphite, **4:63**
 POF₂(CH₃) Methyl difluorophosphite, **4:141**
 POSCl₂(C₂H₅) O-Ethyl dichlorothiophosphate, **4:75**
 PO₂F₂NH₄ Ammonium difluorophosphate, **2:157**
 PO₃(C₂H₅)₂H Diethyl phosphite, **4:58**
 PO₃(C₈H₁₇)₂H Dioctyl phosphite, **4:61**
 PO₃Cl(C₂H₅)₂ Diethyl monochlorophosphate, **4:78**
 PO₃FAg₂ Silver monofluorophosphate, **3:109**
 PO₃FK₂ Potassium monofluorophosphate, **3:109**
 PO₃F(NH₄)₂ Ammonium monofluorophosphate, **2:155**
 PO₃FNa₂ Sodium monofluorophosphate, **3:106, 108**
 PO₃H₃ Phosphorous acid, **4:55**
 PO₃NH₂(C₂H₅)₂ Diethyl monoamidophosphate, **4:77**
 (PO₃Na)₂ Sodium polymetaphosphate, **3:104**
 PO₃SK₃ Potassium monothio-phosphate, **5:102**
 PO₃SNa₃ Sodium monothio-phosphate, **5:102**
 PO₄CaH (and +2H₂O) Calcium hydrogen orthophosphate, and 2-hydrate, **4:19, 20, 22**
 PO₄H₃ Orthophosphoric acid, **1:101**
 PO₄UO₂H·4H₂O Uranyl orthophosphate 4-hydrate, **5:151**
 (PO₄)₂CaH₄·H₂O Calcium dihydrogen orthophosphate 1-hydrate, **4:18**
 PSBr₃ Phosphorus(V) sulfobromide, **2:153**
 PSCl₃ Phosphorus(V) sulfochloride, **4:71**
 PSFBr₂ Phosphorus(V) sulfodibromofluoride, **2:154**
 PSF₂Br Phosphorus(V) sulfobromodifluoride, **2:154**
 PSF₃ Phosphorus(V) sulfofluoride, **1:154**
 (PW₁₂O₄₀)H₃·xH₂O 12-Tungstophosphoric acid, **1:132**

