INORGANIC SYNTHESES

Volume IV

Inorganic Syntheses

Volume IV

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to

HAROLD SIMMONS BOOTH

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PREFACE

The reception which has been accorded the earlier volumes of INORGANIC SYNTHESES has been most gratifying to the Board of Editors and has encouraged them to continue the series at an accelerated rate. The resurgence of interest in inorganic chemistry and the rapidly increasing number of its applications lead the editors to hope that these volumes will find increasing usefulness. Conversely, they hope that the publication of INORGANIC SYNTHESES will stimulate interest in inorganic chemistry still further.

The policy of having each synthesis carefully checked in at least one independent laboratory has been continued, as it has been found that the efficiency and usefulness of the syntheses are often greatly increased by the checker. After checking and revision, the syntheses have been edited and then returned to the authors and checkers for final approval.

As in the earlier volumes, the syntheses in Volume IV are arranged on the basis of the Mendeleev periodic classification, with subdivision into A and B groups. The nomenclature is that used in Volumes II and III. Cross references have been used liberally, and the index has been made as complete as possible. The index is cumulative for all four volumes.

Contributions are now being accepted for forthcoming volumes, two of which are in preparation. Manuscripts describing syntheses of a general nature should be sent to Prof. Therald Moeller of the University of Illinois, who will serve as editor of the next general volume. Manuscripts concerning syntheses of hydrides should be sent to Prof. W. C. Johnson of the University of Chicago, who, with Prof. H. I. Schlesinger, is preparing a volume on that subject. All manuscripts should be submitted in triplicate and should follow, as nearly as possible, the style used in the earlier volumes. After a brief introduction, the procedure should be described in detail. This should be followed by a brief description of the chemical and physical properties of the substance under discussion and by analytical data. If the analytical methods are sufficiently distinctive to warrant description, they should be presented in detail. Pertinent references should be placed at the end of the synthesis.

The editors wish, again, to call attention to the fact that INORGANIC SYNTHESES is a periodical publication and that references to articles appearing in it should include the names of the authors of the articles in addition to the name of the editor of the volume.

In dedicating this volume to Prof. Harold S. Booth, the editors wish to acknowledge the invaluable help which Dr. Booth rendered to INORGANIC SYNTHESES. Not only was he one of the founders of the project and the first editor, but he continued to contribute generously of his talents, time, and energy to ensure its continued success. He was an outstanding chemist, an inspiring leader, and best of all, a beloved friend.

The editor-in-chief takes pleasure in thanking his colleagues on the Editorial and Advisory Boards for their help in preparing this volume. Miss Janet D. Scott has been particularly helpful, as she has handled all the problems of nomenclature and indexing. The editor wishes also to thank Mrs. John Maisch for her help in preparing the manuscript, and Daryle H. Busch, without whose excellent help this project could not have been completed for many months.

The editors will consider it a favor if users of INORGANIC SYNTHESES will call to their attention any errors or omissions.

John C. Bailar, Jr.

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CHAPTER IA

See also: Disodium dihydrogen hypophosphate, synthesis 23
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1. LITHIUM NITRIDE

$$6Li + N_2 \rightarrow 2Li_3N$$

Submitted by E. Masdupuy* and F. Gallais*
Checked by T. R. P. Gibb† and H. O. Warren†

Lithium nitride was first prepared by Ouvrard,[1] who heated metallic lithium to dull redness in a stream of nitrogen. Guntz[2] observed shortly afterward that the preparation can be realized with but slight heating, while Deslandres[3] found that the metal absorbs nitrogen even at room temperature. Other early experimental work[4,5] has determined that the compound may best be obtained either at room temperature or at approximately 450°. In the first case, the preparation proceeds slowly; the substance produced is very hygroscopic and retains uncombined nitrogen. When lithium nitride is prepared at the higher temperature, the process is completed in a short time; the substance so obtained is more compact, less hygroscopic, and more easily preserved. For these reasons the second method is preferred.

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† Metal Hydrides, Beverly, Mass.

Procedure

The nitrogen employed should be perfectly dry and free from oxygen and hydrogen. In order to prevent contamination with hydrogen, which may be formed by reduction of water vapor by the hot copper, the nitrogen is passed through a U-tube *A* (Fig. 1) containing Drierite or phosphorus(V) oxide prior to removal of the oxygen. To eliminate the oxygen which the gas contains, it is passed successively over hot powdered copper *B* and through an alkaline solution of sodium dithionite *C*, which is cooled in an ice bath. It is then dried by passing over potassium hydroxide pellets *D*, through sulfuric acid *E*, and then over phosphorus (V) oxide *F*, after which it enters the reaction apparatus *G*. This consists of an iron tube 90 cm. in length and approximately 5 cm. i.d., the ends of which are surrounded by a few turns of lead or copper tubing which serve as cooling coils, using water as a coolant. The central portion of the iron tube is placed in an electric tube furnace *H* about 50 cm. long. This iron tube is fitted with two one-hole rubber stoppers which hold pyrex gas inlet and outlet tubes. The reaction

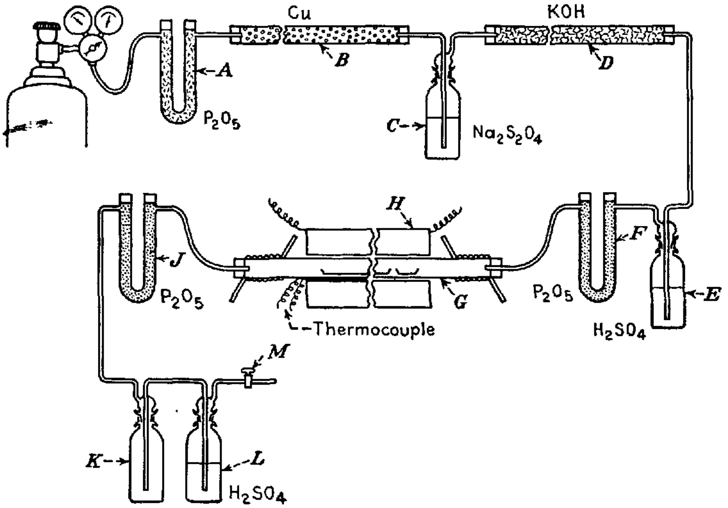

FIG. 1. Apparatus for the preparation of lithium nitride.

tube is preceded in the nitrogen path by the purification train described above and followed by a phosphorus(V) oxide drying tube *J*, a safety flask *K*, a gas-washing bottle containing sulfuric acid *L*, and a glass stopcock *M*, in that order. The sulfuric acid serves both as a washing medium for the gas and as a flowmeter. The external temperature of the reaction tube is determined by means of a thermocouple placed between the tube and the furnace.

Two flat, iron boats are located in the central part of the reaction tube; the boat nearest the point of entry of the nitrogen holds only a small quantity of lithium and serves as a final protection against oxygen and water-vapor contamination, while the second vessel contains the amount of lithium required for the preparation. The apparatus must be thoroughly dried, and all the air must be displaced before the reaction is initiated. Therefore, the reaction tube is first heated gently (200°) for some time in a stream of nitrogen. It is then allowed to cool, and lithium which has been freshly cut into lumps of approximately 0.5 cc. volume is placed in the vessels (1 lump in the first vessel, 10 or 12 lumps in the second). The nitrogen is then allowed to flow for 1 hour to eliminate any air which may have entered the apparatus when the boats were introduced. The temperature is gradually increased to a maximum of 450°. The reaction is most rapid at 370°, at which temperature a sudden strong absorption of nitrogen takes place. In order to prevent air from entering the apparatus during this phase of the preparation (suckback), it is advisable to close the stopcock *M* near the exhaust end of the train. The flow of nitrogen may also be increased. If care is taken, the pressure regulator on the nitrogen tank may be set up to about 4 p.s.i. without causing undue hazard. The gas-washing bottles must be equipped with "horns" which are wired to prevent popping when the pressure builds up after the reaction subsides.* When the absorption is no longer

* As an additional safety precaution, a T-tube with a long vertical arm may be incorporated in the train between wash bottle *E* and tube *F*. The

vigorous, the pressure regulator is set back and the stopcock is *slowly* opened. The temperature is maintained at 450° until nitrogen is no longer absorbed, after which the furnace is allowed to cool while nitrogen still passes through the system.

The lithium nitride produced in the second vessel will be 95 to 99% pure, depending on the purity of the lithium that was used in the reaction. On the basis of ammonia obtained by hydrolysis, the ratio Li:N is very nearly 3:1. Pure lithium nitride may also be produced in the first vessel if the purification of the nitrogen is complete, but this sample of nitride is sometimes contaminated with small quantities of lithium oxide or hydroxide.

Properties

When prepared at high temperature, lithium nitride forms as porous, puffy lumps which are a dark violet in color. Its crystalline nature is apparent on viewing a section of the substance. It is quickly altered by air and must be preserved in an atmosphere of nitrogen. It melts between 840 and 845°. Lithium nitride is extremely reactive at temperatures near its melting point, attacking iron, nickel, copper, and even platinum, silica, and porcelain. It begins to react with iron at 500°, and for this reason the preparation outlined here must be carried out at temperatures of 450° or lower. Its high reactivity may be related, to some extent, to the fact that it exists in an ionic lattice.[6] It evolves nitrogen when electrolyzed.[7]

References

1. Ouvrard: *Compt. rend.*, **114**, 120 (1892).
2. Guntz: *ibid.*, **120**, 777 (1895).

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open end of the vertical arm is immersed in a test tube, 70 to 100 cm. in length, filled with sulfuric acid or mercury. The flow of nitrogen through the horizontal arm of the T-tube is kept adjusted so that some of it bubbles out of the bottom opening. A coarse sintered-glass disk sealed near the top of the vertical arm serves as a further safety device since it prevents, or at least greatly impedes, suckback.

3. DESLANDRES: *ibid.*, **121**, 886 (1895).
4. GUNTZ: *ibid.*, 945.
5. DAFERT and MIKLAUZ: *Monatsh.*, **31**, 981 (1910).
6. ZINTL and BRAUER: *Z. Elektrochem.*, **41**, 102 (1935).
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2. EXTRACTION OF CESIUM FROM POLLUCITE

Although cesium may be recovered from minerals such as lepidolite[1] and beryl,[2] the chief source of this metal is the relatively rare mineral pollucite.* The isolation of a pure compound of cesium usually depends upon the insolubilities of the "double salts" such as the chloroplatinates, the alums, and the double chlorides with tin, lead, and antimony.[3–5] Of these, the compound having the composition $(CsCl)_3(SbCl_3)_2$ is most commonly employed.[6] Use of this material is based upon the observations first recorded by Setterberg[7] and elaborated by the work of Wells[8,9] and others.[10–12] Procedure A outlined below is based primarily upon the work of Wells with $(CsCl)_3(SbCl_3)_2$.[4,5,8]

Pollucite contains enough aluminum to form an alum when treated with sulfate, and the use of this sparingly soluble alum as a means of recovering the cesium value is well known.[13,14] Procedure B given here uses sulfuric acid for the treatment of the mineral, giving the alum directly, eliminating the usual preliminary decomposition of the mineral with hydrochloric acid or hydrofluoric acid.

Other methods which have been suggested for the separation of cesium from pollucite include the conversion of the mineral to carbonates, followed by the extraction of cesium carbonate with ethanol,[15] and the precipitation of cesium iododichloride. The use of cesium iododichloride was first suggested by Wells.[8] This provides the basis for procedure C.

* Approximately $Cs_4Al_4H_2Si_9O_{27}$.

Procedure A*

Cesium Antimony(III) Chloride Method and Preparation of Cesium Nitrate

Submitted by George W. Watt†
Checked by Wm. C. Smith‡

One hundred grams of pollucite§ is ground to −100 mesh in a ball mill, placed in a 600-ml. beaker together with 100 ml. of concentrated hydrochloric acid (12*N*), covered with a watch glass, and digested at the boiling temperature for 4 hours. The mixture is stirred at frequent intervals, and concentrated hydrochloric acid is added from time to time to keep the volume at approximately 100 ml. over the entire digestion period. The hydrochloric acid solution is decanted through a fritted-glass filter, and the residue is covered with 100 ml. of 12 *N* hydrochloric acid and again extracted as described above. The second extract is combined with the first, and the residual solid is collected on the filter and washed twice with 25-ml. portions of water. The residue is dried and weighed in order to determine the total weight of ore dissolved during the two extractions. For most samples of pollucite the extraction is complete when 40 to 50% has been dissolved. If the weight loss is not within the range indicated, the digestion is repeated. The solid residue is finally discarded.

Cesium is precipitated as $(CsCl)_3(SbCl_3)_2$ by diluting the combined filtrate and washings with an equal volume of water and adding a solution that is 20 *M* in antimony(III) chloride and 6 *M* in hydrochloric acid until no further precipitation occurs.‖ The precipitate is filtered through a

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[*] This procedure is readily amenable to being scaled up by at least a factor of 10.

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[‡] University of Illinois, Urbana, Ill.

[§] Most of the pollucite samples used by the author were obtained from the A. D. Mackay Co., New York, N.Y.

[‖] The solubility of the double salt with antimony(III) chloride is about 10 g./l.[6] On the basis of this solubility, 14.2 ml. and 44.4 ml. of the antifritted-glass funnel and washed three times with 10-ml. portions of water. The filtrate and washings are discarded.

A gross separation of cesium and antimony is accomplished by transferring the precipitate to 2500 ml. of boiling distilled water contained in a 4-l. beaker and agitated vigorously with a motor-driven stirrer. The resulting precipitate of antimony(III) oxychloride is digested for 30 minutes, washed with three 25-ml. portions of water, and discarded. The separation from antimony is completed by saturating the hot filtrate with hydrogen sulfide. If a precipitate of antimony sulfide forms, the solution is cooled to room temperature, and the precipitate is removed by filtration and washed with three 25-ml. portions of water. The washings are added to the filtrate, and the precipitate is discarded.

The filtrate from the antimony separation is boiled to expel hydrogen sulfide and to reduce the total volume by approximately one-half. One hundred milliliters of concentrated nitric acid (16 *N*) is added to this solution. The resulting solution is evaporated to a volume of approximately 150 ml. and filtered. The precipitate is washed once with 10 ml. of distilled water, and the combined filtrate and washing are collected in a 250-ml. beaker. This solution is concentrated by evaporation until the formation of crystals is first evident. It is then cooled in an ice-salt bath. The resulting crystals of cesium nitrate 1–hydrogen nitrate[16] are separated by filtration, washed twice with 10-ml. portions of cold 50% ethanol, and air-dried. Complete conversion of the 1–hydrogen nitrate to the unsolvated salt is ensured by heating the air-dried product for 1 hour in a vacuum oven at 110°. If a product of exceptionally high purity is desired, the nitrate may be recrystallized from water.

Although additional crops of crystals may be obtained from the original mother liquor, either by further concen-

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mony(III) chloride solution will precipitate 99% and 99.9% of the cesium, respectively.

tration and cooling or by dilution with ethanol, these products are usually relatively impure. It is preferable to collect these residues (and the mother liquors from any recrystallizations) and recycle them during the extraction of the next batch of ore.

By the above procedure a sample of average pollucite gives a yield of cesium nitrate of about 19 g. This is a convenient starting material for the preparation of other cesium compounds.

Procedure B

Cesium Alum Method

Submitted by Robert West* and Robert P. Anderson*
Checked by Lewis I. Krimen† and Therald Moeller†

Pollucite is broken into pea-sized lumps with a hammer and then ground in a ball mill until fine enough to pass through a 120-mesh sieve. One hundred grams of the screened pollucite‡ is mixed with 400 ml. of 50% sulfuric acid (7.1 *M*) in a 1-l. round-bottomed flask and refluxed gently for 30 hours. The mixture is diluted with 250 ml. of water, heated to boiling, and filtered with suction, using a large, coarse, sintered-glass funnel. The silica residue is washed well with hot water.

The hot solution is cooled to 0°, and the well-defined octahedra of cesium alum are collected on a sintered-glass funnel and washed with cold water. A small second crop of crystals is obtained when the filtrate is concentrated to about 450 ml. and cooled. The yield is about 110 g., or nearly 90% (for Varuträsk pollucite).

Properties

Cesium alum crystallizes in colorless octahedra which melt at 117°. This compound is more insoluble than the other alkali-metal alums and is remarkable for its high

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* Harvard University, Cambridge, Mass.

† University of Illinois, Urbana, Ill.

‡ Swedish pollucite obtained from Ward's Natural Science Establishment was used in both procedures B and C.

temperature coefficient of solubility. At 100°, 12 g. is soluble in 100 g. of water; at 0°, only 0.19 g. is soluble.[13] Because of this property, the cesium compound is readily prepared in a high state of purity by recrystallizing it from water.[14]

Procedure C*

Cesium Iododichloride Method

SUBMITTED BY ROBERT WEST† AND ROBERT P. ANDERSON†
CHECKED BY LEWIS I. KRIMEN‡ AND THERALD MOELLER‡

Pollucite is ground to 120 mesh as described in procedure B above. One hundred grams of the screened material is mixed with 400 ml. of concentrated hydrochloric acid (12 *M*) in a 1-l. round-bottomed flask, which is connected to a reflux condenser, and refluxed gently for 30 hours. The resulting solution is filtered with suction, using a large Büchner funnel, and the silica residue is washed with about 150 ml. of water.

The filtrate and washings are transferred to a beaker§ or evaporating dish and concentrated nearly to dryness on a steam bath, to remove excess hydrogen chloride. The concentrated solution is diluted to about 400 ml. with water, and concentrated aqueous ammonia (28%, sp. gr. 0.90) is added until the solution is definitely basic. Six grams of ammonium carbonate (0.05 mol) is then added, and the mixture is stirred and heated on the steam bath for 15 minutes. The suspension is filtered with suction on a large Büchner funnel, and the residue is washed three times by slurrying with dilute (1:10) ammonia.

A small amount of ammonium oxalate is added to the filtrate and washings to test for the presence of calcium.

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* Based in part upon a method developed many years ago by the late Prof. L. M. Dennis at Cornell University.

† Harvard University, Cambridge, Mass.

‡ University of Illinois, Urbana, Ill.

§ It has been found convenient to carry out the entire procedure in 800-ml. beakers, thus minimizing splattering losses during the numerous evaporations.

If a precipitate results, more oxalate is added until a precipitate no longer forms, and the liquors are filtered.

The filtrate is then evaporated nearly to dryness in a weighed beaker or evaporating dish. About 50 ml. of concentrated nitric acid (16 *M*) is added, and the solution is evaporated to dryness. This operation is repeated (usually three or four times) until frothing stops, and there is no change in color upon the addition of more nitric acid, at which point all the ammonium ion has been decomposed. The mixture is then heated above 100° on a hot plate.* When boiling stops and the temperature of the melt approaches 170°, the nitrate mixture is cooled slowly with stirring until it solidifies.

The solid nitrates are then weighed and dissolved in the smallest possible amount of hot water. If the solution is not clear, it is filtered to remove dehydrated silica. The nitrate solution is diluted until 50 ml. of the solution contains 20 g. of dry nitrates. The solution is heated to boiling, and two parts by weight of solid iodine is added for every three parts of dry nitrates. A volume of pure concentrated hydrochloric acid (12 *M*) equal to three times the volume of the solution is added. The solution is kept warm until the iodine is completely dissolved, the color of free iodine has disappeared, and all the nitric oxide has been expelled. Slow cooling now produces long, orange needles of $CsICl_2$; more rapid cooling gives orange plates. The crystals are collected on a sintered-glass funnel and washed several times with small amounts of 9 *M* hydrochloric acid. A second crop of crystals is obtained by concentrating the filtrate to one-fourth its original volume.