- P_2I_4 Diphosphorus tetraiodide, **2:143**
 $P_2O_6Na_2H_2 \cdot 6H_2O$ Disodium dihydrogen hypophosphate, **4:68**
 $P_2O_7H_4$ Pyrophosphoric acid, **3:96, 97**
 $P_2O_7Na_2H_2$ Disodium dihydrogen pyrophosphate, **3:99**
 $P_2O_7Na_4$ Tetrasodium pyrophosphate, **3:100**
 $P_3O_9Na_3 \cdot 6H_2O$ Sodium trimetaphosphate, **3:104**
 $P_3O_{10}Na_5$ Sodium triphosphate, **3:101, 103**
 $P_4O_{12}Na_4 \cdot 4H_2O$ Sodium tetrametaphosphate 4-hydrate, **5:98**
 $P_4O_{13}Na_6$ Sodium tetrphosphate, **5:99**
 $PbBr_6H_2$ Hexabromoplumbic(IV) acid, **1:48**
 $Pb(C_2H_3O_2)_4$ Lead(IV) acetate, **1:47**
 $PbCl_6H_2$ Hexachloroplumbic(IV) acid, **1:48**
 PbO_2 Lead(IV) oxide, **1:45**
 PbO_3H_2 "Metaplumbic acid," **1:46**
 $Pb(SCN)_2$ Lead(II) thiocyanate, **1:85**
 $Pd(CN)_4K_2 \cdot 1(\text{and } 3)H_2O$ Potassium tetracyanopalladate(II), **2:245, 246**
 $[Pd(NH_3)_2(NO_2)_2]$ *trans*-Dinitrodiamminepalladium, **4:179**
 $Pr(NO_3)_3$ Praseodymium(III) nitrate, **5:41**
 Pr_2O_3 Praseodymium(III) oxide, **5:39**
 $Pt(CN)_4K_2$ Potassium tetracyanoplatinate(II), **5:215**
 $[Pt(C_2H_4)Cl_2]_2$ Tetrachloro(diethylene)diplatinum(II), **5:210**
 $[Pt(C_2H_4)Cl_3]K$ Potassium trichloro(ethylene)platinate(II), **5:211, 214**
 $[Pt(C_2H_4)_2Cl_2]$ Dichloro(diethylene)platinum(II), **5:215**
 $[Pt(C_6H_6)_2Cl_2]_2$ Tetrachloro(di-propylene)diplatinum(II), **5:214**
 $[Pt(C_6H_5CH=CH_2)Cl_2]_2$ Tetrachloro(distyrene)diplatinum(II), **5:214**
 $PtCl_2$ Platinum(II) chloride, **5:208, 209**
 $PtCl_4$ Platinum(IV) chloride, **2:253**
 $PtCl_4H_2$ Tetrachloroplatinic(II) acid, **2:251; 5:208, 210**
 $PtCl_4K_2$ Potassium tetrachloroplatinate(II), **2:247**
 $[Pt(NH_3)_2Cl_2]$ Dichlorodiammineplatinum(II), **2:253**
 $[Pt(NH_3)_4]Cl_2$ Tetrammineplatinum(II) chloride, **2:250; 5:210; 1-hydrate, 2:252**
 $[Pt(NH_3)_4][PtCl_4]$ Tetrammineplatinum(II) tetrachloroplatinate(II), **2:251**
- R**
- RbN_3 Rubidium azide, **1:79**
 $ReCl_3$ Rhenium(III) chloride, **1:182**
 $ReCl_5$ Rhenium(V) chloride, **1:180**
 $ReCl_6K_2$ Potassium hexachlororhenate(IV), **1:178**
 ReO_2 Rhenium(VI) oxide, **3:186**
 ReO_4NH_4 Ammonium perrhenate, **1:177, 178**
 Re_2O_7 Rhenium(VII) oxide, **3:188**
 Re_2S_7 Rhenium(VII) sulfide, **1:177**
- S**
- $(SCN)_2$ Thiocyanogen, **1:84, 86**
 $(SCN)_2Ba$ Barium thiocyanate, **3:24**
 $(SCN)_2Pb$ Lead(II) thiocyanate, **1:85**
 SF_6 Sulfur(VI) fluoride, **1:121; 3:119**
 SH_2 Hydrogen sulfide, **1:111; 3:14, 15**

- SOBr_2 Thionyl bromide, **1**:113
 SO_2 Sulfur dioxide, **2**:160
 SO_2Cl_2 Sulfuryl chloride, **1**:114
 $\text{SO}_2\cdot\text{N}(\text{CH}_3)_3$ Trimethylamine-sulfur dioxide, **2**:159
 $\text{SO}_3\cdot\text{C}_5\text{H}_5\text{N}$ Pyridine-sulfur trioxide, **2**:173
 $\text{SO}_3\cdot\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ Dimethylaniline-sulfur trioxide, **2**:174
 $\text{SO}_3\text{Cl}(\text{C}_2\text{H}_4\text{Cl})$ 2-Chloroethyl chlorosulfonate, **4**:85
 $(\text{SO}_3\text{H})\text{Cl}$ Chlorosulfonic acid, **4**:52
 $(\text{SO}_3\text{H})\text{NH}_2$ Sulfamic acid, **2**:176, 177, 178
 $(\text{SO}_3\text{H})\text{ONH}_2$ Hydroxylamine-*O*-sulfonic acid, **5**:122, 123
 SO_3KH Potassium hydrogen sulfite, **2**:167
 $4\text{SO}_3\text{KH}\cdot\text{S}_2\text{O}_5\text{K}_2$, **2**:167
 SO_3K_2 Potassium sulfite, **2**:165, 166
 $\text{SO}_3\text{K}_2\cdot\text{N}_2\text{O}_2$ Potassium *N*-nitrosohydroxylamine-*N*-sulfonate, **5**:117, 120
 $(\text{SO}_3\text{K})_3\text{N}$ Potassium nitridotrisulfate, **2**:182
 $(\text{SO}_3[\text{NC}_6\text{H}_5])\text{NHC}_6\text{H}_5$ Pyridinium *N*-phenylsulfamate, **2**:175
 $(\text{SO}_3\text{NH}_4)\text{NH}_2$ Ammonium sulfamate, **2**:175, 180
 $\text{SO}_3(\text{NH}_4)_2\cdot\text{N}_2\text{O}_2$ Ammonium *N*-nitrosohydroxylamine-*N*-sulfonate, **5**:120
 $(\text{SO}_3\text{NH}_4)_2\text{NH}$ Diammonium imidodisulfate, **2**:180
 $(\text{SO}_2\text{NH}_4)_2\text{NNH}_4\cdot\text{H}_2\text{O}$ Triammonium imidodisulfate, **2**:179, 180
 SO_3NaH Sodium hydrogen sulfite, **2**:164
 SO_3Na_2 (and $+7\text{H}_2\text{O}$) Sodium sulfite, **2**:162, 164, 165
 $\text{SO}_3\text{Na}_2\cdot\text{N}_2\text{O}_2$ Sodium *N*-nitrosohydroxylamine-*N*-sulfonate, **5**:119
 $\text{SO}_3\cdot\text{O}(\text{CH}_2\text{CH}_2)_2\text{O}$ Dioxane-sulfur trioxide, **2**:174
 $2\text{SO}_3\cdot\text{O}(\text{CH}_2\text{CH}_2)_2\text{O}$ Dioxane-bis-(sulfur trioxide), **2**:174
 SO_4HNO Nitrosylsulfuric acid, **1**:55
 SO_4Na_2 Sodium sulfate, **5**:119
 $\text{S}_2\text{O}_5\text{Cl}_2$ Disulfur pentoxydichloride, **3**:124, 126
 $\text{S}_2\text{O}_5\text{K}_2$ Potassium pyrosulfite, **2**:165, 166; $\frac{2}{3}$ -hydrate, **2**:165
 $\text{S}_2\text{O}_5\text{K}_2\cdot 4\text{SO}_3\text{KH}$, **2**:167
 $\text{S}_2\text{O}_5\text{Na}_2$ (and $+7\text{H}_2\text{O}$) Sodium pyrosulfite, **2**:162, 164, 165
 $\text{S}_2\text{O}_6\text{Ba}\cdot 2\text{H}_2\text{O}$ Barium dithionate, **2**:170
 $\text{S}_2\text{O}_6\text{Ca}\cdot 4\text{H}_2\text{O}$ Calcium dithionate, **2**:168
 $\text{S}_2\text{O}_6\text{Na}_2\cdot 2\text{H}_2\text{O}$ Sodium dithionate, **2**:170
 $2\text{SbCl}_3\cdot 3\text{CsCl}$ Antimony(III) cesium chloride, **4**:6
 SbF_3 Antimony(III) fluoride, **4**:134
 SbI_3 Antimony(III) iodide, **1**:104
 SeCNK Potassium selenocyanate, **2**:186
 SeCNNa Sodium selenocyanate, **2**:186, 187
 SeCl_2 Selenium(II) chloride, **5**:127
 $[\text{SeCl}_3]^+[\text{AlCl}_4]^-$ Selenium(IV) chloride, compound with aluminum chloride, **5**:127
 SeCl_4 Selenium(IV) chloride, **5**:125, 126
 SeF_6 Selenium(VI) fluoride, **1**:121
 SeH_2 Hydrogen selenide, **2**:183, 184
 SeOCl_2 Selenium(IV) oxychloride, **3**:130
 SeO_2 Selenium(IV) oxide, **1**:117, 119; **3**:13, 15, 127, 129, 131
 $\text{SeO}_2\text{Cl}_2\text{H}_2$ Dichloroselenious acid, **3**:132
 SeO_3Sr Strontium selenite, **3**:20
 SeO_4H_2 Selenic acid, **3**:137
 $\text{Se}[\text{S}_2\text{CN}(\text{CH}_3)_2]_2$ Selenium(II) dimethylthiocarbamate, **4**:93
 $\text{Se}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$ Selenium(II) diethylthiocarbamate, **4**:93