The crystals are air-dried overnight and then heated for a few minutes on a steam bath to drive off the last of the hydrogen chloride. The yield is about 61 g., or 85% based on the published analysis of Varuträsk pollucite.[17] If a

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* Cesium is present as the hydrogen nitrate solvate, which melts at approximately 100°.

very pure cesium salt is required, the iododichloride can be recrystallized from hot 8 *M* hydrochloric acid.

Cesium iododichloride can be converted quantitatively to cesium chloride by heating for several hours at 150 to 200°, until the powder is pure white in color and no longer smells of iodine monochloride.

Analysis

Since the principal impurities in cesium compounds are other alkali metals, analysis by conventional methods is difficult. Unrecrystallized cesium iododichloride prepared by this method was analyzed spectroscopically and found to contain 0.01 to 1.0% rubidium and traces of other metals.

Properties

Cesium iododichloride crystallizes in beautiful orange rhombohedral needles or plates. The compound is stable indefinitely in closed containers but slowly whitens when exposed to air, reverting to cesium chloride. The cesium trihalides are more stable thermally and less soluble than those of the other alkali metals.

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CHAPTER IB

3. SILVER(II) OXIDE

$$4AgNO_3 + 2K_2S_2O_8 + 8NaOH \rightarrow 4AgO + K_2SO_4 + 3Na_2SO_4 + 2NaNO_3 + 2KNO_3 + 4H_2O$$

Submitted by Robert N. Hammer* and Jacob Kleinberg*
Checked by Henry F. Holtzclaw, Jr.,† and K. W. R. Johnson†

Silver(II) oxide has been made by the hydrolytic action of boiling water on a substance of the approximate formula $Ag_7O_8NO_3$, a material which is obtained by the electrolytic oxidation of silver(I) nitrate solutions.[1–4] A more rapid and convenient process for the preparation of this oxide involves the oxidation of silver(I) nitrate by means of potassium peroxydisulfate in an alkaline medium.[5,6]

Procedure

Seventy-two grams of sodium hydroxide (1.8 mols) in pellet form is added portionwise, with constant stirring, to 1 l. of water, which is maintained at approximately 85°. Seventy-five grams of potassium peroxydisulfate (0.28 mol) in the form of an aqueous slurry is added to the hot alkaline solution; this is followed by the addition of 51 g. of silver(I) nitrate (0.30 mol) dissolved in a minimum amount of water. The temperature of the resulting mixture is raised to 90°, and stirring is continued for approximately 15 minutes.

The precipitate of black silver(II) oxide is filtered on a large Büchner funnel, and sulfate ion is removed by washing with water which has been made slightly alkaline with sodium hydroxide. The product is air-dried. Yield, 35 g. (94%). *Anal.* Calcd. for AgO: Ag, 87.08. Found: Ag,

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† University of Nebraska, Lincoln, Neb.

86.93, 86.90 (by gravimetric chloride method, after dissolution of the product in 3 *N* nitric acid).

Properties

There are many indications that AgO is a true oxide, rather than a peroxide, and is, therefore, properly named silver(II) oxide. The compound does not give free hydrogen peroxide when acidified but behaves in a manner more characteristic of a compound in which the metal ion is present in a strongly oxidizing valence state, which may be stabilized by coordination. In dilute acid, oxygen is immediately evolved; in concentrated acid, intensely colored solutions are formed (brown in nitric acid and olive green in sulfuric acid). These latter solutions are relatively stable, though they gradually decompose with an accompanying liberation of oxygen, and have been shown to possess paramagnetism which is quantitatively consistent with the expected magnetic moment of the postulated silver(II) species.[7] In the solid state, this oxide is stable when heated to 100°, but it decomposes at higher temperatures. The solid possesses semiconductor properties and is diamagnetic. These phenomena have been explained by Neiding and Kazarnovskii[7] on the assumption that the silver is actually trivalent in its crystal lattice with both O-Ag and Ag-Ag bonds. The difference in the specific volumes of AgO and Ag_2O is less than would be expected if AgO were a peroxide.[7] Equilibration of silver(II) oxide with dilute nitric acid gives the black paramagnetic oxynitrate ($Ag_7O_8NO_3$), a substance in which part of the silver is apparently in the tripositive state.

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4. GOLD POWDER AND POTASSIUM TETRABROMOAURATE(III)

Submitted by B. P. Block*
Checked by S. A. Bartkiewicz† and Therald Moeller,† and by J. D. Chrisp,‡ P. Gentile,‡ and L. O. Morgan‡

The most inexpensive way to obtain gold compounds is to purchase metallic gold and prepare the desired compounds from the metal, because gold(III) chloride, the only readily available compound, costs about the same, gram for gram, as pure gold. Ordinarily, gold is supplied as the massive metal, a form which reacts fairly slowly, so it is convenient to convert the gold to powder form before use. This may be accomplished by dissolving the gold in aqua regia, removing the excess nitric acid, and then reducing the tetrachloroauric(III) acid solution back to metal. Many substances will reduce gold(III) chloride solutions to gold,[1,2] but frequently the gold produced is, at least in part, colloidal and difficult to manage. Hydroquinone will reduce such gold solutions quantitatively.[3] It is convenient to work with and produces no colloidal gold.

Balard, in his paper describing the discovery of bromine,[4] reported the reaction of gold with bromine to give gold(III) bromide. Shortly thereafter Bonsdorff prepared potassium tetrabromoaurate(III) 2-hydrate by the reaction of potassium bromide with a gold(III) bromide solution which had been made by dissolving gold in a mixture of nitric acid and hydrobromic acid.[5] He later found that the water of hydration could be removed by gentle heating.[6] Schottländer employed the reaction of gold with bromine in the pres-

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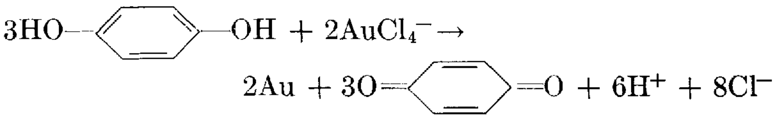
‡ University of Texas, Austin, Tex.

ence of potassium bromide to prepare potassium tetrabromoaurate(III) 2-hydrate,[7] whereas Gutbier and Huber treated a solution of tetrachloroauric(III) acid with hydrobromic acid and potassium bromide for this purpose.[8] The reaction used by Schottländer is probably the most convenient.

Procedure

A. GOLD POWDER

$$Au + HNO_3 + 4HCl \rightarrow HAuCl_4 + NO + 2H_2O$$



A 10-g. piece of gold (0.051 mol) is dissolved in a mixture of 50 ml. of concentrated (12 *M*) hydrochloric acid and 13 ml. of concentrated (16 *M*) nitric acid. Heating the mixture to 90° will hasten the process somewhat, but then aqua regia has to be added occasionally to maintain a constant volume. It is simpler to allow the mixture to stand at room temperature until all the gold has dissolved. The resulting solution is evaporated to about 10 ml., 30 ml. of concentrated hydrochloric acid is added, and the evaporation is repeated. The solution is diluted with 20 ml. of water and filtered through a medium sintered-glass funnel, and the flask and filter are washed with small amounts of water. The filtrate with the added washings is heated to boiling, and a solution of 10 g. of hydroquinone (0.091 mol) in 100 ml. of hot water is added slowly. The mixture is maintained at about 90° for 1 hour, cooled, and filtered through an extraction thimble, which is then placed in a Soxhlet extractor and extracted with methanol. Fifteen minutes after the methanol circulating through the thimble has become colorless, the thimble is removed, and the contents are allowed to dry in the air. The yield of gold powder is essentially quantitative.

B. POTASSIUM TETRABROMOAURATE(III)

$$KBr + Au + \tfrac{3}{2}Br_2 \rightarrow KAuBr_4$$

Nine and eighty-six hundredths grams of gold powder (0.050 mol), 5.95 g. of potassium bromide (0.050 mol), and 100 ml. of water are placed in a 300-ml. flask. Ten milliliters of bromine (0.195 mol) is added to the mixture, and the temperature is then kept at 55° for 6 hours. At the end of this period, a stream of clean compressed air is passed over the solution, which is still maintained at 55°, until it has evaporated to dryness. The residue is dissolved in 50 ml. of methanol, and the resulting solution is filtered through a medium sintered-glass funnel. The flask and filter are washed with methanol and the washings combined with the filtrate. Evaporation of this solution to dryness at 40° with a compressed-air stream gives a practically quantitative yield of anhydrous potassium tetrabromoaurate(III) (27.8 g.).* The solid should be stored in a desiccator until required. No special precautions need be taken to protect it from light. *Anal.* Calcd. for $KAuBr_4$: Au, 35.47; Au + KBr, 56.9. Found: Au, 35.3, 34.9,† 34.8;† Au + KBr, 56.8.

Properties

Potassium tetrabromoaurate(III) is a reddish-purple crystalline solid which begins to decompose at 120°.[9] It is readily soluble in water, methanol, and ethanol. It slowly absorbs water from the atmosphere to form the 2-hydrate, which loses its water of hydration at 60°.[6]

References

1. Mellor: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 3, pp. 595–603, Longmans, Green & Co., Inc., New York and London, 1923.
2. Lenher: *J. Am. Chem. Soc.*, **35**, 546 (1913).

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* The yield is sometimes a fraction over 100%. This is probably due to the presence of a small amount of unreacted bromine or to the presence of some water of hydration, as is indicated by the analyses.

† These data were supplied by checkers Bartkiewicz and Moeller.

3. Beamish, Russell, and Seath: *Ind. Eng. Chem., Anal. Ed.*, **9**, 174 (1937).
4. Balard: *Ann. chim. et phys.*, [2] **32**, 337 (1826).
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CHAPTER IIA

5. CALCIUM DIHYDROGEN ORTHOPHOSPHATE 1-HYDRATE

(Calcium Tetrahydrogen Di-orthophosphate 1-Hydrate)

$$CaCO_3 + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 \cdot H_2O + CO_2$$

Submitted by A. Tovborg Jensen* and J. Rathlev*
Checked by Therald Moeller† and Robert W. Haisty†

Calcium dihydrogen orthophosphate 1-hydrate has been reported to be deliquescent; however, its alleged deliquescence may be attributed to contamination with orthophosphoric acid. The following procedure gives a crystalline product which is perfectly stable when exposed to air. The salient point in the preparation of the stable compound is the washing of the crystals with acetone.

Procedure

Fifty grams of calcium carbonate (0.5 mol), 110 g. of 89% orthophosphoric acid (1.0 mol), and 200 ml. of 60% orthophosphoric acid (the liquor from the crystallization step in an earlier run is suitable) are kneaded in a mortar until the evolution of carbon dioxide has stopped. The mixture is added to 250 ml. of 60% orthophosphoric acid. The resulting slurry is heated until the solid components dissolve and, if necessary, is filtered with suction through a funnel equipped with a sintered-glass disk. In order to obtain large crystals of the product, the clear solution must be cooled very slowly to 0°. The crystalline product is filtered, washed seven or eight times with 70-ml. portions of

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† University of Illinois, Urbana, Ill.

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acetone, and then dried in air. The yield is 92 g. (73% based on calcium carbonate), or 111 g. (88%) if the 60% orthophosphoric acid used for crystallization is the liquor from a previous run and is therefore saturated with calcium dihydrogen orthophosphate 1-hydrate.

Properties

Calcium dihydrogen orthophosphate 1-hydrate crystallizes as large, white, shining, triclinic plates which may be up to 1 mm. in diameter. The refractive indexes* for the crystals are 1.528, 1.518, and 1.501.[1] No increase in weight is detectable when calcium dihydrogen orthophosphate 1-hydrate is exposed to the air at room temperature for long periods of time.

References

1. Bale, *et al.: Ind. Eng. Chem., Anal. Ed.*, **17**, 491 (1945).
2. Hill and Hendricks: *Ind. Eng. Chem.*, **28**, 443 (1936).

6. CALCIUM HYDROGEN ORTHOPHOSPHATE 2-HYDRATE AND CALCIUM HYDROGEN ORTHOPHOSPHATE

Submitted by A. Tovborg Jensen† and J. Rathlev†

The nature of the calcium orthophosphate precipitated from an aqueous solution containing calcium and orthophosphate ions depends on the pH of the solution. The solubility products of the different calcium orthophosphates at room temperature[1] indicate that the pH must be less than 4 in order to obtain calcium hydrogen orthophosphate 2-hydrate (brushite) and avoid supersaturation with Bjerrum hydroxyapatite.‡ On the other hand, the largest

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* There is a slight disagreement in the optical properties reported by Bale *et al.*,[1] and those reported in reference 2, particularly in the values given for α which are 1.501 and 1.496 as given by Bale *et al.* and by Hill and Hendricks, respectively.

† Royal Veterinary and Agricultural College, Copenhagen, Denmark.

‡ This compound is a colloidal hydroxyapatite, containing about 5% water, which is formed by slow precipitation from calcium chloride and disodium hydrogen orthophosphate solutions at 100° and pH of 9 to 10.

yields of brushite are obtained at the highest permissible pH values. The basic phosphate which precipitates at room temperature is much more soluble than Bjerrum hydroxyapatite, and the small amounts of it which form locally redissolve at pH 4 to 5 and are converted to pure brushite, which is then precipitated. High local values of pH must be avoided as much as possible, or the basic phosphates formed will not redissolve completely.

Brushite is not stable much above room temperature. It dehydrates to form the anhydrous salt (monetite), but not in a manner applicable to synthesis. However, if calcium hydrogen-orthophosphate is precipitated at 100° at a pH of 4 to 5, monetite is formed.

The following procedure permits a close control of pH at every stage of the reaction and gives a high yield of product in a good state of purity.

Procedure

A. CALCIUM HYDROGEN ORTHOPHOSPHATE 2-HYDRATE

(Brushite)

$$Na_2HPO_4 \cdot 2H_2O + CaCl_2 \cdot 6H_2O \rightarrow CaHPO_4 \cdot 2H_2O + 2NaCl + 6H_2O$$

Checked by Therald Moeller* and Stephen J. Bodnar*

Ninety grams of disodium hydrogen orthophosphate 2-hydrate (0.5 mol) and 5 g. of potassium dihydrogen orthophosphate (0.037 mol) are dissolved in 1 l. of hot water. This solution is cooled to room temperature, and is now almost saturated with respect to disodium hydrogen orthophosphate. A calcium chloride solution is prepared by dissolving 110 g. of the 6-hydrate (0.5 mol) in 1 l. of water. Using dropping funnels, the two solutions are added slowly at the same rate to a solution of 10 g. of potassium dihydrogen orthophosphate dissolved in 0.5 l. of water, which is contained in a 3-l. beaker and maintained at room tem-

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* University of Illinois, Urbana, Ill.

perature. The solution is stirred mechanically during the addition.

The pH of the reaction medium is initially 4. In order that the pH may be maintained between 4 and 5, methyl red is added in equal concentrations to each of the three solutions; any change in pH is then detected by comparison with the color of a standard solution. If necessary, the pH of the reaction medium is adjusted by adding potassium dihydrogen orthophosphate.

Care must be taken to add both reagents at the same rate and slowly enough to allow the local precipitate of the more basic phosphates to redissolve before the next drop is added. In the first few minutes, the supernatant liquor is slightly turbid because of the precipitation of amorphous phosphates; however, it soon becomes clear.

After 2½ to 3 hours, the operation is finished. The mother liquor is sucked from the crystals, which are then washed three times with 330-ml. portions of a solution containing 0.16 ml. of 45% orthophosphoric acid in 1 l. of water. The crystals are then washed with 250 ml. of ethanol and dried in air. In order to obtain a pure product, it is necessary to perform the washing operations rapidly and without interruption (maximum period of time, 20 minutes), because the dissolution of some of the brushite during the washing process causes an increase in the pH of the wash solution which may subsequently cause contamination of the product with highly hydrated basic phosphates. The last portion of the wash solution has a pH of approximately 5. The yield is 83 g. (96%). The most convenient and sensitive test for purity depends on loss of weight when the product is ignited at 900° and in that manner converted to calcium pyrophosphate ($Ca_2P_2O_7$). *Loss of weight upon ignition at* 900°. Calcd.: 26.17. Found: 26.20, 26.30.

B. CALCIUM HYDROGEN ORTHOPHOSPHATE

(Monetite)

$$Na_2HPO_4 \cdot 2H_2O + CaCl_2 \cdot 6H_2O \xrightarrow{100°} CaHPO_4 + 2NaCl + 8H_2O$$

Checked by Therald Moeller,* Michael Kondzella,* and Robert Lokken*

The procedure for the preparation of monetite is the same as that given for brushite in part A, except that the reaction medium is kept at 100° throughout the course of the reaction. The wash solutions are slightly different. The product is first washed with three 330-ml. portions of an orthophosphoric acid solution with a pH of approximately 3, and then with 250 ml. of absolute ethanol. The yield is 65 g. (95%). *Loss of weight upon ignition at* 900°. Calcd.: 6.62. Found: 7.13. (This represents an excess of water, over that required by the equation, of 0.0416 mol per mol of calcium hydrogen orthophosphate.)

Properties

Brushite forms white monoclinic (2) crystals with n_D 1.553, 1.5450, 1.5394.[2] Its water of crystallization is lost slowly below 100°. It is further dehydrated at red heat to calcium pyrophosphate.

Monetite forms white triclinic ($\bar{1}$) crystals with refractive indexes 1.63, 1.61, 1.60.[3]† At red heat it is dehydrated to calcium pyrophosphate.

References

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4. Hill and Hendricks: *Ind. Eng. Chem.*, **28**, 443 (1936).

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† Hill and Hendricks[4] report the refractive indexes for monetite as follows: α, 1.587; β, 1.615; γ, 1.640.

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CHAPTER IIIA

See also: Aluminum(III) iodide, synthesis 39
Gallium(II) chloride, synthesis 37

7. ALUMINUM PHOSPHIDE

$$4Al + P_4 \rightarrow 4AlP$$

Submitted by Wayne E. White* and A. H. Bushey*
Checked by Henry F. Holtzclaw, Jr.,† and Frank W. Hengeveld†

The relative ease with which a good-quality aluminum phosphide may be made suggests the possibility of greater laboratory use of this compound as a source for phosphine.

The early chemical literature has recorded the existence of several different aluminum phosphides, but it now appears that only one exists, namely, AlP.[1]

Procedure

By the simple procedure given here aluminum phosphide of 75% purity, or greater,‡ can be obtained if the reactants are of good quality and if care is taken to avoid excessive contact with the air during the reaction between the aluminum and phosphorus. A product of considerably higher purity can be obtained if the phosphorus is purified, −400-mesh aluminum is used,[1] and the reaction is carried out in a hydrogen atmosphere.

Six grams of pure, dry red phosphorus (0.193 g.-atom.) is mixed intimately with 4.5 g. of flake-type aluminum powder (0.167 mol) having low oxide content (*e.g.*, Alcoa No. 422). The mixture is transferred to an iron crucible

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† University of Nebraska, Lincoln, Neb.

‡ The checkers reported purities of 92% and 80% on the two runs which they made.

of such size (approximately 25 ml. capacity) that the packed mixture occupies one-third to one-half its volume. The crucible must be provided with a close-fitting cover. The crucible containing the mixture is placed in a hood and on an iron plate, which serves to conduct away part of the heat produced in the subsequent reaction. A piece of magnesium ribbon is inserted into the mixture with about 2 cm. extending above the surface and not more than 1 cm. below. The magnesium is ignited, and the crucible cover is immediately set in place. The high temperature produced by the burning magnesium initiates the highly exothermic reaction between the aluminum and phosphorus.

The excess phosphorus condenses in the yellow form on the cover and in the upper part of the crucible. When the crucible cover is removed, the excess phosphorus burns. As soon as the burning of the phosphorus has subsided somewhat, the crucible is placed in a desiccator. The phosphide appears as a dark-colored, rather fluffy mass. Usually, there is little difficulty in preventing contamination from the excess phosphorus and its oxide, since they tend to stick to the crucible and its cover. The ash of the magnesium is easily picked out. The product is then loosened with a spatula and removed from the crucible.

The phosphide must be protected from moist air, since it reacts readily with moisture to produce phosphine. Care must always be taken to avoid inhalation of the very toxic phosphine gas.

Analysis

A weighed sample of the aluminum phosphide is treated with water and acid, in order to produce phosphine from the aluminum phosphide and hydrogen from the unreacted metallic aluminum. These gases are swept by a stream of nitrogen into an absorption vessel containing mercury(II) chloride solution. Phosphine reacts according to the equation

$$PH_3 + 3HgCl_2 \rightarrow P(HgCl)_3 + 3HCl$$

The liberated acid is titrated to obtain a measure of the phosphide phosphorus. The gas emerging from the solution is swept into a hot copper oxide tube to convert the hydrogen to water; the latter is collected in a weighed drying tube.

Aluminum oxide in the sample is determined by exposing another sample of the product to a stream of dry, oxygen-free hydrogen chloride at 500°. Metallic aluminum and aluminum phosphide are volatilized under these conditions as aluminum chloride so that the residue may be weighed directly as aluminum oxide.

Properties

Aluminum phosphide (AlP) exists as dark gray to dark yellow crystals with the cubic zinc blende structure.[2] The length of an edge of the unit cube (a_0) is 5.451 Å. Aluminum phosphide does not melt or decompose thermally at temperatures up to 1000°. It is readily hydrolyzed to give phosphine.

References

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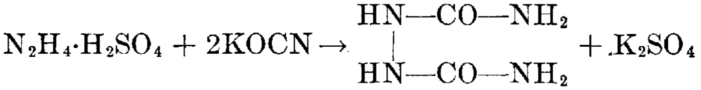
CHAPTER IV

See also: Silicon tetrafluoride, synthesis 47
- Germanium(IV) fluoride, synthesis 48
- Tin(IV) iodide, synthesis 40
- Zirconium and hafnium tetrachlorides, synthesis 41
- Diethyl phosphite, synthesis 19
- Dioctyl phosphite, synthesis 20
- Alkyl dichlorophosphites, synthesis 21
- 2-Chloroethyl dichlorophosphite, synthesis 22
- Diethyl monoamidophosphate, synthesis 26
- Diethyl monochlorophosphate, synthesis 27
- 2-Chloroethyl chlorosulfonate and (2-chloroethoxy)trichlorosilane, synthesis 30
- Xanthates and dithiocarbamates of selenium(II) and tellurium (II), synthesis 32
- Iron(II) formate, synthesis 52

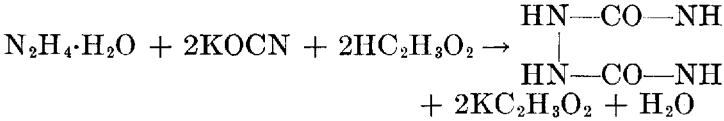
8. BIUREA

(Hydrazidicarbamide)

(1,2-Dicarbamylhydrazine)



$$N_2H_4 \cdot H_2SO_4 + 2KOCN \rightarrow \begin{array}{l} HN{-}CO{-}NH_2 \\ | \\ HN{-}CO{-}NH_2 \end{array} + K_2SO_4 \qquad (A)$$



$$N_2H_4 \cdot H_2O + 2KOCN + 2HC_2H_3O_2 \rightarrow \begin{array}{l} HN{-}CO{-}NH_2 \\ | \\ HN{-}CO{-}NH_2 \end{array} + 2KC_2H_3O_2 + H_2O \qquad (B)$$

Submitted by L. F. Audrieth* and Elizabeth B. Mohr*
Checked by H. E. Ritchey† and W. R. Tuxhorn†

Biurea has been prepared by the reaction of urea with hydrazine hydrate[1,2] or with hydrazinium hydrogen sulfate

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* University of Illinois, Urbana, Ill. Experimental work was undertaken under Ordnance Contract W-11-022-ORD-11329. Publication has been approved by the Office of Public Information of the Office of Chief of Ordnance.

† Virginia Military Institute, Lexington, Va.

(hydrazine sulfate)[3] at elevated temperatures and also by the action of sodium hypobromite upon an aqueous solution of semicarbazide hydrochloride.[4] The preferred methods represent modifications of Thiele's procedure[5,6] involving the condensation of potassium cyanate with hydrazine sulfate or hydrazine hydrate in the presence of an acetate buffer.

Procedure A

Preparation from Hydrazine Sulfate. Sixty-five grams of hydrazine sulfate (0.5 mol) is added to a mixture of 30 g. of glacial acetic acid (0.5 mol) in 1000 ml. of water. Eighty-nine grams of potassium cyanate* (1.1 mol) dissolved in 300 ml. of water is added to this solution portionwise with constant stirring. Considerable gas evolution takes place, and the temperature rises to about 40°. The acetic acid serves to adjust the final pH to approximately 4.8.

After the mixture has been allowed to digest for 4 hours at room temperature with constant stirring, the biurea is filtered by suction and washed with 300 ml. of water, followed by ethanol and ether. The dry product should weigh from 53 to 55 g. (90 to 93% yield). The biurea is quite pure and need not be recrystallized.

Procedure B

Preparation from Hydrazine Hydrate. Hydrazine hydrate may be substituted for hydrazine sulfate in the preparation of biurea. In this case it is necessary to supply enough additional acetic acid to compensate for the absence of sulfuric acid. Thus, 29 g. of 85% hydrazine hydrate (0.5 mol) and 90 g. of glacial acetic acid (1.5 mol) are dissolved in 500 ml. of water. Eighty-nine grams of potas-

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* This quantity represents a 10% excess of pure potassium cyanate. Commercial cyanate generally contains impurities requiring suitable adjustment of amounts of reagent. The major impurity is carbonate, which in part accounts for the vigorous gas evolution when the cyanate is added to the hydrazine sulfate solution.

sium cyanate (1.1 mols) in 300 ml. of water is added to this solution. This must be done carefully and in 50-ml. portions, since vigorous gas evolution takes place. The final pH is about 5.4. After 4 hours of digestion, the biurea is recovered as described in A. The yield and the purity of the product are the same as when hydrazine sulfate is used.

Properties

Biurea is a dense, white crystalline compound which melts with decomposition at 245 to 246°. It is soluble in water to the extent of less than 0.10 g./100 g. of water at 0° and is insoluble in alcohol and ether. It dissolves without decomposition in warm concentrated potassium hydroxide. It is nonhygroscopic and undergoes no decomposition when heated at 110° for 48 hours.

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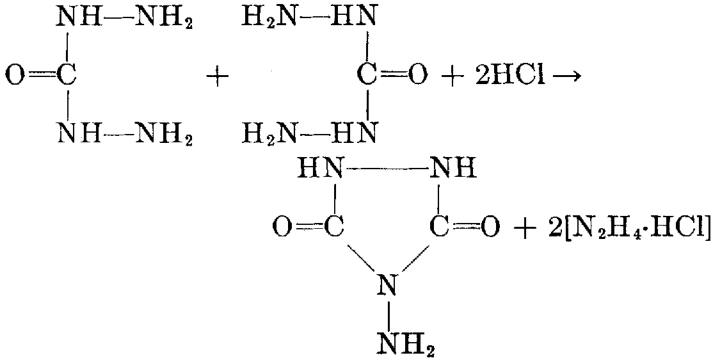
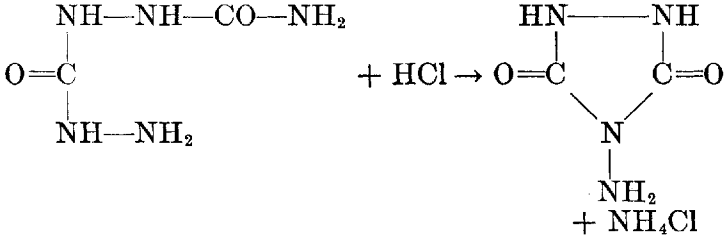
9. URAZINE


(*A*)


(*B*)

Submitted by L. F. Audrieth* and Elizabeth B. Mohr*
Checked by Emanuel Davis† and W. R. Tomlinson, Jr.†

Many of the *N*-alkyl and *N*-aryl derivatives of urazine have been synthesized and characterized, but the parent substance is not well known. In the past, urazine has been prepared by thermal deammonation of carbohydrazide-*N*-carboxamide [eq. (1)],[1] fusion of hydrazidicarbamide with hydrazinium hydrogen sulfate [eq. (2)],[2] fusion of carbohydrazide with urea [eq. (3)],[3] action of sodium hypobromite on semicarbazide [eq. (4)],[4] reaction of dichlorourea with concentrated ammonia [eq. (5)],[5] and the reaction between 1,2 hydrazine carboxylic ester and hydrazine hydrate

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* University of Illinois, Urbana, Ill. Experimental work was undertaken under Ordnance Contract W-11-022-ORD-11329. Publication has been approved by the Office of Public Information of the Office of Chief of Ordnance.

† Chemical Research Laboratory, Picatinny Arsenal, Dover, N.J.

[eq. (6)][6]. However, none of these procedures gives urazine in good yield.

$$CO(NH{\cdot}NH_2)NH{\cdot}NHCONH_2 \rightarrow C_2H_4N_4O_2 + NH_3 \qquad (1)$$

$$(-NHCONH_2)_2 + N_2H_4{\cdot}H_2SO_4 \rightarrow C_2H_4N_4O_2 + NH_4HSO_4 + NH_3 \qquad (2)$$

$$CO(NH{\cdot}NH_2)_2 + CO(NH_2)_2 \rightarrow C_2H_4N_4O_2 + 2NH_3 \qquad (3)$$

$$2CO(NH_2)(NH{\cdot}NH_2) + 2NaBrO \rightarrow C_2H_4N_4O_2 + 2NaBr + 2NH_3 + O_2 \qquad (4)$$

$$2CO(NHCl)_2 + 4NH_3 + 2H_2O \rightarrow C_2H_4N_4O_2 + 2NH_4OCl + 2NH_4Cl \qquad (5)$$

$$(-NHCOOC_2H_5)_2 + N_2H_4{\cdot}H_2O \rightarrow C_2H_4N_4O_2 + 2C_2H_5OH \qquad (6)$$

The methods recommended here involve acid-catalyzed desolvation reactions, which lead to better yields of the desired compound.

Procedure A

Preparation from Carbohydrazide. One hundred seventeen grams of carbohydrazide (1.3 mols) and 108 ml. of 12 *M* hydrochloric acid (1.3 mols) are mixed in a 400-ml. beaker equipped with a mechanical stirrer and a 360° thermometer. The mixture is heated slowly on a hot plate with constant stirring. At first, there is vigorous effervescence, which may cause spattering, but this gradually subsides as evaporation continues. The temperature rises to about 215° and remains there for approximately an hour. Heating is stopped when the temperature rises above 220°. The over-all time of reaction is 4 hours. To the cooled melt, 125 ml. of water is added, and the mixture is heated to effect solution of soluble by-products (principally hydrazine hydrochloride). After the solution has cooled to room temperature, the urazine is filtered and washed with water, ethanol, and ether. The yield of dry product is 55 g. (73%). The product melts with decomposition at 271 to 272°.

The impure urazine is recrystallized by dissolving it in

1200 ml. of 0.1 *M* hydrochloric acid at 95°, filtering, and cooling to room temperature with constant stirring. The urazine crystallizes in the form of large, brilliant, white crystals; it is filtered and washed with water, ethanol, and ether. The product weighs about 44 g. (80% yield based on the crude product) and melts with decomposition at 275°.

Procedure B

Preparation from Carbohydrazide-*N*-carboxamide. Twenty-six and six-tenths grams of carbohydrazide-*N*-carboxamide (0.2 mol) and 16.7 ml. of 12 *M* hydrochloric acid (0.2 mol) are heated together in a 200-ml. beaker until the temperature of the mixture rises to 210°. This usually requires between 60 and 90 minutes. The melt is then cooled and treated with 35 ml. of water. The suspension is heated briefly to effect complete solution and is then cooled to room temperature. The crystalline urazine is filtered and washed with water, ethanol, and ether. The product weighs about 11.5 g. (50% yield) and melts with decomposition at 270 to 272°. Purification is effected by recrystallization from 0.1 *M* hydrochloric acid, as described above.

Properties

Urazine melts with decomposition at 276°, but it is quite stable over long periods of time at 110°. It is soluble in water to the extent of 0.32 g./100 g. at 0° and 4.02 g./100 g. at 65°. It is difficultly soluble in alcohol and completely insoluble in boiling acetic acid and in ether.

Urazine is a weak acid (pH of a saturated solution at 25° is 3.4). The following salts have been described: $NH_4C_2H_3N_4O_2 \cdot H_2O$, $N_2H_5C_2H_3N_4O_2$, $NaC_2H_3N_4O_2 \cdot H_2O$, $AgC_2H_3N_4O_2$, $Ba(C_2H_3N_4O_2)_2 \cdot 3H_2O$. The silver and barium salts are quite insoluble in water.

Urazine reduces ammoniacal silver nitrate but does not reduce Fehling solution. When shaken with benzaldehyde, it reacts readily to form 4-benzalaminourazole, $C_6H_5CH{-}C_2H_2N_4O_2$, which melts at 253°.

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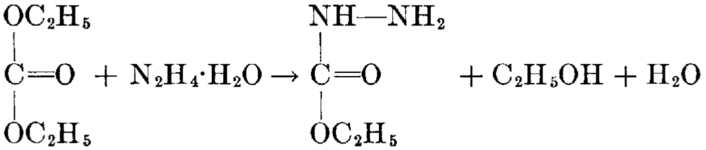
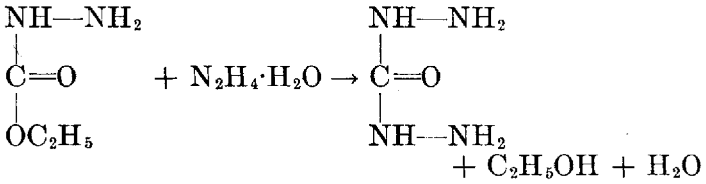
10. CARBOHYDRAZIDE



$$\begin{array}{l} OC_2H_5 \\ | \\ C{=}O \\ | \\ OC_2H_5 \end{array} + N_2H_4{\cdot}H_2O \rightarrow \begin{array}{l} NH{-}NH_2 \\ | \\ C{=}O \\ | \\ OC_2H_5 \end{array} + C_2H_5OH + H_2O \quad (1)$$



$$\begin{array}{l} NH{-}NH_2 \\ | \\ C{=}O \\ | \\ OC_2H_5 \end{array} + N_2H_4{\cdot}H_2O \rightarrow \begin{array}{l} NH{-}NH_2 \\ | \\ C{=}O \\ | \\ NH{-}NH_2 \end{array} + C_2H_5OH + H_2O \quad (2)$$

Submitted by Elizabeth B. Mohr,* J. J. Brezinski,* and L. F. Audrieth*
Checked by H. E. Ritchey† and R. F. McFarlin†

Carbohydrazide has been prepared by the reaction between diphenyl carbonate and hydrazine hydrate[1] and also by the action of dilute acid on tris(benzalamino)guanidine.[2] Curtius and Heidenreich[3] synthesized carbohydrazide by long refluxing of a mixture of diethyl carbonate and hydrazine hydrate. Kesting[4] increased the yield by distilling off volatile products and unreacted materials after the 48-hour reflux period.

The procedures outlined below represent modifications of the Kesting synthesis in that the volatile products are removed by fractional distillation as they are formed; thus

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* University of Illinois, Urbana, Ill. Experimental work was undertaken under Ordnance Contract W-11-022-ORD-11329. Publication has been approved by the Office of Public Information of the Office of the Chief of Ordnance.

† Virginia Military Institute, Lexington, Va.

only a relatively short heating time is required. Directions are given for carrying out the synthesis both as a single-batch operation and as a semicontinuous procedure[5] in which the mother liquor remaining after removal of the product is used for the next batch. Higher cumulative yields are obtainable in the latter case.

Procedure

Single-batch Preparation. Three hundred fifty-four grams of diethyl carbonate (3.0 mols) and 388 g. of 85% hydrazine hydrate (6.6 mols) are placed in a 1-l. round-bottomed flask equipped with a thermometer. The reactants are only partially miscible at first; the flask is shaken until a single phase is formed. This process [eq. (1)] is accompanied by the evolution of heat, causing the temperature to rise to about 55°.

The flask is then connected, preferably through a standard-taper joint, to a fractionating column filled with Raschig rings to a depth of about 22 cm. A still head, fitted with a thermometer and a water-cooled condenser, is attached to the fractionating column.

A Glas-col heater regulated by a variable transformer is employed to heat the reaction mixture. Distillation of the alcohol and water is quite rapid (5 ml./min.) for the first 30 minutes but decreases as the reaction proceeds. Heating is continued for 4 hours, during which time 325 to 350 ml. of distillate is collected at a vapor temperature of 80 to 85°; the pot temperature rises from 96 to 119°.

The pot liquor is cooled to 20° and allowed to stand for at least 1 hour. Crystals of carbohydrazide separate and are filtered and dried as completely as possible by suction. The crude product weighs approximately 165 g. (60% yield).

If necessary, purification may be effected by recrystallization from water. The product is dissolved in 110 ml. of hot water, and the solution is filtered free of insoluble material. Precipitation is then effected by adding approximately 500 ml. of 95% ethanol. After standing for at least 1 hour at 20°, the precipitate is filtered and washed with ether. The pure carbohydrazide weighs about 133 g., representing a recovery of 80% of the crude material and a 49% over-all yield based on the amount of diethyl carbonate employed.

Semicontinuous Procedure. The yield of carbohydrazide may be increased markedly by recycling the mother liquor with fresh reagents.

A stock solution is prepared by shaking 856 g. of diethyl carbonate (7.25 mols) with 938 g. of 85% hydrazine hydrate (15.95 mols) until a single liquid phase is formed. The equipment described above is used to effect reaction and removal of volatile products.

A 700-g. quantity of the stock solution is employed in the first step of the synthesis. Distillation of the alcohol-water mixture is carried out under the conditions outlined above, and heating is continued until a temperature of 119° is attained. The crude carbohydrazide is then recovered by cooling and filtering the reaction mixture. The mother liquor is weighed and made up to 700 g. again with fresh stock solution. The data given in Table I represent the results of a typical synthesis in which the mother liquor from two successive steps was recycled with fresh reagent solution.