- $\text{Se}(\text{S}_2\text{COCH}_3)_2$ Selenium(II) methylxanthate, **4:93**
 $\text{Se}(\text{S}_2\text{COC}_2\text{H}_5)_2$ Selenium(II) ethylxanthate, **4:93**
 $\text{SeS}_4\text{O}_6\text{Na}_2 \cdot 3\text{H}_2\text{O}$ Sodium "selenopentathionate" 3-hydrate, **4:88, 89**
 SeSr Strontium selenide, **3:11, 20, 22**
 Se_3Al_2 Aluminum selenide, **2:183, 184**
 SiBr_2H_2 Silane, dibromo-, **1:38**
 SiBr_3H Silane, tribromo-, **1:38, 41**
 SiBr_4 Silicon tetrabromide, **1:38, 40**
 $\text{Si}(\text{CH}_3)_2\text{Cl}_2\text{H}$ Silane, methyl-dichloro-, **3:58**
 $\text{Si}(\text{CH}_3)_3\text{Cl}$ Silane, methyltrichloro-, **3:58**
 $\text{Si}(\text{CH}_3)_2\text{Cl}_2$ Silane, dimethyldichloro-, **3:56**
 $[\text{Si}(\text{CH}_3)_2\text{NH}]_3$ Cyclotrisilazane, hexamethyl-, **5:61**
 $[\text{Si}(\text{CH}_3)_2\text{NH}]_4$ Cyclotetrasilazane, octamethyl-, **5:61**
 $\text{Si}(\text{CH}_3)_3\text{Cl}$ Silane, trimethylchloro-, **3:58**
 $\text{Si}(\text{CH}_3)_3\text{H}$ Silane, trimethyl-, halo derivatives, **5:61**
 $\text{Si}(\text{CH}_3)_2\text{NHC}_6\text{H}_5$ Silane, trimethyl(anilino)-, **5:59**
 $[\text{Si}(\text{CH}_3)_3]_2\text{NCH}_3$ Disilazane, *N*-methylhexamethyl-, **5:58**
 $[\text{Si}(\text{CH}_3)_3]_2\text{NH}$ Disilazane, hexamethyl-, **5:56**; compound with BF_3 , **5:58**
 $[\text{Si}(\text{CH}_3)_3]_2\text{O}$ Disiloxane, hexamethyl-, **5:58**
 $\text{Si}(\text{CH}=\text{CH}_2)(\text{CH}_3)_2$ Silane, vinylmethyldichloro-, **3:58, 61**
 $\text{Si}(\text{CH}=\text{CH}_2)(\text{CH}_3)_3$ Silane, vinyltrimethyl-, **3:58, 61**
 $\text{Si}(\text{CH}=\text{CH}_2)_2\text{Cl}_3$ Silane, vinyltrichloro-, **3:58**
 $\text{Si}(\text{CH}=\text{CH}_2)_2\text{Cl}_2$ Silane, divinyl-dichloro-, **3:58, 61**
 $\text{Si}(\text{C}_2\text{H}_3\text{O}_2)_4$ Silicon tetraacetate, **4:45**