TABLE I. THE PREPARATION OF CARBOHYDRAZIDE ON A SEMICONTINUOUS BASIS

Run No.	Stock soln. added, g.	Diethyl carbonate added, mols	Distillate removed, ml.	Mother liquor remaining, g.	Crude product, g.	Carbohydrazide cumulative yield	
						g.	%
1	700	2.82	300	260	165	165	65
2	440	1.78	300	229	189	354	86
3	471	1.91	275	294	155	509	87

Properties

Carbohydrazide is a white crystalline compound melting with decomposition at 153 to 154°. It is very soluble in water but insoluble in alcohol, ether, chloroform, and benzene. It reacts with benzaldehyde to form dibenzalcarbohydrazide, $O{=}C(NHN{=}CHC_6H_5)_2$, which melts at 198°.[6] In the presence of nitrous acid, carbohydrazide is converted into carbonyl azide, $CO(N_3)_2$, a highly explosive compound.[3]

Carbohydrazide forms crystalline salts with 1 and 2 mols of hydrochloric acid, 1 mol of sulfuric acid, and 1 mol of oxalic acid. The two chlorides are very soluble in water, while the sulfate and oxalate are only slightly soluble. Phosphoric and nitric acids also form salts with carbohydrazide, but these materials have never been isolated in a crystalline form.[7]

The pH of a 1% aqueous solution of carbohydrazide is in the neighborhood of 7.4.[7] This solution is gradually decomposed when heated with acid or base.

References

1. Cazeneuve and Moreau: *Compt. rend.*, **129**, 1255 (1899).
2. Stolle: *Ber.*, **37**, 3548 (1904).
3. Curtius and Heidenreich: *ibid.*, **27**, 55 (1894).
4. Kesting: *ibid.*, **57**, 1321 (1924).
5. Brazaitis and Tarika: Chemical Engineering Project Reports, University of Illinois, 1949.
6. Curtius and Heidenreich: *J. prakt. Chem.*, [2] **52**, 454 (1895).
7. Beck: thesis, University of Illinois, 1948.

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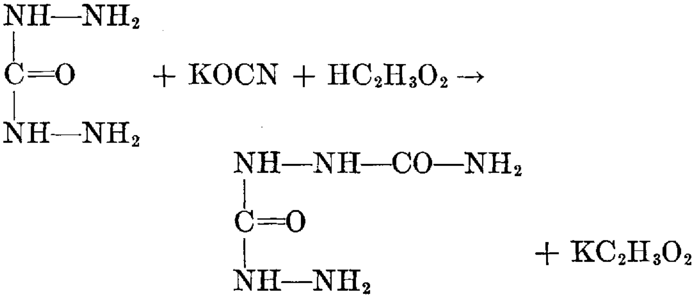
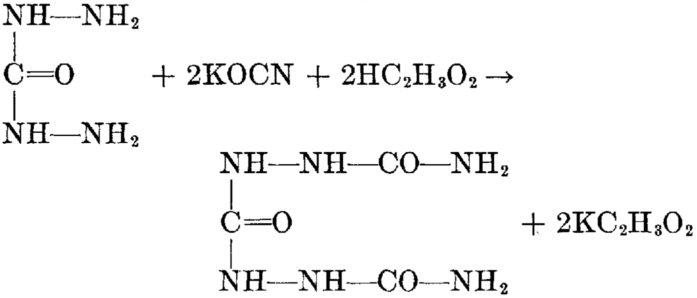
11. CYANATE CONDENSATION PRODUCTS OF CARBOHYDRAZIDE



$$\begin{array}{l}\mathrm{NH{-}NH_2}\\ |\\ \mathrm{C{=}O}\\ |\\ \mathrm{NH{-}NH_2}\end{array} + \mathrm{KOCN} + \mathrm{HC_2H_3O_2} \rightarrow \begin{array}{l}\mathrm{NH{-}NH{-}CO{-}NH_2}\\ |\\ \mathrm{C{=}O}\\ |\\ \mathrm{NH{-}NH_2}\end{array} + \mathrm{KC_2H_3O_2}$$

(*A*)



$$\begin{array}{l}\mathrm{NH{-}NH_2}\\ |\\ \mathrm{C{=}O}\\ |\\ \mathrm{NH{-}NH_2}\end{array} + 2\mathrm{KOCN} + 2\mathrm{HC_2H_3O_2} \rightarrow \begin{array}{l}\mathrm{NH{-}NH{-}CO{-}NH_2}\\ |\\ \mathrm{C{=}O}\\ |\\ \mathrm{NH{-}NH{-}CO{-}NH_2}\end{array} + 2\mathrm{KC_2H_3O_2}$$

(*B*)

Submitted by L. F. Audrieth* and Elizabeth B. Mohr*

Many hydrazine derivatives condense readily with potassium cyanate to give *N*-substituted semicarbazides. Carbohydrazide reacts with 1 or 2 mols of potassium cyanate to form carbohydrazide-*N*-carboxamide or carbohydrazide-*N*,*N*′-dicarboxamide.

A. CARBOHYDRAZIDE-*N*-CARBOXAMIDE

Checked by Samuel Helf† and K. G. Ottoson†

This compound was first isolated as a secondary reaction product in the formation of diaminoguanidine hydrobromide and guanazine from the reaction of cyanogen bromide

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* University of Illinois, Urbana, Ill. Experimental work was carried out under Ordnance Contract W-11-022-ORD-11329. Publication has been approved by the Office of Public Information of the Office of the Chief of Ordnance.

† Chemical Research Laboratory, Picatinny Arsenal, Dover, N.J.

with 2 mols of hydrazine.[1] Pellizzari and Roncagliolo[2] prepared carbohydrazide-*N*-carboxamide in good yield by the dropwise addition of glacial acetic acid to an equimolar mixture of carbohydrazide and potassium cyanate until the permanent disappearance of the phenolphthalein color. This procedure has been improved to give better yields and a more nearly pure and uniform product.

Procedure

The reaction is carried out in a 2-l. beaker above which is suspended a 500-ml. dropping funnel for slow addition of the cyanate solution. A mechanical stirrer is employed to agitate the mixture throughout the reaction and digestion processes.

Ninety-nine grams of carbohydrazide (1.10 mols) is dissolved in a solution containing 120 g. of glacial acetic acid (2.00 mols) and 1000 ml. of water. To this, a solution of 81 g. of potassium cyanate (1.00 mol) in 350 ml. water is added dropwise over a period of about 2 hours. The mixture is digested at room temperature for 5 hours. The precipitate is then removed by filtration and washed very thoroughly with water, alcohol, and ether. The dry product weighs approximately 115 g. (86%) and melts with decomposition at 227 to 228°.

Properties

Carbohydrazide-*N*-carboxamide is a white, nonhygroscopic, crystalline substance which is insoluble in water and in alcohol and other organic solvents. It is soluble in mineral-acid solutions, from which it may be reprecipitated by the addition of ammonia; however, it dissolves in sodium hydroxide with decomposition.

This compound reduces Fehling solution and ammoniacal silver nitrate readily. It is quite stable for long periods of time at 110°. When heated for 1 hour at 226°, it cyclizes to form urazine (synthesis 9). It condenses with aldehydes and ketones; the hydrochloride reacts with additional potassium cyanate to give carbohydrazide-*N*,*N*′-dicarboxamide.

B. CARBOHYDRAZIDE-*N*,*N*′-DICARBOXAMIDE

Checked by C. F. Dieter* and K. G. Ottoson*

Pellizzari and Roncagliolo[2] prepared this compound by reaction of carbohydrazide in dilute acetic acid with 2 mols of potassium cyanate and also by condensation of carbohydrazide-*N*-carboxamide hydrochloride with 1 mol of cyanate. The former procedure does not give a pure product, probably because of the preferential formation of the less soluble carbohydrazide-*N*-carboxamide. The latter reacts with hydrochloric acid to form the hydrochloride, which is water-soluble. Prior condensation of carbohydrazide to form the *N*-carboxamide is advantageous, since the hydrochloride of this compound will undergo further reaction with cyanate to give the desired product by precipitation from water. When the procedure outlined below is followed, it is not necessary to recrystallize the carbohydrazide-*N*,*N*′-dicarboxamide unless an extremely pure material is desired.

Procedure

Thirteen and three-tenths grams of carbohydrazide-*N*-carboxamide (0.10 mol) is dissolved in a solution of 9.2 ml. of 12 *M* hydrochloric acid (0.11 mol) in 100 ml. of water. The resulting solution is filtered, if necessary, and to it is added a solution of 8.9 g. of potassium cyanate (0.11 mol) dissolved in 100 ml. of water. After a short time, precipitation begins. The resulting suspension is digested at room temperature for 5 hours with constant stirring. The crystals are filtered and washed with water, alcohol, and ether. The yield of carbohydrazide-*N*,*N*′-dicarboxamide thus obtained weighs about 15.0 g. (85%). A small sample melts with decomposition at 225°, or at 232° when heated rapidly.

If a material of greater purity is desired, the product may

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be recrystallized from 125 ml. of hot 3% hydrochloric acid solution. The recovery of purified carbohydrazide-*N*,*N'*-dicarboxamide is about 50%.

Properties

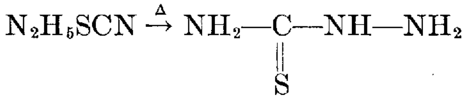
This compound melts with decomposition at 232°, is relatively nonhygroscopic, and is difficultly soluble in cold water and dilute acids. However, it dissolves to the extent of 4.72 g./100 g. of water at 65°. A saturated aqueous solution hydrolyzes to a noticeable extent at 65°.

References

1. Pellizzari and Cantoni: *Gazz. chim. ital.*, **35**, I, 291 (1905).
2. Pellizzari and Roncagliolo: *ibid.*, **37**, I, 434 (1907).

12. THIOSEMICARBAZIDE

$$(N_2H_5)_2SO_4 + Ba(SCN)_2 \rightarrow BaSO_4 + 2N_2H_5SCN$$



$$N_2H_5SCN \xrightarrow{\Delta} NH_2{-}\underset{\underset{\displaystyle S}{\|}}{C}{-}NH{-}NH_2$$

Submitted by John J. Pitha* and John P. Olatta*
Checked by Eugene Lieber,† S. H. Patinkin,† and R. D. Pratt†

Directions for the preparation of thiosemicarbazide as given in the literature[1] are lacking in detail, and so a good yield of the desired material in pure form is not assured. The procedure described here is a modification of that described by Freund[1] with emphasis on the temperature of conversion of hydrazinium thiocyanate to thiosemicarbazide. Thiosemicarbazide is a useful intermediate in the preparation of guanidine derivatives, which are of interest because of their high nitrogen content.

Procedure

A solution of 27.5 ml. of concentrated sulfuric acid (0.5 mol) in 500 ml. of water is added slowly, with stirring, to a solution of 59 g. of 85% hydrazine hydrate (1 mol) in 500

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† Illinois Institute of Technology, Chicago, Ill.

ml. of water in a 2-l. beaker. A solution of 145 g. of barium thiocyanate 2-hydrate (0.5 mol) in 500 ml. of water is added to the solution of hydrazinium sulfate. The barium sulfate precipitate is stirred thoroughly and is then digested on a steam bath for 2 hours or more before filtering. For quick removal of the barium sulfate precipitate, the slurry is filtered by suction through a mat of filter-paper pulp between two pieces of filter paper,* using a fairly large (14-cm.) Büchner funnel. The clear, or only slightly cloudy, filtrate is then evaporated in a large evaporating dish on a steam bath until the total volume has been reduced to about 200 ml. At this point it may be necessary to filter the solution again. The clear solution is then transferred to a round-bottomed flask fitted with a thermometer well. The solution is boiled until its temperature reaches 110°. A reflux condenser is then attached to the flask, and the solution is maintained at the boiling point for 30 minutes. Upon cooling, a mass of crystals separates; these are removed by filtration. The filtrate is returned to the flask, and the refluxing at 100° is repeated. Five fractions of crystals are obtained from the solution in this manner. The crude thiosemicarbazide is purified by recrystallization from 50% ethanol. The yield of recrystallized material varies from 40 to 50% of theory, depending on the completeness of the conversion of the salt to product.†

Properties

Pure thiosemicarbazide is a white crystalline mass, which is very soluble in water and in ethanol. The reported melting point of the material is 181°, but this is not a reliable criterion of purity. The melting point appears to depend on the kind of crystal obtained by recrystallization. The crystals obtained range from those of micro size to long

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* Whatman ashless tablets are recommended.

† The checkers have pointed out that the synthesis can be simplified, though with some loss of yield and purity, by simple evaporation of the filtered solution of hydrazine thiocyanate to a volume of 75 ml., or until a yellow precipitate begins to form.

needles or large plates. They melt in the range 170 to 181°, and all give identical x-ray diffraction patterns. A qualitative test for the presence of the thiocyanate ion, using iron(III) chloride in acid solution, showed that all were about equally pure. A variety of transitions can be observed to take place during the process of melting.

Reference

1. Freund and Schander: *Ber.*, **29**, 2500 (1896).

13. IODOTRICHLOROSILANE AND DIIODODICHLOROSILANE

$$HSiCl_3 + I_2 \rightarrow SiICl_3 + HI$$
$$SiICl_3 + HI \rightarrow SiI_2Cl_2 + HCl$$

Submitted by Robert West* and Eugene G. Rochow*
Checked by C. A. Burkhard†

Various methods have been used to obtain equilibrium mixtures of the iodochlorides of silicon. These include passing a mixture of silicon tetrachloride and hydrogen iodide through a hot tube[1] or an electric discharge,[2] passing iodine monochloride over silicon at dull red heat,[1] and treating silicon tetrachloride with fused potassium iodide.[3] Although Besson mentioned that iodotrichlorosilane could be prepared from trichlorosilane and iodine in a Carius tube,[1] the conditions and yield data were not published. This reaction is more safely carried out in a pressure vessel, as described below.

Procedure

The reaction is carried out in a steel bomb of approximately 1 l. capacity, fitted with a thermocouple or thermometer, and equipped for rocking. The vessel should be capable of withstanding at least 2000 p.s.i. It is charged with 254 g. of iodine (1.0 mol) and 169 g. of trichlorosilane

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† Research Laboratory, General Electric Company, Schenectady, N.Y.

(1.25 mol). The bomb is sealed,* placed in the rocker, and heated to 240 to 250°. This temperature is maintained for 15 hours with continual rocking.† After cooling to room temperature, the bomb is cautiously vented outdoors, or in a well-ventilated hood, to release the large volume of hydrogen iodide which is formed in the reaction.

The contents are transferred to a distilling pot and distilled through a fractionating column at atmospheric pressure. The receivers and the distilling head should be protected from atmospheric moisture by calcium chloride drying tubes, and a rubber tube should lead from the top of the distilling head to a hood or a beaker of water, to carry away the dissolved hydrogen iodide which escapes during the early part of the distillation. The forerun consists principally of $HSiCl_3$ and $SiCl_4$, which distill below 60°. Iodotrichlorosilane is collected at 110 to 116°. The temperature is then raised, and diiododichlorosilane is collected at 168 to 173°. Since the boiling points of the principal products and contaminants differ by 50° or more, good separations can be achieved by fairly rapid distillation through a column of only moderate efficiency.‡

The products are purplish in color because of decomposition and the presence of codistilled iodine. The color can be removed by shaking with mercury or copper and decanting through a glass-wool plug. The yield of iodotrichlorosilane is about 110 g. (42%) and that of diiododichlorosilane is about 55 g. (16%, based on the iodine used). The products should be stored in dark glass bottles or ampoules in a refrigerator.

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* The authors closed the bomb with a valve immediately above the head of the bomb. If any considerable length of tubing extends between the bomb and the valve, iodine will sublime into the tubing and correspondingly reduce the amount available for reaction, thus decreasing the yield.

† Lower temperatures decrease the yield of both iodotrichlorosilane and diiododichlorosilane.

‡ The 25 g. of residue remaining may contain triiodochlorosilane and silicon tetraiodide.

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Properties

Iodotrichlorosilane and diiododichlorosilane are heavy, colorless liquids, which fume slightly in air and hydrolyze vigorously in water. Both decompose slowly at room temperature, liberating iodine; light accelerates their decomposition.

Compound	B.p.	n_D^{25}	Sp.gr.$_4^{25}$
$SiICl_3$	113.5	1.507_0	2.092
SiI_2Cl_2	172	1.605_3	2.647

References

1. Besson: *Compt. rend.*, **112,** 611, 1314 (1891).
2. Besson and Fournier: *ibid.*, **152,** 603 (1911).
3. Forbes and Anderson: *J. Am. Chem. Soc.*, **66,** 931 (1944).

14. CYCLOHEXYLTRICHLOROSILANE

$$C_6H_{10} + SiHCl_3 \xrightarrow{\substack{\text{organic}\\ \text{peroxide}}} C_6H_{11}SiCl_3$$

Submitted by Charles A. Burkhard* and Robert H. Krieble*
Checked by William S. Tatlock† and Eugene G. Rochow†

The peroxide-catalyzed addition of trichlorosilane or methyldichlorosilane to olefins affords a new method of synthesizing organochlorosilanes.[1] It is possible to effect reaction between trichlorosilane and pentene, cyclohexene, isobutylene, and acetylene. A similar reaction takes place between trichlorosilane and both vinyltrichlorosilane and allyltrichlorosilane. In each case, the corresponding alkyl silicon derivatives can be isolated. The synthesis of cyclohexyltrichlorosilane is described below as an example of the general procedure. Cyclohexyltrichlorosilane has also been prepared by the Grignard reaction.[2]

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† Harvard University, Cambridge, Mass.

Procedure

A mixture of 57 g. (0.69 mol) of cyclohexene, 135 g. (1.0 mol) of trichlorosilane, and 10 ml. of diacetyl peroxide in dimethylphthalate (0.026 *M*)* is placed in a glass-lined autoclave and heated at 100° for 24 hours. The product is distilled through a stainless-steel, packed, 13-plate column.† The lower-boiling fractions consist of unreacted cyclohexene and trichlorosilane. The fraction boiling at 198.6 to 200° comprises the desired material, amounting to 49.5 g. (30%) in a typical run. (If allowance is made for unreacted cyclohexene, the yield amounts to 64%.) The product is analyzed by subjecting the compound to hydrolysis and determining the chlorine content. *Anal.* Calcd. for $C_6H_{11}SiCl_3$: Cl, 48.9. Found: Cl, 48.4.

Properties

Cyclohexyltrichlorosilane reacts with water, alcohols, Grignard reagents, and amines to give siloxanes, ethers, cyclohexyl-substituted organosilanes, and silylamines, respectively.

References

1. Burkhard and Kriebel: *J. Am. Chem. Soc.*, **69**, 2687 (1947).
2. Palmer and Kipping: *J. Chem. Soc.*, **1930**, 1020.

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* The checkers prefer to use 12.6 g. of benzoyl peroxide as the catalyst, because they feel that the use of acetyl peroxide is unsafe. However, the submitters believe that acetyl peroxide *in dimethyl phthalate* is entirely safe and is more convenient to use than the benzoyl peroxide. The disadvantage of using benzoyl peroxide lies in the fact that the benzoyl chloride formed from it boils at almost exactly the same temperature as cyclohexyltrichlorosilane.

† The checkers report that distillation of the solution may be carried out with a modified Claisen flask. The fraction boiling between 190 and 200° is collected but is generally not so pure, based on the hydrolyzable-chlorine content, as material fractionated under conditions permitting closer control.

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15. SILICON TETRAACETATE

$$SiCl_4 + 4(CH_3CO)_2O \rightarrow Si(OOCCH_3)_4 + 4CH_3COCl$$

Submitted by J. H. Balthis*
Checked by E. G. Rochow† and D. G. White†

This procedure for the preparation of silicon tetraacetate was discovered by Friedel and Ladenburg;[1] however, details of their work were not published, and subsequent workers appear to have adopted more complicated methods. The procedure given here is also applicable to the preparation of alkyl- or arylacetoxysilanes of the type $R_nSi(C_2H_3O_2)_{4-n}$ from organochlorosilanes.

Procedure

Two hundred fifty-five grams of silicon tetrachloride (1.5 mols) and 704 g. of acetic anhydride (6.9 mols, 15% excess) are mixed by gentle swirling in a three-necked 1-l. flask *A* (Fig. 2) fitted with a dropping funnel *B* and a filter stick‡ *C* which is connected to a filter flask *D*. The reaction mixture is protected from moist air as shown in Fig. 2. The tubing connecting the filter stick to the filter flask is closed with a screw clamp except during filtration. During the course of the reaction, the filter stick is kept out of contact with the reaction mixture by slipping it up through the stopper. The reaction evolves heat, and the contents of the flask develop a slight coloration. In a short time, large crystals of silicon tetraacetate begin to form. The mixture is allowed to stand for several days and is then cooled in a Dry Ice–acetone bath. The supernatant liquid, consisting of acetyl chloride and excess acetic anhydride, is removed

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* Chemical Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Del.

† Harvard University, Cambridge, Mass.

‡ The checkers prefer a glass tube to the filter stick, because they found that the fritted-glass filtering area of the filter stick may become clogged. Only slight loss in yield is associated with the use of an open tube, since the product forms as a crystalline mass in the bottom of the flask rather than as individual crystals.

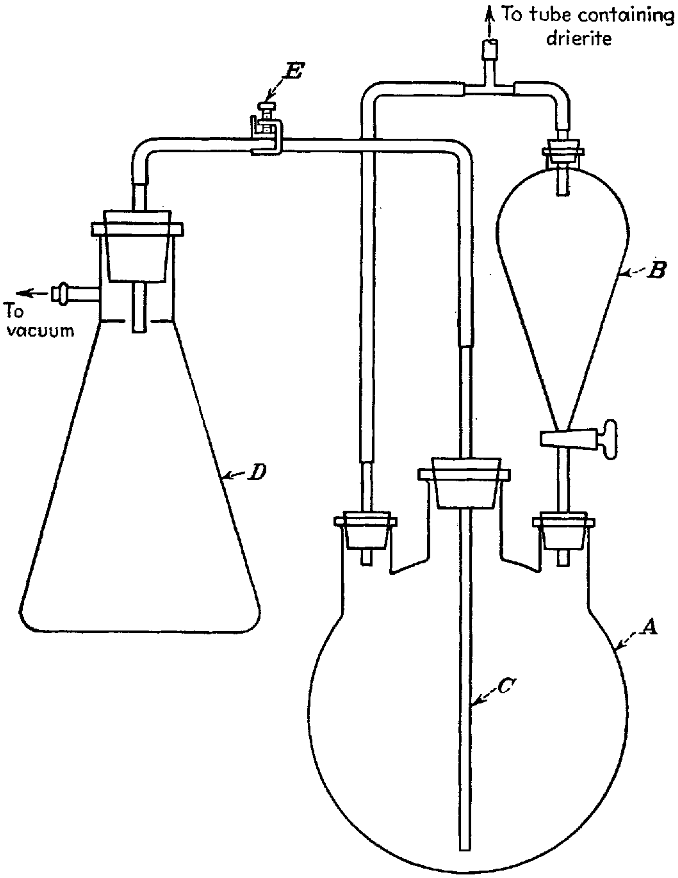

FIG. 2. Apparatus for the preparation of silicon tetraacetate.

through the filter stick *C*.* Care must be taken in disposing of the liquid since it reacts violently with water.

The silicon tetraacetate is twice recrystallized by dissolving it in acetic anhydride at 100°† and cooling to 0°.

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* The mother liquor may be separated from the product by distillation; however, this leads to discoloration of the silicon tetraacetate. For this reason, purification by recrystallization is preferable. When the procedure given here is applied to the preparation of organoacetoxysilanes, distillation is usually necessary. In this case, the acetyl chloride is removed at atmospheric pressure, and the excess acetic anhydride and product are separated by fractional distillation under reduced pressure.

† It is advisable *not* to use a steam bath when recrystallizing the silicon

The first recrystallization requires 100 ml. of solvent, and the second, 75 ml. While still in the reaction flask, the purified silicon tetraacetate is subjected to a preliminary drying at room temperature *in vacuo;* it is then dried further at 100° for several hours. The yield is 335 g. (84.6%, based on silicon tetrachloride).

Properties

Silicon tetraacetate is a colorless, crystalline solid, which reacts vigorously with water and hydrolyzes rapidly when exposed to moist air. It melts at 110°[1] and decomposes at 160 to 170° with evolution of acetic anhydride.[1] It is moderately soluble in inert organic liquids such as acetone and benzene.

Reference

1. FRIEDEL and LADENBURG: *Ann.*, **145**, 174 (1868).

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tetraacetate, because of the violence with which both the product and the solvent react with water.

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CHAPTER V

See also: Lithium nitride, synthesis 1
Iron(II) bromide 6-ammoniate, synthesis 53
Acidopentamminecobalt(III) salts, synthesis 56
Nitrosylpentamminecobalt(II) chloride, synthesis 55
trans-Dinitrodiamminepalladium(II), synthesis 58
cis- and *trans*-Dinitrobis(ethylenediamine)cobalt(III) nitrate, synthesis 57
Pyridine and picoline addition compounds of chromium(VI) oxide, synthesis 33
Biurea, synthesis 8
Urazine, synthesis 9
Carbohydrazide, synthesis 10
Cyanate condensation products of carbohydrazide, synthesis 11
Thiosemicarbazide, synthesis 12
Dithiocarbamates of selenium(II) and tellurium(II), synthesis 32
Aluminum phosphide, synthesis 7
Phosphorus(III) fluoride, synthesis 49
Methyl chlorofluorophosphite and methyl difluorophosphite, synthesis 46
Calcium dihydrogen orthophosphate 1-hydrate, synthesis 5
Calcium hydrogen orthophosphate, synthesis 6
Arsenic(III) fluoride, synthesis 50
Bismuth(III) iodide, synthesis 38
Vanadium(II) chloride, synthesis 42
Vanadium(III) chloride, synthesis 43
Tantalum(V) bromide, synthesis 44

16. NITROSYL CHLORIDE

$$NaNO_2 + 2HCl \rightarrow NOCl + NaCl + H_2O$$

SUBMITTED BY J. R. MORTON* AND H. W. WILÇOX*
CHECKED BY THERALD MOELLER† AND DELWIN C. EDWARDS†

Nitrosyl chloride has been prepared from hydrogen chloride and nitrosylsulfuric acid,[1] from sodium chloride and nitrosylsulfuric acid,[2] from nitrogen dioxide and moistened potassium chloride,[3] by the combination of nitric oxide and

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chlorine under the influence of a catalyst,[4] and by passing dry hydrogen chloride into liquid nitrogen(III) oxide.[5] This procedure uses a modification of the last-named method. The process is advantageous in that there are no intermediates to purify and the crude nitrosyl chloride contains only oxides of nitrogen, which are easily removed by refluxing and by distillation.

Procedure

Caution: *This preparation should be carried out in a hood.* A gas-drying tower *A* (Fig. 3), which has a capacity of 900 ml., is plugged at the bottom with a paraffined rubber stopper *B* and is fitted at the top with a two-hole rubber stopper. The dimensions specified should be adhered to as closely as possible; the use of larger apparatus causes excessive loss of the product. A dropping funnel *C* and a short L-tube *D* are inserted in the stopper in the top of the drying tower. The stem of the dropping funnel should extend nearly to the bottom of the drying tower. The three drying tubes *E*, *F*, and *G* contain, respectively, sodium nitrite

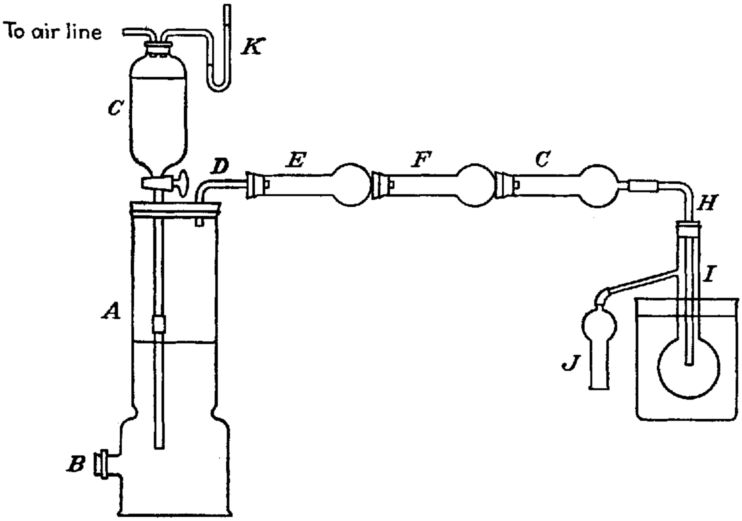

FIG. 3. Apparatus for the preparation of nitrosyl chloride.

(to absorb hydrogen chloride), potassium chloride which has been moistened with an amount of water equivalent to 2.4% of its dry weight (to absorb nitrogen dioxide), and anhydrous calcium chloride. The side arm of the 100-ml. distilling flask *I* is connected to a drying tube *J* filled with anhydrous calcium chloride.

Six hundred milliliters of concentrated hydrochloric acid (7.2 mols) is placed in the drying tower. A concentrated solution of 103.5 g. of sodium nitrite (1.5 mols) in approximately 150 ml. of water is placed in the dropping funnel. The dropping funnel is fitted with a two-hole rubber stopper, which is connected to an air line and to a manometer *K*. The solution of sodium nitrite is kept under a pressure of 100 mm. to ensure its flow into the hydrochloric acid and to prevent bubbles of nitrosyl chloride from backing up into the dropping funnel. The receiver *I* is surrounded with a mixture of solid carbon dioxide and acetone.

When the receiver has been thoroughly cooled, a small stream of the sodium nitrite solution is allowed to flow into the hydrochloric acid. The rate of flow of the sodium nitrite solution must be carefully regulated to maintain a slow evolution of nitrosyl chloride. Excessive pressure may develop if the sodium nitrite is added too rapidly. When nitrosyl chloride is seen issuing from the drying tube *J*, the drying tube is stoppered.* A precipitate of sodium chloride causes cloudiness in the hydrochloric acid, but this settles out, leaving a clear, red solution of nitrosyl chloride and sodium chloride in the hydrochloric acid.

When all the sodium nitrite solution has run into the hydrochloric acid, the stopcock is closed and the stopper is removed from the drying tube *J*. After the reaction has subsided, tube *H* is then withdrawn, and if any of the nitrosyl chloride has solidified, it is allowed to melt while

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* Stoppering is necessary because, when the sodium nitrite solution is added to the concentrated hydrochloric acid, the reaction proceeds vigorously and unevenly until approximately one-third to one-half of the sodium nitrite solution has been added. This may cause some nitrosyl chloride to be forced through the receiver without being liquefied.

the receiver is out of the Dry Ice–acetone bath. After all the nitrosyl chloride has melted, it is poured into a 200-ml. round-bottomed flask *A* (Fig. 4), which is immersed in the cooling bath from which the receiver was removed. A porcelain chip is added, and the flask is attached to a reflux system; this consists of a fractionating column *B* (Fig. 4), of the Vigreux type, which is surrounded by a Dry Ice–acetone bath. The cooling bath consists of an inverted 2-l. bottle *C* the bottom of which has been removed. The nitrosyl chloride is allowed to reflux for approximately 30 minutes by surrounding the flask with water at 20°. During the refluxing, the nitrosyl chloride must be protected from moisture.

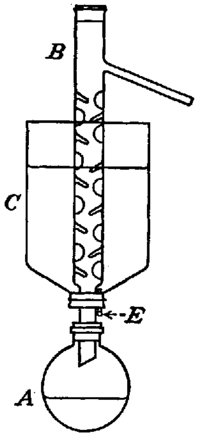

FIG. 4. Apparatus for the distillation of nitrosyl chloride.

At the end of the refluxing period a new receiver, suitable for sealing, is attached to the side arm of the fractionating column. This new receiver is surrounded by an acetone–solid carbon dioxide bath. A portion of the cold acetone is removed from the bath surrounding the fractionating column through the valve *E*, and warm acetone is added. The forerun (3 to 4 ml.) of nitrosyl chloride is discarded or added to the crude product obtained in the next run; the last 2 ml. remaining in the distilling flask is also discarded. The nitrosyl chloride is then redistilled, if desired, to obtain a product of enhanced purity. The yield varies from 45 to 55 g. (46 to 56%, based on sodium nitrite). The procedure, including assembly of the apparatus, takes approximately 6 hours. Redistilled nitrosyl chloride is analyzed for chlorine according to the method given in reference 6. *Anal.* Calcd. for NOCl: Cl, 54.16. Found: Cl, 53.93, 53.98.

Properties

The properties of nitrosyl chloride have been described in an earlier synthesis.[6]

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17. NITRYL CHLORIDE

(Nitroxyl Chloride)

$$HNO_3 \cdot nH_2O + H_2SO_4 \cdot nSO_3 \rightarrow HNO_3 + (1 + n)H_2SO_4$$
$$HNO_3 + ClSO_3H \rightarrow H_2SO_4 + NO_2Cl$$

Submitted by Ralph Kaplan* and Harold Shechter*
Checked by Thomas C. Castorina† and W. R. Tomlinson, Jr.†

Critical surveys have shown that the older methods for the preparation of nitryl chloride are inefficient and yield impure products.[1–7] Reasonably pure nitryl chloride was first prepared by Schumacher and Sprenger[1–3] in 1929 by the reaction of nitrosyl chloride with ozone; the preparation from chlorosulfonic acid and nitric acid was reported later.[4] Recently, Schmeisser has obtained nitryl chloride from nitrogen(V) oxide and phosphorus(V) chloride.[5] The reaction of chlorosulfonic acid with nitric acid[8–10] is probably the most convenient method for preparing large quantities of nitryl chloride of satisfactory purity.

Procedure

Chlorosulfonic Acid. Chlorosulfonic acid is best purified by distillation[11,12] of the technical product at atmospheric pressure in a glass apparatus protected from the atmosphere by a drying tube containing anhydrous calcium chloride. The fraction distilling at 149 to 151° at 745 mm. is collected and stored in a glass-stoppered bottle.

Anhydrous Nitric Acid. One hundred per cent nitric acid may be prepared by distillation of a mixture of concen-

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† Chemical Research Section, Picatinny Arsenal, Dover, N.J.

trated nitric acid and excess fuming sulfuric acid at atmospheric pressure in a glass apparatus. However, it is more convenient and less time-consuming to use fuming nitric acid to which is added the amount of fuming sulfuric acid necessary to combine with the water present.

Nitryl Chloride. Caution: *The operations are performed in a well-ventilated hood which is darkened to prevent photochemical decomposition of the product.* All connections in the apparatus are of ground glass. Openings in the system are fitted with drying tubes containing anhydrous calcium chloride.

A 500-ml., three-necked, round-bottomed flask is equipped with a dropping funnel, an efficient motor-driven, glass stirrer* sealed with mercury or sulfuric acid, and a distilling head to which a test-tube receiver (125 to 150 ml. capacity) is to be connected.† The still head is cooled with Dry Ice. One hundred grams of fuming nitric acid (1.45 mols) (sp. gr. 1.50; 91.6% acid) is placed in the flask and cooled to 0°. Stirring is begun and 123 g. of fuming sulfuric acid (30% sulfur trioxide) is added dropwise. The receiver, which also serves as a storage vessel, is then put in place and immersed in a freezing mixture (−80°). The mixed acids in the reaction flask are maintained at 0° and vigorously stirred while 168.9 g. of chlorosulfonic acid (1.45 mols) is added slowly from the dropping funnel over a period of 3 to 4 hours, or at such a rate that brown fumes of oxides of nitrogen do not appear above the reaction mixture. After the addition of each drop of chlorosulfonic acid, gaseous nitryl chloride is immediately evolved. After the addition of chlorosulfonic acid is complete, the cooling bath is removed, and the mixture is stirred for an additional 30 minutes, while the product distills and is collected.

The product is a dense, pale yellow liquid with a melting

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* Efficient stirring is necessary to prevent localized overheating and subsequent decomposition of the product.

† The receiver is not opened to the system until the nitric acid and the sulfuric acid have been mixed; otherwise, sulfur trioxide fumes pass into it during this operation.

point of −145 ± 2° and a boiling point of −17 to −15°. The slight yellow color of the product may be attributed to the presence of traces of chlorine and nitrogen dioxide, although the freezing-point curve of this product indicates an almost complete absence of impurities.[1–3] In a simple distillation from one test tube to another, with a calibrated alcohol thermometer (the bulb of which is wrapped with glass wool to promote ebullition) immersed in the liquid, less than 2% distills below −16°. Pure nitryl chloride is colorless. A purification procedure, employing high-vacuum technique at low temperatures, is described by Schmeisser.[5] The yield is 95 to 108 g. (81 to 91%). *Anal.* Calcd. for NO_2Cl: Cl, 43.6. Found: Cl, 44.9.

Properties

Nitryl chloride is a colorless gas having a vapor density of 2.81 g./l. at 100°. It decomposes above 120° and condenses at −15° to a colorless liquid. At 0° the specific gravity of the liquid is 1.37; at 16°, 1.33. Nitryl chloride solidifies as a white, crystalline mass at −145°. Its vapor pressures at temperatures between −80° and −15° and its heat of vaporization have been determined.[1–3] The structure of nitryl chloride is not known with certainty.[5]

On long storage, even at the temperature of −80°, nitryl chloride darkens in color. Decomposition is probably accelerated by light. The compound is a corrosive, toxic substance possessing a chlorinelike odor. It attacks organic matter rapidly, sometimes explosively. Its chemical properties have been studied.[5,8–10]

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18. PHOSPHOROUS ACID

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

SUBMITTED BY D. VOIGT* AND F. GALLAIS*
CHECKED BY L. E. NETHERTON†

The usual method of preparing phosphorous acid from phosphorus(III) chloride and water is complicated by the necessity of avoiding any rise in temperature which might lead to the formation of phosphoric acid by disproportionation. This tendency to disproportionate makes direct reaction between equivalent weights of pure phosphorus(III) chloride and water, or concentration of dilute solutions of phosphorous acid by evaporation on a steam bath, impossible.

Of the numerous procedures proposed to prevent too vigorous a reaction, that of Grosheintz,[1,2] which involves passing a current of air successively through warm phosphorus(III) chloride and ice-cold water to give a solution from which phosphorous acid crystallizes, is perhaps the most interesting. However, since it is difficult to remove hydrochloric acid completely from the crystalline product, it is preferable to add water to a solution of phosphorus(III) chloride in carbon tetrachloride and to remove hydrogen chloride and water successively from the resulting sirupy liquid.

Procedure

Six hundred milliliters of carbon tetrachloride and 200 g. of freshly distilled phosphorus(III) chloride (1.46 mols) are placed in a 1.5-l., three-necked flask which is equipped with a 125-ml. dropping funnel, a mechanical stirrer, and a con-

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denser connected to a potassium hydroxide tower (Fig. 5). The flask is cooled by means of an ice bath, the stirrer is started, and 75 g. of water (4.17 mols) is added drop by drop from the dropping funnel over a period of 1 hour. Inasmuch as the maximum evolution of heat occurs at the beginning of the reaction, initial quantities of water must be added very slowly. After all the water has been added, the ice bath is removed and the rate of stirring is increased.