 $\text{Si}(\text{C}_2\text{H}_4\text{Cl})\text{Cl}_2$ Silane, (chloroethyl)trichloro-, **3:60**
 $[\text{Si}(\text{C}_2\text{H}_5)_2\text{NH}]_3$ Cyclotrisilazane, hexaethyl-, **5:62**
 $[\text{Si}(\text{C}_2\text{H}_5)_2\text{NH}]_4$ Cyclotetrasilazane, octaethyl-, **5:62**
 $\text{Si}(\text{C}_6\text{H}_{11})\text{Cl}_2$ Silane, cyclohexyltrichloro-, **4:43**
 SiCl_4 Silicon tetrachloride, **1:44**
 SiF_4 Silicon tetrafluoride, **4:145**
 SiF_6Ba Barium hexafluorosilicate, **4:145**
 SiICl_3 Silane, iodotrichloro-, **4:41**
 SiI_2Cl_2 Silane, diiododichloro-, **4:41**
 $(\text{SiMo}_{12}\text{O}_{40})\text{H}_4 \cdot x\text{H}_2\text{O}$ 12-Molybdosilicic acid, **1:127, 128**
 $\text{Si}(\text{NHC}_6\text{H}_5)_4$ Silane, tetraanilino-, **5:61**
 $\text{Si}(\text{OC}_2\text{H}_4\text{Cl})\text{Cl}_3$ Silane, (2-chloroethoxy)trichloro-, **4:85, 86**
 SiO_2 Silica gel, **2:95**; (correction), **5:55**
 $\text{SiOH}(\text{CH}_3)_3$ Silanol, trimethyl-, **5:58**
 $\text{Si}(\text{OH})_2(\text{C}_6\text{H}_5)_2$ Silanediol, diphenyl-, **3:62**
 $(\text{SiW}_{12}\text{O}_{40})\text{H}_4 \cdot x\text{H}_2\text{O}$ 12-Tungstosilicic acid, **1:129, 131**
 Si_2Br_6 Disilicon hexabromide, **2:98**
 Si_2Cl_6 Disilicon hexachloride, **1:42**
 $(\text{Si}_2\text{O}_2\text{H}_2)_x$ "Silicooxalic acid," **2:101**
 $\text{Si}_2\text{O}_2\text{H}_2$ "Silicoformic anhydride," **1:42**
 Si_3Cl_8 Trisilicon octachloride, **1:44**
 $\text{Sm}(\text{NO}_3)_3$ Samarium(III) nitrate, **5:41**
 SnI_4 Tin(IV) iodide, **4:119**
 SrCl_2 Strontium chloride, **3:21**
 SrNO_3 Strontium nitrate, **3:17**
 SrS Strontium sulfide, **3:11, 20, 21, 23**
 SrSO_4 Strontium sulfate, **3:19**
 SrSe Strontium selenide, **3:11, 20, 22**
 SrSeO_3 Strontium selenite, **3:20**