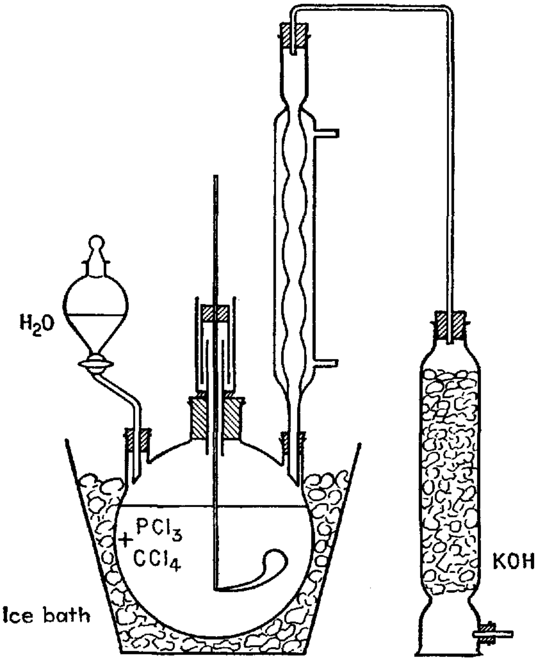

FIG. 5. Apparatus for the preparation of phosphorous acid.

The system is then stirred for 1 hour, after which the sirupy solution* is transferred to a separatory funnel and washed four times with volumes of carbon tetrachloride equivalent to its own volume, to remove the dissolved

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* If the phosphorous acid crystallizes in the reaction flask, it may be conveniently redissolved by adding 3 or 4 ml. of water, after which the purification may be accomplished as outlined in the procedure.

hydrogen chloride. The washed solution is filtered through sintered glass, using suction, and is placed in a round-bottomed flask connected with a vacuum pump or an aspirator through a Büchner flask containing solid sodium hydroxide (Fig. 6). Connection between the two flasks is made with a short glass tube of large bore. Vacuum is maintained until gas evolution has almost stopped. Then the round-bottomed flask is warmed to 60° on a steam bath while pumping is continued for a few hours to remove the last traces of hydrogen chloride and water. The phosphorous acid is then crystallized, either by supercooling or by allowing it to stand in a desiccator. The yield is about 114 g. (90%). By acidimetric or oxidimetric analysis,[3] the purity is shown to be about 99.5%.

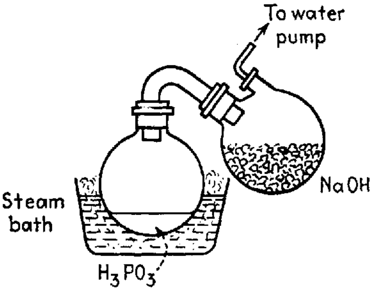
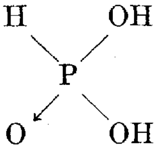


FIG. 6. Apparatus for the removal of hydrogen chloride and water from phosphorous acid.

Properties

Phosphorous acid forms white, snowy crystals which are extremely hygroscopic. Its melting point is between 73 and 74°, its specific gravity in the liquid state, 1.597^{76}_{4}. The physical and chemical properties of phosphorous acid[4-7] indicate that the molecule has structure I and not structure II.



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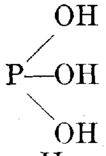

II

It has, therefore, been proposed that the name phosphonic acid should be used, rather than phosphorous acid.

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19. DIETHYL PHOSPHITE

$$3C_2H_5OH + PCl_3 \rightarrow (C_2H_5O)_2POH + C_2H_5Cl + 2HCl$$

Submitted by J. E. Malowan*
Checked by T. P. Traise† and T. M. Beck†

Diethyl phosphite was probably first prepared in 1854 by the reaction between alcohol and phosphorus(III) chloride.[1] It can also be prepared from phosphorus(III) oxide and alcohol,[2] from phosphorous acid and diazoethane,[3] or from lead phosphite and ethyl iodide.[4]

Diethyl phosphite is generally produced by the reaction of phosphorus(III) chloride with absolute alcohol. Good yields are difficult to obtain unless special precautions are taken. The by-product hydrogen chloride tends to react with the diethyl phosphite to form additional ethyl chloride and phosphorous acid:

$$(C_2H_5O)_2POH + 2HCl \rightarrow 2C_2H_5Cl + H_3PO_3$$

Various methods have been proposed to prevent this secondary reaction from occurring by removing the hydrogen chloride rapidly, either by applying a vacuum to the reactor, by bubbling a dry inert gas through the mixture, by adding pyridine to combine with the hydrogen chloride, or

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by adding low-boiling solvents like pentane, carbon tetrachloride, or ether to the mixture. Yields are often below 80% and may be as low as 40%. The method of Heider and Gann,[5] which is recommended here, provides an alternative procedure. It depends on the use of refluxing hexane to remove the hydrogen chloride.

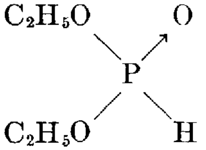
Procedure

Two hundred seventy-five grams of phosphorus(III) chloride (2.0 mols) and 275 g. of hexane (3.2 mols) are placed in a 2-l. three-necked, round-bottomed flask. The flask is equipped with a stirrer, a dropping funnel, and a reflux condenser protected by a drying tube at the upper end. The contents of the flask are heated to refluxing, and a mixture of 276 g. of alcohol (6.0 mols) with an equal amount of hexane is added slowly over a period of 2 to 3 hours, with constant stirring and refluxing. After all the alcohol has been added, the refluxing is continued for an additional 30 minutes. The reaction mixture is then cooled rapidly and transferred to a distilling flask equipped with a short fractionating column, a thermometer, and a glass capillary. Diethyl phosphite has a tendency to bump or boil over during distillation; this difficulty is alleviated by admitting a slow current of air through the capillary.

A distilling head with a thermometer (to show the vapor temperature), a condenser, and a receiver are connected to the fractionating column, and vacuum is applied. Vigorous boiling of the flask contents begins, caused by the escape of the remaining hydrogen chloride and ethyl chloride. After these substances have been expelled, the pressure falls. At 25 mm. the vapor temperature of the distilling diethyl phosphite is about 90°. The temperature in the flask increases slowly to about 100°, then rapidly to about 130° toward the end of the distillation, with an accompanying increase in pressure to 50 to 60 mm., which indicates the beginning of decomposition. The distillation is stopped when this occurs. The yield is 75 to 90% based on phosphorus(III) chloride. *Anal.** Calcd. for $C_4H_{11}O_3P$: P, 22.5. Found: P, 21.8, 22.0. The residue has a deep yellow to orange color and consists of phosphorous acid and the lower phosphorus oxides.

Properties

Diethyl phosphite is a colorless liquid with a slight odor; Nylen[6] reports it to be odorless if purified by two distillations. It has the following properties: b.p., 187 to 188° at 760 mm., 77.0 to 77.5° at 13 mm.; sp. gr., 1.0961^{0}_{4}; $n_{\gamma}^{18.4}$, 1.4164 or 1.4165.[7] Diethyl phosphite is miscible with most organic solvents. It is rapidly hydrolyzed by water or moist air, forming phosphorous acid and alcohol. It is decomposed by heating, with the evolution of some phosphine. Since it is a very good solvent for oxidized oils and varnishes, it may be used for removal of old paints. The compound behaves as though it exists in two tautomeric forms:



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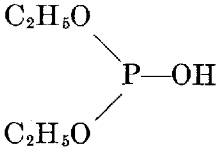

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* Analytical data are provided by the checkers.

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20. DIOCTYL PHOSPHITE

$$(C_2H_5O)_2POH + 2C_8H_{17}OH \rightarrow (C_8H_{17}O)_2POH + 2C_2H_5OH$$

Submitted by John E. Malowan*
Checked by T. P. Traise† and A. D. F. Toy†

Dioctyl phosphite can be produced by the usual method of preparing phosphite esters, *i.e.*, by allowing octanol to react with phosphorus(III) chloride:

$$3C_8H_{17}OH + PCl_3 \rightarrow (C_8H_{17}O)_2POH + C_8H_{17}Cl + 2HCl$$

This method has several disadvantages: first, about one-third of the octanol is converted to 1-chlorooctane; and, second, the removal of the phosphorous acid, formed incidentally, requires additional steps. The preferred process involves ester exchange reactions, in which a light alkyl or aryl group is replaced by a heavier alkyl or aryl radical.[1–3] In the procedure given here, the reaction is driven in the desired direction by distillation of the more volatile alcohol, leaving the heavier radical in the ester. The method may be applied with minor modifications to the preparation of other phosphite esters whose boiling points are too high to permit their purification by distillation.

Procedure

One hundred ninety-five grams of octanol (1.5 mols) and 114 g. of diethyl phosphite (0.83 mol) are placed in a 1000-ml. three-necked flask equipped with a thermometer, a glass capillary tube, and a short fractionating column. The amount of diethyl phosphite used represents an excess of 10%. The flask is connected to a distilling head which is equipped with a thermometer and attached to a condenser and a receiver. The contents of the flask are heated at a rate such that the temperature reaches 150° in 1 to 2 hours.

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[†] Victor Chemical Works, Chicago Heights, Ill.

Ethanol begins to distill when the temperature reaches 125 to 135°. The vapor temperature on top of the fractionating column will rise slowly from 80 to about 105°. The flask contents are then permitted to cool, vacuum is applied, and the distillation is again started. To prevent bumping and boiling over, air is permitted to bubble slowly through the contents of the distilling flask by way of the glass capillary. If the pressure is about 30 mm., the temperature may be permitted to rise in about 45 minutes to 150° with an accompanying vapor temperature of 90°. At this point the excess diethyl phosphite has distilled over and the heating is stopped. The total distillates will weigh about 64.0 g., and the residual dioctyl, phosphite, 223.3 g. (95%). *Anal.* Calcd. for $(C_8H_{17}O)_2POH$: P, 10.1. Found: P, 10.5.

For further purification, the product may be distilled at a pressure of less than 0.1 mm. (preferably in a Hickman still). Over-all yield is 74%.

Properties

Dioctyl phosphite is a colorless liquid, with the following properties: m.p., -13 to $-14°$; b.p., 190 to 191 at 3.0 mm., 173° at 0.5 mm.; sp. gr., 0.9286_0^{20}; n_D^{20}, 1.4420.[4] It cannot be distilled without decomposition, except in high vacuum. It is soluble in common solvents but insoluble in water and undergoes hydrolysis slowly.

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21. ALKYL DICHLOROPHOSPHITES

$$PCl_3 + ROH \rightarrow ROPCl_2 + HCl$$

Submitted Simultaneously by J. E. Malowan* and by Donald Ray Martin† and Philip J. Pizzolato†
Checked by T. P. Traise‡ and T. M. Beck‡ and by John F. Suttle§ and Franklin B. Barker§

Ethyl dichlorophosphite and methyl dichlorophosphite have been prepared by the reaction of 1 mol of the appropriate alcohol with 1 mol of phosphorus(III) chloride.[1] The ethyl compound has also been prepared from triethyl phosphite and phosphorus(III) chloride.[2] The method outlined below is essentially the former; however, several improvements have been incorporated. Among the difficulties encountered in the preparation of these compounds are the following: Side reactions occur between the generated hydrogen chloride and the ester, giving an alkyl chloride and phosphorous acid; disproportionation may occur; in the case of the ethyl ester, the necessary vacuum distillation causes losses of the relatively low boiling product.

Procedure

Two hundred seventy-five grams of phosphorus(III) chloride (2 mols) is weighed into a 500-ml., round-bottomed, three-necked flask equipped with standard-taper ground-glass joints and cooled by means of an ice-salt or Dry Ice bath. The necks of the flask are fitted, respectively, with a dropping funnel, a mercury-sealed, motor-driven stirrer,‖

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* Central Research Department, Monsanto Chemical Company, Dayton, Ohio. (This author worked with ethyl dichlorophosphite.)

† University of Illinois, Urbana, Ill. (These authors worked with methyl dichlorophosphite.)

‡ Victor Chemical Works, Chicago Heights, Ill. (These checkers worked with ethyl dichlorophosphite.)

§ University of New Mexico, Albuquerque, N.M. (These checkers worked with methyl dichlorophosphite.)

‖ Barker and Suttle (checkers of the preparation of the methyl ester) and a barium oxide drying tube to protect the reaction mixture from moist air. With continuous agitation, 2 mols of alcohol is added from the dropping funnel at such a rate that 2 to 3 hours are required to complete the addition. The actual rate of addition of alcohol in any instance is controlled by the efficiency of the cooling, because the temperature in the reaction flask should be kept in the range −5 to −10° or lower. After all the alcohol has been added, stirring is continued for an additional 15 minutes.

In the case of the ethyl ester, vacuum distillation should follow immediately unless the reaction products are kept in the cooling bath. A good fractionating column is required to separate the components of the mixture. The fractionating column is attached to an efficient condenser through which cold water is circulating and to a receiver cooled to about −20° in a Dry Ice bath. The barium oxide tube is replaced by a glass stopper. The pressure is kept at about 100 mm.; this prevents decomposition and at the same time does not make condensation of the product especially difficult. A slow current of dry air is bubbled through the solution by means of a capillary, to facilitate smooth boiling. After the reaction flask is removed from the cooling bath, the hydrogen chloride and ethyl chloride escape. The distillation of the unreacted phosphorus(III) chloride follows, with a vapor temperature of about 30°. The ethyl dichlorophosphite is obtained at 54 to 60°, depending on the pressure. When the still contents are low in volume and have acquired a dark orange color and when the thermometer in the flask shows a rapid temperature rise to about 95 to 100°, the distillation is stopped. The yield of the ethyl compound is 126 g. [43%, based on total phosphorus(III) chloride, or 52%, based on the phosphorus(III) chloride which has reacted.] *Anal.*[*] Calcd. for

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obtained satisfactory results with a magnetic stirrer when working with quantities of reactants equal to one-half the amounts used in the procedure above.

[*] Analytical data are provided by the checkers.

$C_2H_5OPCl_2$: P, 21.1; Cl, 48.3. Found: P, 20.6, 20.9; Cl, 47.7, 48.3.

The methyl dichlorophosphite is distilled at atmospheric pressure. The yield of crude product is about 185 g. (70%). A second distillation gives a product of enhanced purity in a yield of 160 g. (60%). *Anal.** Calcd. for CH_3OPCl_2: P, 23.3; Cl, 53.4. Found: P, 23.1; Cl, 53.1.

Care must be exercised in disposing of the waste phosphorus(III) chloride and the distillation residue. The waste phosphorus(III) chloride may be added in small increments to a large volume of cold water. Each portion is permitted to react and dissolve before the next portion is added. If phosphorus(III) chloride is added to warm water, the reaction is violent and flashes of flame may appear on the surface of the water.

Properties

Ethyl dichlorophosphite is a colorless liquid, with an irritating odor. It fumes when exposed to air. It has the following physical constants: sp. gr., 1.30526^0_4; b.p., 117.5°; n_D^{20}, 1.47176. It decomposes at 165° to ethyl chloride, phosphorus, phosphine, and phosphoric acid.[3] It reacts with water to form hydrogen chloride and phosphorous acid, and with alcohols to form esters. When ammonia is passed through ethyl dichlorophosphite, ethyl phosphenimidate (ethoxyphosphimide), $C_2H_5OP{=}NH$, is formed.

Methyl dichlorophosphite is a colorless, somewhat viscous liquid having the following physical constants: sp. gr., 1.406^0_4; b.p., 93.0° (760 mm.); m.p., $-91.0 \pm 0.4°$. The vapor pressure may be expressed by the equation

$$\log p_{\text{mm.}} = 7.8300 - \frac{1812.6}{T}$$

Methyl dichlorophosphite hydrolyzes readily and fumes in air. It reacts rapidly with aqueous sodium hydroxide. Mercury is attacked slowly by the compound, as is Lubriseal stopcock grease. It reacts with sublimed antimony-

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(III) fluoride below 10° and under a pressure of 50 mm. to produce methyl chlorofluorophosphite and methyl difluorophosphite.

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22. 2-CHLOROETHYL DICHLOROPHOSPHITE

(Phosphorus(III) β-Chloroethoxydichloride)

$$PCl_3 + ClC_2H_4OH \rightarrow ClC_2H_4OPCl_2 + HCl$$

Submitted by Donald Ray Martin,* W. Douglas Cooper,* Dwight R. Spessard,† and Harold Simmons Booth†
Checked by T. M. Beck‡ and E. N. Walsh‡

The reaction between an alcohol and the halide of a nonmetal (usually phosphorus) is well known in the synthesis of alkyl halides. Usually the reaction is conducted with an excess of alcohol and/or in basic media; thus

$$3ROH + PX_3 \rightarrow 3RX + H_3PO_3$$

Until recent years, comparatively little attention has been given to the inorganic products of these reactions. By maintaining an excess of the nonmetallic halide, stepwise replacement of a halogen atom by an alkoxy radical may be achieved.

$$\begin{aligned} ROH + PX_3 &\rightarrow ROPX_2 + HX \\ ROH + ROPX_2 &\rightarrow (RO)_2PX + HX \\ ROH + (RO)_2PX &\rightarrow (RO)_3P + HX \end{aligned}$$

In this synthesis, the reaction is confined primarily to the first step by adding 1 mol of ethylene chlorohydrin to 1 mol of precooled phosphorus(III) chloride.

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‡ Victor Chemical Works, Chicago Heights, Ill.

2-Chloroethyl dichlorophosphite may also be prepared by allowing ethylene oxide to condense with phosphorus(III) chloride.[1]

Procedure

The apparatus and procedure for the preparation of 2-chloroethyl dichlorophosphite are essentially the same as described for the analogous silicon and sulfuryl compounds (synthesis 30). One hundred thirty-seven and one-half grams of reagent-grade phosphorus(III) chloride (1.0 mol) is allowed to react with 80.5 g. of freshly distilled, anhydrous ethylene chlorohydrin (1.0 mol) in a 500-ml. flask under the conditions set forth in the cited synthesis. Approximately 1 hour is required for the introduction of the ethylene chlorohydrin.

After all the ethylene chlorohydrin has been added, stirring is continued while the reaction mixture is allowed to warm slowly to room temperature to facilitate the evolution of dissolved hydrogen chloride.

The remaining mixture of reaction products is distilled under a pressure of 40 mm. in an efficient fractionating column. The desired product is collected as a fraction boiling between 77 and 81° (40 mm.). The yield of purified 2-chloroethyl dichlorophosphite is about 131 g. (72%). *Anal.* Calcd. for $ClC_2H_4OPCl_2$: C, 13.24; H, 2.21; P, 17.10; Cl, 58.62. Found: C, 13.08; H, 2.28; P, 17.49; Cl, 58.52.

Properties

2-Chloroethyl dichlorophosphite is a colorless liquid having a specific gravity of 1.515 at 0°. It solidifies to a white solid at $-142 \pm 1°$. A second crystalline phase may be obtained by allowing the first phase to warm to room temperature. The higher-melting phase was not obtained directly from the liquid phase, nor was a definite temperature for the transition between the two phases observed. The boiling point has been reported to be 172 to 175° (747.8 mm.)[1] and 162.4° (760 mm.).[2]

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2-Chloroethyl dichlorophosphite fumes in moist air and hydrolyzes readily in water. It reacts vigorously with ethanol and propylene glycol and is soluble in dioxane, acetone, and diethyl ether. 2-Chloroethyl dichlorophosphite is obtained when the dichloride is allowed to react with antimony(III) fluoride at room temperature under a pressure of 50 mm.

References

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23. DISODIUM DIHYDROGEN HYPOPHOSPHATE

$$2P(red) + 2NaClO_2 + 8H_2O \rightarrow Na_2H_2P_2O_6 \cdot 6H_2O + 2HCl$$

Submitted by Elmer Leininger* and Thomas Chulski*
Checked by Therald Moeller,† Gladys H. Quinty,† and Robert L. Rebertus†

The methods commonly used for preparation of disodium dihydrogen hypophosphate depend upon the oxidation of yellow or red phosphorus. Yellow phosphorus may be oxidized by air[1] or by copper(II) nitrate.[2,3] Red phosphorus may be oxidized by chlorite,[4] hypochlorite,[5,6] alkaline permanganate,[7] hydrogen peroxide,[7] or iodine.[8] The phosphorus(III) halides, upon hydrolysis and treatment with iodine, yield some hypophosphate.[9–11] Electrolytic oxidation of a phosphide of copper, nickel, or silver[3] has also been used.

Of the various methods for preparing disodium dihydrogen hypophosphate, the one depending upon the oxidation of red phosphorus with sodium chlorite seems to be the best, considering both the yield and the simplicity of the procedure. In this reaction, phosphites and orthophosphates

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are also formed; however, the disodium dihydrogen hypophosphate is easily separated because of its limited solubility in cold water.

Procedure

The special reaction chamber *A* (Fig. 7) may be made from the outer jacket of a Liebig condenser by cutting a 15- or 20-cm. length from one end so as to include one tubulature. The end near the tubulature is closed with a one-hole rubber stopper through which a 30-cm. length of glass tubing of 1-cm. i.d. is inserted. While the reaction is taking place, cold water is passed through the central tube to moderate the reaction.

Enough pieces of broken porcelain *B* or large glass beads are put in the outer portion of the vessel to cover the tubulature opening. A 1- to 2-cm. depth of asbestos *C* is packed above the porcelain chips, and then alternate layers of red phosphorus *D* and glass beads *E* are packed into the column. A total weight of approximately 30 g. of phosphorus (0.24 mol) is used. Care should be exercised in the loading to obtain a compact filling which will not settle when suction is applied.

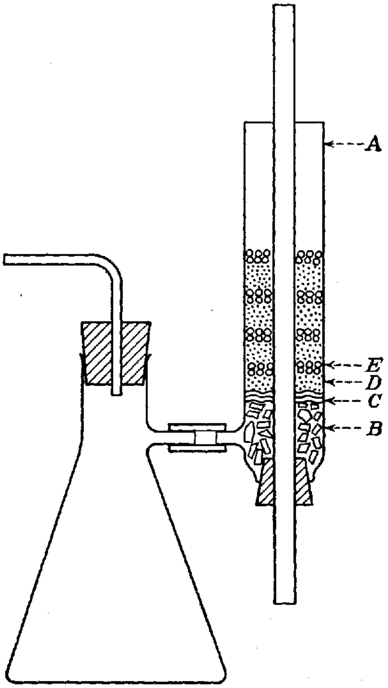

Fig. 7. Apparatus for the preparation of disodium dihydrogen hypophosphate.

A solution consisting of 54 g. of technical (83%) sodium chlorite (0.50 mol)* in 450 ml. of water is then put into

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* Mathieson Alkali Works.

a dropping funnel which is placed above the reaction vessel with the tip of the stem just inside the top of the chamber. The chlorite solution is allowed to drop into the chamber at a rate of 20 to 35 drops/min. (1 to 2 ml./min.). Cold water is circulated through the central tube during the reaction. The filter flask is connected to a water pump, and sufficient suction is applied to draw the solution through the column and at the same time retain a small volume (5 to 10 ml.) of the solution above the phosphorus. If the reaction is allowed to take place too rapidly, chlorine dioxide may be evolved with boiling and spattering. The addition of the chlorite solution requires from 4 to 7 hours.

Twelve grams of decolorizing carbon is placed in the solution of the phosphorus compounds contained in the flask, and the mixture is allowed to stand overnight or is shaken in a mechanical shaker for several hours. After the carbon is removed by filtration, the solution is brought to a pH of 5.4 (glass electrode) by addition of a 15% solution of sodium hydroxide. It is then heated to boiling, filtered to remove the coagulated impurities, and allowed to stand overnight at room temperature. The crystals are filtered, washed several times with ice-cold water, and either air-dried or dried in a desiccator over anhydrous disodium dihydrogen hypophosphate.

The yield is 23 g. of $Na_2H_2P_2O_6 \cdot 6H_2O$, which is approximately 30%, based on the weight of sodium chlorite consumed.

The salt may be recrystallized from water with a loss of 1 to 2 g. of product.

Properties

Disodium dihydrogen hypophosphate hexahydrate is a stable, colorless, crystalline compound. It loses its water of crystallization completely at 110°. The solubility of the hydrate is 2.0 g./100 ml. of water at 25°. Solutions of the compound are quite stable, but upon heating or the addition of acids, hypophosphate tends to disproportionate to phos-

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phite and orthophosphate. It is oxidized to orthophosphate only with great difficulty.

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24. PHOSPHORUS(V) SULFOCHLORIDE

(Thiophosphoryl Chloride)

Several procedures have been reported for the synthesis of phosphorus(V) sulfochloride. These include the reaction of phosphorus(V) chloride with hydrogen sulfide,[1,2] of phosphorus(III) chloride with sulfur,[3,4] of carbon tetrachloride with phosphorus(V) sulfide,[5] and of phosphorus(V) chloride with phosphorus(V) sulfide.[6] The second and fourth methods form the bases for the two syntheses presented here.

Procedure A

Preparation from Phosphorus(III) Chloride, Aluminum Trichloride, and Elemental Sulfur

$$PCl_3 + AlCl_3 \rightarrow AlCl_3 \cdot PCl_3$$
$$AlCl_3 \cdot PCl_3 + S \rightarrow PSCl_3 + AlCl_3$$

Submitted by Therald Moeller,* Homer J. Birch,* and Niels C. Nielsen*
Checked by Frederic B. Dutton† and Reed F. Riley†

This method of synthesis is essentially that of Knotz.[4] Phosphorus(III) chloride and sulfur are caused to react in

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the presence of anhydrous aluminum(III) chloride to form the sulfochloride. It is assumed, however, that the aluminum and phosphorus(III) chlorides form a molecular addition compound, which then reacts with sulfur to give the product and regenerate the catalyst. Under strictly anhydrous conditions, the yield is nearly quantitative.

One hundred three grams of phosphorus(III) chloride (0.75 mol), 24 g. of powdered sulfur (0.75 g.-atom), and 2.0 g. of white, anhydrous aluminum chloride (0.015 mol)* are placed in a dry 300-ml. round-bottomed flask with a single standard-taper opening. The flask is immediately connected to two efficient condensers, which are joined in series and arranged for refluxing. A calcium chloride drying tube fashioned from 0.75-in. glass tubing (to permit rapid pressure release) is attached to the open end of the condenser system. The flask is heated on a hot plate until the aluminum chloride dissolves and the strongly exothermic reaction begins. This normally occurs at 40 to 50° and is followed by an immediate rise in temperature to about 120°. The efficient condenser is necessary to prevent losses by volatilization. All but a small quantity of sulfur should react. If appreciable quantities of unreacted sulfur remain, the flask is heated until the reaction is complete. The resulting clear, brownish solution is cooled and then distilled, using a Liebig condenser. It is necessary to provide ample protection from atmospheric moisture during the distillation. A few porcelain chips are added to the flask to facilitate smooth boiling. A tarry residue remains; this should be removed from the flask before it hardens. The distillate is colorless and boils at 122 to 123°. The yield is 113 to 117 g. (89 to 92%, based on sulfur). Losses are largely mechanical and may be attributed to the presence

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* The ratio $1PCl_3:1S:0.02AlCl_3$ is critical. The quantities of reagents employed are optional provided that the ratio is maintained. Excess phosphorus(III) chloride renders separation of the final product difficult, whereas excess aluminum chloride causes the reaction to go too rapidly for adequate control. The aluminum chloride used should be white. The yellow form promotes a more rapid reaction; however, the resulting yields are lower.

of gelatinous aluminum chloride, which causes incomplete distillation of the product. All-glass equipment is desirable, although reaction of the product with cork or rubber appears to be slow.

Procedure B

Preparation from Phosphorus(V) Sulfide and Phosphorus(V) Chloride

$$P_2S_5 + 3PCl_5 \rightarrow 5PSCl_3$$

Submitted by Donald Ray Martin* and Wilmer M. Duvall*
Checked by Frederic B. Dutton† and Reed F. Riley†

The older literature reports the synthesis of phosphorus(V) sulfochloride by reaction of phosphorus(V) chloride with phosphorus(V) sulfide in a sealed tube at 120°. Experience has shown that pressures as great as 700 p.s.i. may result under these conditions, indicating that an autoclave or bomb should be used. In the absence of these, the reactor shown in Fig. 8 is suitable. It consists of an oil bath containing a lecture bottle fitted with a pipe plug (iron pipe size, ½ in.), a thermometer, and a knife type of immersion heater. Although no difficulty has been experienced in the use of this reactor, it is well to keep it behind a barricade during the reaction.

In a hood, 211 g. of powdered phosphorus(V) chloride (1.01 mols) is intimately mixed with 75 g. of powdered phosphorus(V) sulfide (0.338 mol) in a 500-ml. beaker. This mixture is then transferred to the lecture bottle. Use of a 150-mm. short-stemmed funnel and a stirring rod facilitates this transfer and keeps the pipe threads clean. After treatment with pipe-joint compound, the pipe plug is screwed into place. (A satisfactory pipe-joint compound can be made by grinding litharge and glycerol together.)

The oil bath is maintained at 150° for 45 minutes with a 500-watt immersion heater. When cool, the reactor is

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opened, and the contents are poured into a 500-ml. round-bottomed flask with a standard-taper neck. Distillation in ungreased standard-taper equipment yields the product as a colorless liquid. The crude product is obtained in approximately 80% yield; distillation yields 70% of the theoretical amount of phosphorus(V) sulfochloride having a 2° boiling range. By extending the reaction time to 2 hours, the yield of purified product may be increased to about 76%.

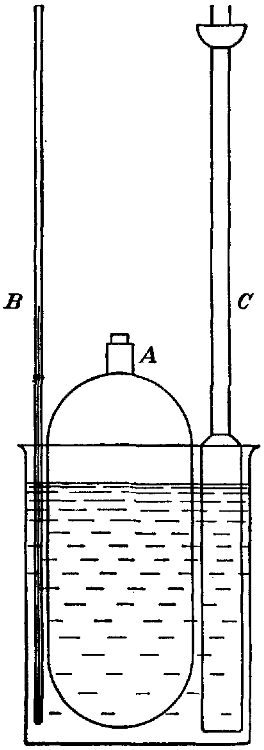

Fig. 8. Apparatus for the preparation of phosphorus(V) sulfochloride from phosphorus(V) sulfide and phosphorus(V) chloride.

Properties

Phosphorus(V) sulfochloride is a colorless, fuming liquid with boiling point 125° and specific gravity 1.635. The alpha form solidifies at −40.8°, while the beta form solidifies at −36.2°.[7] The compound hydrolyzes slowly in water and rapidly in alkaline solution. In water, the hydrolysis products are orthophosphoric acid, hydrochloric acid, and hydrogen sulfide. Phosphorus(V) sulfochloride is soluble in benzene, carbon tetrachloride, carbon disulfide, and chloroform. It reacts with ethanol, yielding *O*-ethyl dichlorothiophosphate[8] (synthesis 25).

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25. *O*-ETHYL DICHLOROTHIOPHOSPHATE

(Phosphorus(V) Ethoxysulfodichloride)

$$PSCl_3 + C_2H_5OH \rightarrow C_2H_5OPSCl_2 + HCl$$

Submitted by Donald Ray Martin,* Harold Simmons Booth,† and Fred E. Kendall‡
Checked by G. A. McDonald§

O-Ethyl dichlorothiophosphate is prepared most conveniently by allowing ethanol to react with phosphorus(V) sulfochloride.[1–3]

Procedure

One hundred four milliliters of phosphorus(V) sulfochloride (1.0 mol) is placed in a 500-ml. three-necked flask. The flask is fitted with a mercury-sealed stirrer, a water-cooled condenser to which a drying tube containing barium oxide is attached in a horizontal position, and a 250-ml. dropping funnel containing 58 ml. of anhydrous ethanol (1.0 mol). All joints may be rubber stoppers or, preferably, nonlubricated standard-taper ground-glass joints.

The reactor is placed in an ice bath in a *hood*. The contents of the reactor are stirred vigorously while the ethanol is added at a rate of about 0.5 ml./min. The ice bath is removed after all the ethanol has been added, and stirring is continued until the reaction mixture reaches room temperature.

The apparatus originally attached to the three necks of the reactor is quickly replaced by stoppers (rubber or ground glass) and a Vigreux fractionating column adapted for vacuum distillation. The pressure within the system is *slowly* reduced to about 25 mm. After the dissolved hydrogen chloride and the unreacted ethanol have been removed, the contents of the still pot are heated slowly. A fraction obtained over the range from room temperature up

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to about 45° is primarily unreacted phosphorus(V) sulfochloride. The desired product, *O*-ethyl dichlorothiophosphate, is collected at about 57° under a pressure of 25 mm. The yield is about 70 g. (39%). *Anal.* Calcd. for $C_2H_5OPSCl_2$: P, 17.31; S, 17.91; Cl, 39.61. Found: P, 17.15, 17.30;* S, 17.82, 17.90;* Cl, 39.62, 39.40.*

Properties

O-Ethyl dichlorothiophosphate is an oily, colorless liquid which freezes to a white solid at $-78.4 \pm 0.5°$. It is thermally unstable at temperatures above 90°. The vapor pressure is expressed by the equation

$$\log p_{\text{mm.}} = 7.7846 - \frac{2108.1}{T}$$

The boiling point at 20 mm. is 52.0°; specific gravity, $1.4395_4^{20°}$.

The compound displays no tendency to hydrolyze in air or in water. It reacts slowly with aqueous sodium hydroxide. It is soluble in ethanol, acetone, ether, and carbon tetrachloride.

O-Ethyl dichlorothiophosphate reacts with sublimed antimony(III) fluoride in the presence of a small amount of antimony(V) chloride to yield *O*-ethyl chlorofluorothiophosphate and *O*-ethyl difluorothiophosphate.[3] No reaction has been observed when the vapors are in contact with mercury. Steel is attacked very slightly by the liquid. The liquid in small quantities has no vesicant action upon the hands.

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* These data were supplied by the checker.

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26. DIETHYL MONOAMIDOPHOSPHATE

$$(C_2H_5O)_2POH + CCl_4 + 2NH_3 \rightarrow (C_2H_5O)_2PONH_2 + CHCl_3 + NH_4Cl$$

Submitted by J. E. Malowan*
Checked by T. P. Traise† and T. M. Beck†

Diethyl monoamidophosphate can be produced by the ammonolysis of diethyl monochlorophosphate or preferably by the reaction of diethyl phosphite with carbon tetrachloride and ammonia, as described by Atherton, Openshaw, and Todd[1] and further elaborated by Steinberg.[2]

Procedure

One hundred thirty-eight grams (1.0 mol) of diethyl phosphite (synthesis 19) and 153.8 g. of carbon tetrachloride (1.0 mol) are diluted with 400 g. of dry benzene and placed in a 2-l. three-necked flask, which is equipped with a stirrer, a thermometer, and gas inlet and outlet tubes. The outlet tube is connected to a drying tube to prevent access to moist air. The flask is kept in a salt-ice bath and agitated while ammonia is admitted at such a rate that the temperature does not exceed 5°. Three to four hours are required. The reaction is complete when the escape of ammonia through the outlet tube is detectable and heat is no longer evolved. When this occurs, the ammonia flow is stopped, but agitation is continued for an additional 15 minutes; the solution should still possess a strong odor of ammonia. The ammonium chloride produced is filtered on a Büchner funnel with suction and washed with benzene. It may be dried and weighed as a check on the reaction.

The filtrate is heated in a flask, under atmospheric pressure, to distill out the benzene and chloroform. Vacuum is then applied, and the flask is heated to 80 to 90° to drive off the last traces of the solvents.

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The residue is nearly colorless and solidifies to a crystalline mass on cooling. The yield is approximately 90%. *Anal.** Calcd. for $(C_2H_5O)_2PONH_2$: P, 20.2; N, 9.1. Found: P, 20.7, 21.7; N, 8.8, 8.7.

Properties

Diethyl monoamidophosphate forms colorless, needlelike crystals, which melt at 46 to 47°. It is very soluble in water, alcohol, acetone, ether, carbon tetrachloride, and a number of other organic solvents but insoluble in hexane. It is very hygroscopic and liquefies when exposed to moist air.

References

1. Atherton, Openshaw, and Todd: *J. Chem. Soc.*, **1945**, 660.
2. Steinberg: *J. Org. Chem.*, **15**, 637 (1950).

27. DIETHYL MONOCHLOROPHOSPHATE

$$(C_2H_5O)_2POH + Cl_2 \rightarrow (C_2H_5O)_2POCl + HCl$$

Submitted by J. E. Malowan†
Checked by T. P. Traise‡ and T. M. Beck‡

Diethyl monochlorophosphate has been prepared by the reaction of triethyl phosphate with phosphorus(V) oxychloride, by treating diethyl phosphite with sulfuryl chloride,[1] from diethyl phosphite and carbon tetrachloride in the presence of a tertiary amine,[2] from ethanol and phosphoryl chloride in a medium of pyridine and benzene,[3] and by the chlorination of diethyl phosphite.[4,5] The last procedure is simple and gives good yields.

Procedure

One hundred thirty-eight grams of diethyl phosphite (1.0 mol) is placed in a three-necked flask, equipped with a close-fitting stirrer, gas inlet and outlet tubes, and a thermometer, and then cooled in an ice-salt bath. The gas outlet tube is

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* Analytical data are furnished by the checkers.

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‡ Victor Chemical Works, Chicago Heights, Ill.

connected to a drying tube to prevent access of moist air. Since hydrogen chloride is generated, the experiment must be conducted in a *hood.*

Chlorine is slowly conducted into the diethyl phosphite with constant stirring and at such a rate that the temperature does not exceed 5°. When the liquid acquires a light yellow color from free chlorine, in from 2 to 3 hours, the chlorine flow is stopped and the product is transferred to a distilling flask. A short fractionating column is attached, and this column is connected to a condenser and a receiver.

When vacuum is applied, the liquid bubbles vigorously as the free chlorine and hydrogen chloride escape. After this boiling subsides, heating is started. With a pressure of 20 mm., distillation begins at 100 to 110°. The vapor temperature is 103.0 to 104.5°. When the distillation is complete, the temperature in the flask rises rapidly to 150°, with the pressure increasing to about 35 mm., indicating decomposition. The distillation is stopped when this occurs. The yield of diethyl monochlorophosphate is 80 to 90%. *Anal.** Calcd. for $C_4H_{10}O_3ClP$: P_2O_5, 41.5; Cl, 20.6. Found: P_2O_5, 41.2, 41.0; Cl, 21.6, 21.5.