T

- TaBr₅ Tantalum(V) bromide, **4**:
130
- TaF₅ Tantalum(V) fluoride, **3**:179
- TeBr₆K₂ Potassium hexabromo-
tellurate(IV), **2**:189
- TeCl₄ Tellurium(IV) chloride, **3**:
140
- TeCl₆(NH₄)₂ Ammonium hexa-
chlorotellurate(IV), **2**:189
- TeF₆ Tellurium(VI) fluoride, **1**:121
- TeO₂ Tellurium(IV) oxide, **3**:143
- TeO₆H₆ Telluric acid, **3**:145, 147
- Te(S₂CN(CH₃)₂)₂ Tellurium(II)
dimethyldithiocarbamate, **4**:93
- Te(S₂CN(C₂H₅)₂)₂ Tellurium(II)
diethyldithiocarbamate, **4**:93
- Te(S₂COCH₃)₂ Tellurium(II)
methylxanthate, **4**:93
- Te(S₂COC₂H₅)₂ Tellurium(II) eth-
ylxanthate, **4**:93
- TeS₄O₆Na₂·2H₂O Sodium "tellsu-
ropentathionate" 2-hydrate, **4**:
88, 89
- ThBr₄ Thorium bromide, **1**:51;
ammoniates, **1**:54; hydrates,
1:53
- Th(C₅H₇O₂)₄ Thorium acetylaceto-
nate, **2**:123; ½-ammoniate,
2:125; compound with aniline,
2:125
- ThCl₄ Thorium chloride, **5**:154
- ThOBr₂ Thorium oxybromide,
1:54
- TiBr₃ Titanium(III) bromide, **2**:
116
- TiBr₄ Titanium(IV) bromide, **2**:
114
- [Ti(C₅H₇O₂)₃]FeCl₄ Tris(2,4-pen-
tanediono)titanium(IV) tetra-
chloroferrate(III), **2**:120
- [Ti(C₅H₇O₂)₃]₂TiCl₆ Bis[tris(2,4-
pentanediono)titanium(IV)]
hexachlorotitanate(IV), **2**:119
- TiO₂ Titanium(IV) oxide, **5**:79, 81
- TiS₂ Titanium(IV) sulfide, **5**:82, 85

U

- U(C₂O₄)₂·6H₂O Uranium(IV) oxa-
late, **3**:166
- U(C₂O₄)₄K₄·5H₂O Potassium tet-
raoxalatouranate(IV), **3**:169
- UCl₃ Uranium(III) chloride, **5**:145
- UCl₄ Uranium(IV) chloride, **5**:143,
148
- UCl₅ Uranium(V) chloride, **5**:144
- UO₂ Uranium(IV) oxide, **5**:149
- UO₂Cl₂ Uranyl chloride, **5**:148
- UO₂(C₉H₆NO)₂ Bis(8-quinolino)-
dioxouranium(VI), **4**:101; com-
pound with 8-quinolinol, **4**:101
- UO₂HPO₄·4H₂O Uranyl ortho-
phosphate 4-hydrate, **5**:150
- U₃O₈ Uranium(IV)(VI) oxide, **5**:
149

V

- VCl₂ Vanadium(II) chloride, **4**:126
- VCl₃ Vanadium(III) chloride, **4**:
128; 6-hydrate, **4**:130
- VCl₄ Vanadium(IV) chloride, **1**:
107
- [V(NH₃)₆]Cl₃ Hexamminevanadi-
um(III) chloride, **4**:130
- VO(C₅H₇O₂)₂ Vanadium(IV) oxy-
(acetylacetonate), **5**:113-115
- VOCl₂ Vanadium(V) oxychloride,
1:106; (correction), **4**:80
- VO₃NH₄ Ammonium metavanada-
te, **3**:117
- V₂O₃ Vanadium(III) oxide, **1**:106;
(correction for V₂O₂), **4**:80

W

- W(CO)₆ Tungsten hexacarbonyl,
5:135
- WCl₆ Tungsten(VI) chloride, **3**:
163
- WF₆ Tungsten(VI) fluoride, **3**:181

$W_2Cl_9K_3$ Potassium enneachloro-
ditungstate(III), **5:139**

Y

$Y(NO_3)_3$ Yttrium nitrate, **5:41**

Z

$ZnCl_2$ Zinc chloride, **5:154**

$ZrBr_4$ Zirconium bromide, **1:49**

$Zr(C_5H_7O_2)_4$ Zirconium acetyl-
acetate, **2:121**; 10-hydrate,
2:121

$ZrCl_4$ Zirconium chloride, **4:121**

$ZrOBr_2$ Zirconium oxybromide, **1:**
51

$ZrOCl_2$ Zirconium oxychloride,
3:76

$ZrOCl_2 \cdot 8H_2O$ Zirconium oxychlo-
ride 8-hydrate, **2:121**

ZrO_2 Zirconium oxide, **3:76**