Properties

Diethyl monochlorophosphate is a colorless liquid of irritating, unpleasant odor, with boiling point 89° (at 15 mm.), n_D^{25}, 1.4150. It fumes in moist air and reacts vigorously with water. It reacts with ammonia to give ethylamidophosphate and with amines to give substituted ethylamidophosphates.[5]

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* The analytical data are furnished by the checkers.

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28. VANADIUM(III) OXIDE AND VANADIUM(V) OXYTRICHLORIDE (CORRECTION)[1]

$$V_2O_5 + 2H_2 \rightarrow V_2O_3 + 2H_2O$$
$$2V_2O_3 + 6Cl_2 \rightarrow 4VOCl_3 + O_2$$

Submitted by F. E. Brown* and F. A. Griffitts*
Checked by G. B. Heisig† and L. A. Enberg†

Doctor H. C. Mattraw‡ has called attention to the fact that, in the synthesis of vanadium(V) oxytrichloride[1] ($VOCl_3$), as described in part A of synthesis 38 of Volume I, the reduction of vanadium(V) oxide by hydrogen was incorrectly said to yield vanadium(II) oxide (hypovanadous oxide), V_2O_2, instead of vanadium(III) oxide, V_2O_3, which is in fact produced under the conditions specified, as indicated in the above equations. The chlorination of the resulting oxide, mixed with an equal weight of decolorizing charcoal, yields vanadium(V) oxytrichloride, as correctly described in part B.

Attention should also have been called in Volume I to the vapor-pressure data of Flood, Gørrissen and Veimo,[2] which are not in accord with those of Brown and Griffitts,[1,3] especially at lower temperatures. Flood and coworkers give the following values, those in the second column being calculated on the basis $Q = 8.7$ kcal., and those in the third column being the measured values.

Temp.	Calcd. vapor press., mm.	Measured vapor press., mm.
−15.0	1.75	1.9
0.0	4.6	4.4
11.5	8.4	8.0
19.1	13.0	15.5
31.1	24.0	28.3
40.0	35.0	42.0
50.0	55.0	64.0
60.0	85.0	93.0
80.0	175.0	
100.0	340.0	
127.0	(760.0)	(760.0)

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Flood and coworkers report the freezing point of vanadium(V) oxytrichloride to be −79.5°.

References

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2. Flood, Gørrissen, and Veimo: *J. Am. Chem. Soc.*, **59,** 2494 (1937).
3. Brown and Griffitts: *Iowa State Coll. J. Sci.*, **9,** 89 (1934).

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CHAPTER VIA

See also: Thiosemicarbazide, synthesis 12
Phosphorus(V) sulfochloride, synthesis 24
O-Ethyl dichlorothiophosphate, synthesis 25

29. SODIUM SUPEROXIDE

$$Na_2O_2 + O_2 \rightarrow 2NaO_2$$

SUBMITTED BY STEPHEN E. STEPHANOU,* EDGAR J. SEYB, JR.,* AND JACOB KLEINBERG*
CHECKED BY R. H. SHAKELY† AND W. H. SCHECHTER†

The rapid oxidation of sodium in liquid ammonia[1] under carefully controlled conditions yields a material of the empirical formula $NaO_{1.67}$, which corresponds to a mixture of 4 mols of sodium superoxide with 1 mol of sodium peroxide. A more practicable method for preparing sodium superoxide, and one which results in a product of relatively high purity, involves the direct combination of sodium peroxide and oxygen at elevated temperatures and pressures.[2]

Procedure

The apparatus employed (Fig. 9) consists of a stainless-steel bomb *A* of about 180 ml. capacity‡ equipped with such an arrangement of needle valves that the system can be completely evacuated or filled with oxygen under pres-

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‡ The bomb, tubing, and other accessories were obtained from the American Instrument Company, Inc., of Silver Springs, Md. The equipment was supplied as a hydrogenation apparatus and was adapted for use with oxygen by the removal of all oil and grease by means of carbon tetrachloride and acetone and replacement of the valve packing with a special oil-free material obtained from the Puritan Compressed Gas Corporation, Kansas City, Kan. The seat of each needle valve was lubricated with a trace of mutton fat.

sure. The heating jacket *B* is insulated with a layer of magnesia about 1 in. thick. An iron-constantan thermocouple *H* is inserted in the wall of the bomb and is connected to a Brown electronic recorder; regulator *C* permits temperature control. The voltage across the heating elements of the bomb jacket *B* is adjusted by means of the powerstat *D*.

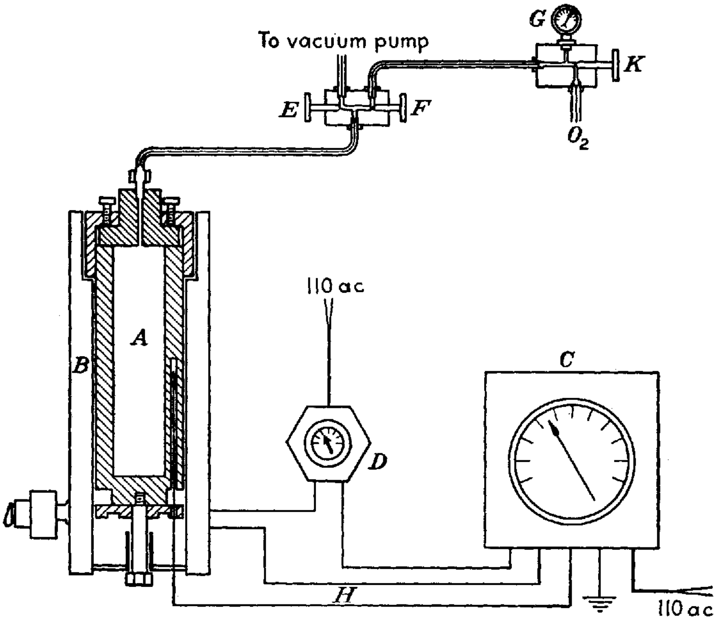

FIG. 9. Apparatus for the preparation of sodium superoxide.

A weighed sample, approximately 10 g., of sodium peroxide* (0.13 mol.) is placed inside a pyrex container† which fits snugly into the bomb, and the system is evacuated to 1 to 3 mm. pressure for several hours. Oxygen from a cylinder is added slowly through valve *F* until a pressure of

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[*] Sodium peroxide of especially large surface area and high purity should be used. This can be obtained from the Mine Safety Appliances Company, Pittsburgh, Pa.

[†] The pyrex container is fitted with a ground-glass stopper. There is a small opening at the joint which permits adjustment and allows access of oxygen during the course of the run.

approximately 2000 p.s.i. is attained. Valve *K* is then closed, and the bomb is heated to 450 to 475° for approximately 6 hours. (After this time the oxygen pressure as shown by pressure gage *G* has reached an approximately constant value.) The bomb is cooled to room temperature, and the product is removed. It is then analyzed for available oxygen by decomposition with a catalyst solution which is 2 *M* with respect to hydrochloric acid and 1 *M* in iron(III) chloride.[3] From the corrected volume of oxygen evolved per gram of product, on the assumption that only superoxide and peroxide are present, the weight per cent of sodium superoxide is calculated by means of the equation

$$\left(\frac{\text{ml. } O_2 \text{ evolved/g. product} - 144}{162}\right) \times 100 = \%\ NaO_2$$

where the numerator of the parenthetical term represents milliliters of oxygen evolved per gram beyond that required for pure sodium peroxide, and the denominator is the difference in milliliters of oxygen evolved per gram between *pure* sodium superoxide and sodium peroxide. Under the conditions described above, a yield of approximately 13.5 g. (96%) of superoxide is obtained.

To avoid decomposition due to exposure to atmospheric moisture, both starting material and product are handled in a dry box containing phosphorus(V) oxide.

Properties

The material obtained in the bomb is a bright orange, sintered mass which may be readily pulverized in a mortar to a yellow, hygroscopic powder. Upon exposure to moisture, it evolves oxygen and gradually loses its color, leaving a white residue, which is a mixture of peroxide and hydroxide. Sodium superoxide appears to be stable indefinitely when stored in a desiccator over phosphorus(V) oxide.

Sodium superoxide, which contains the $:\ddot{\mathrm{O}}\overset{\cdots}{—}\ddot{\mathrm{O}}:^{-}$ ion, has an effective magnetic moment of approximately 2 Bohr magnetons. The crystal structure is like that of sodium

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chloride, with O_2^- ions occupying the halide positions with disorderly orientation.[4]

References

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2. Stephanou, Schechter, Argersinger, and Kleinberg: *ibid.*, 1819.
3. Schechter, Sisler, and Kleinberg: *ibid.*, **70**, 267 (1948).
4. Templeton and Dauben: *ibid.*, **72**, 2251 (1950).

30. 2-CHLOROETHYL CHLOROSULFONATE AND (2-CHLOROETHOXY)TRICHLOROSILANE

[β-Chloroethoxylsulfuryl Chloride and (β-Chloroethoxy)silicon Trichloride]

Submitted by Donald R. Martin,* John F. Suttle,† and Harold Simmons Booth‡
Checked by Frederic B. Dutton§

The solvolytic behavior of the halides of many of the nonmetals (*e.g.*, PX_3, BX_3, SiX_4, SOX_2) is well known. The alcoholysis of these inorganic molecules has been used generally for introducing halogen into organic molecules. This synthesis is a modification of the method first used to prepare 2-chloroethyl chlorosulfonate in which ethylene chlorohydrin is added to sulfuryl chloride.[1] The general reaction is also applied here to the alcoholysis of silicon tetrachloride to produce the new compound (2-chloroethoxy) trichlorosilane. 2-Chloroethyl chlorosulfonate has also been synthesized by the reaction of ethylene chloride and fuming sulfuric acid[2] and by passing chlorine into bis(2-chloroethyl) sulfite.[3]

Procedure

A. 2-CHLOROETHYL CHLOROSULFONATE

$$ClC_2H_4OH + ClSO_2Cl \rightarrow ClC_2H_4OSO_2Cl + HCl$$

One hundred sixty milliliters of sulfuryl chloride (2.0 mols) is placed in a 500-ml. three-necked flask. The flask

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is fitted with a mercury-sealed glass stirrer, a water-cooled condenser to which a drying tube containing Drierite is attached, and a dropping funnel containing 132 ml. of ethylene chlorohydrin (2.0 mols). All joints are nonlubricated standard-taper ground-glass joints.

The reactor is placed in an ice bath, and its contents are stirred vigorously while the ethylene chlorohydrin is added dropwise at a rate of approximately 2 ml./min. (hood). The reaction mixture is maintained at 0° until the addition is completed. Stirring is continued for 45 minutes after all the ethylene chlorohydrin has been added, while the reaction mixture is allowed to warm slowly to room temperature.

The apparatus originally attached to the three necks of the flask is quickly replaced with two glass stoppers and a Vigreux fractionating column adapted for vacuum distillation. The pressure within the distillation apparatus is cautiously reduced to about 25 mm. After the dissolved hydrogen chloride and other volatile compounds cease to be evolved, the reaction products are heated slowly to about 100°. All the distillate which is removed below 100° is discarded. The clear product is collected between 100 and 101°. The yield is 196 ml. (85%). *Anal.** Calcd. for $ClC_2H_4OSO_2Cl$: Cl, 39.61; S, 17.91. Found: Cl, 38.57; S, 17.02.

B. (2-CHLOROETHOXY)TRICHLOROSILANE

$$ClC_2H_4OH + SiCl_4 \rightarrow ClC_2H_4OSiCl_3 + HCl$$

The procedure for the preparation of (2-chloroethoxy)-trichlorosilane is the same as that given in part A above, with a few modifications. The reaction is carried out in a 1-l. flask rather than in the 500-ml. flask described above; the rest of the apparatus is the same as in part A.

Two hundred twenty-six milliliters of silicon tetrachloride (2.0 mols) is allowed to react with 68 ml. of ethylene chlorohydrin (1.0 mol). This excess of silicon tetrachloride is used to reduce the probability of secondary reactions which might produce di-, tri-, and/or tetraalkoxy derivatives.

* These data were supplied by the checker.

In order to reduce the rate of reaction, the ethylene chlorohydrin is diluted with 200 ml. of anhydrous ethyl ether.

After the reaction has been carried out, the apparatus is arranged for distillation as previously described (part A), and the reaction flask is heated at atmospheric pressure to facilitate removal of the dissolved hydrogen chloride, ethyl ether, and excess silicon tetrachloride. The vapor temperature is not allowed to rise above 55 to 60°. Vacuum is then applied, and the pressure in the system is lowered slowly to about 33 mm. The desired product distills at 66 to 68° under a pressure of 33 mm. Most of the distillate is obtained at 66°. The yield is about 130 ml., which is approximately 90% based on ethylene chlorohydrin. *Anal.** Calcd. for $ClC_2H_4OSiCl_3$: Cl, 66.3. Found: Cl, 65.90, 66.15.

Properties

2-Chloroethyl chlorosulfonate is a colorless liquid with the following physical constants: sp. gr., 1.580_4^0, $1.555_4^{18.3}$, $1.552_4^{20.5}$;[4] $n_D^{18.3}$, 1.4587; n_D^{21}, 1.4578;[3,4] b.p., 73° (4 mm.), 92° (14.5 mm.),[3] 101° (23 mm.),[4] and 120 to 122° (80 mm.).[2]

This product hydrolyzes very slowly; however, it is rapidly destroyed by sodium hydroxide. It is miscible with alcohol and ether with no apparent reaction. 2-Chloroethyl chlorosulfonate is more stable than ethyl chlorosulfonate. It is quite stable thermally; no polymerization is apparent. Upon long standing, decomposition occurs with the evolution of hydrogen chloride as evidenced by darkening of the liquid.

β-Chloroethoxylsulfuryl chloride is a lacrimator which possesses an odor somewhat similar to that associated with chloropicrin[1] and formaldehyde.[2]

(2-Chloroethoxy)trichlorosilane is a clear, colorless liquid which decomposes if distilled under atmospheric pressure. Its boiling point has been observed to be 63° (25 mm.) and 66° (33 mm.). It reacts with sodium hydroxide and with

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* This datum was supplied by the checker.

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antimony(III) fluoride. The latter reaction yields silicon tetrafluoride. There is no apparent reaction between calcium fluoride or antimony pentachloride and (2-chloroethoxy)trichlorosilane. The latter is quite soluble in tetrachloroethylene.

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2. Ott: German patent 374141, (Apr. 20, 1923); *cf. Chem. Abstracts*, **18**, 2176 (1924).
3. Levaillant: *Compt. rend.*, **189**, 465 (1929).
4. Levaillant: *ibid.*, **187**, 730 (1928).

31. SODIUM "SELENOPENTATHIONATE" 3-HYDRATE* AND SODIUM "TELLUROPENTATHIONATE" 2-HYDRATE*

Submitted by Olav Foss†
Checked by John J. Pitha‡

$$SeO_2 + 4S_2O_3^{=} + 4H^+ \rightarrow S_4O_6^{=} + SeS_4O_6^{=} + 2H_2O$$
$$TeO_2 + 4S_2O_3^{=} + 4H^+ \rightarrow S_4O_6^{=} + TeS_4O_6^{=} + 2H_2O$$

Sodium "selenopentathionate" 3-hydrate, which was first isolated in 1949,[1] is prepared by the reaction used by Norris and Fay[2] for the iodometric analysis of selenious acid. Salts of "telluropentathionic" acid were also first isolated in 1949.[3] The reaction utilized in their preparation was also discovered by Norris and Fay.[2,4] Tellurous acid cannot be analyzed by a procedure analogous to that which Norris and Fay applied to the determination of selenious acid, because "telluropentathionate" is not indifferent to iodine but may be titrated directly with it:[3]

$$TeS_4O_6^{=} + 2I_2 + 2H_2O \rightarrow TeO_2 + S_4O_6^{=} + 4I^- + 4H^+$$

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* Unambiguous names for these compounds will have to await proof of their structures.—Editor.

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‡ Michigan State College, East Lansing, Mich.

Procedure

It is imperative that an excess of selenious acid or tellurous acid be present at every stage of the process, since thiosulfate catalyzes the decomposition of "selenopentathionate" and "telluropentathionate."

A. SODIUM "SELENOPENTATHIONATE" 3-HYDRATE

One hundred thirty grams of sodium thiosulfate 5-hydrate (0.524 mol) is dissolved in 40 ml. of water by heating, and subsequently cooled to 25 to 30°. The resulting solution is added dropwise to a solution of 17.2 g. of selenium dioxide (0.155 mol) in 20 ml. of water and 100 ml. of glacial acetic acid, over a period of about 20 minutes, with mechanical stirring and cooling in an ice-salt mixture. The temperature of the reaction mixture should be about 0°. One hundred fifty milliliters of ethanol is added to the clear, viscous, yellowish-green solution of sodium tetrathionate and sodium "selenopentathionate." After crystallization begins, 50 ml. of ether is added, and cooling and stirring are continued for 15 minutes. The product is filtered, washed with ethanol and with ether, and dried *in vacuo* over sulfuric acid.

The crude product contains about 40 g. of sodium "selenopentathionate" 3-hydrate and about 4 mol per cent of sodium tetrathionate. It is dissolved in 50 ml. of 0.2 *N* hydrochloric acid at about 30°, and the solution is filtered with suction. One hundred milliliters of methanol is added, and the mixture is cooled in an ice-salt mixture. Pure sodium "selenopentathionate" 3-hydrate precipitates and is filtered, washed with ethanol, and dried *in vacuo* over sulfuric acid. The yield is about 25 g. (55%).

B. SODIUM "TELLUROPENTATHIONATE" 2-HYDRATE

One hundred ten grams of sodium thiosulfate 5-hydrate (0.444 mol) in 60 ml. of water is added to a solution of 18.8 g. of tellurium dioxide (0.118 mol) in 45 ml. of concentrated hydrochloric acid (12 *N*) and 75 ml. of glacial acetic acid, over a period of about 15 minutes and under the same conditions as were described for sodium "selenopentathionate." One hundred fifty milliliters of ethanol is added to the mixture, and cooling and stirring are continued for about 15 minutes. It is sometimes necessary to scratch the walls of the beaker with a glass rod in order to start the crystallization. The crude product is filtered, washed with ethanol and with ether, and dried *in vacuo* over sulfuric acid. It contains about 35 g. of sodium "telluropentathionate" 2-hydrate and 2 to 4 mol per cent of tetrathionate. It is recrystallized from about 60 ml. of 0.2 *N* hydrochloric acid at less than 45°. From this point the procedure is as described in part A above. The yield of pure product is about 20 g. (45%).

Properties[1,3,5]

Sodium "selenopentathionate" 3-hydrate crystallizes as small, voluminous, pale yellowish-green leaves or thin plates. It is very soluble in water and appreciably soluble in methanol, but insoluble in ethanol. Aqueous solutions of the substance are yellowish green.

Sodium "telluropentathionate" 2-hydrate crystallizes as small plates or flat needles. A mass of crystals appears yellow with an orange tint; single crystals are yellow with a greenish tint. Dilute aqueous solutions are yellow; concentrated solutions are orange red. The salt is readily soluble in water, though less soluble than the analogous selenium compound. It is insoluble in ethanol and insoluble or very sparingly soluble in methanol. Its water of hydration, like that associated with sodium "selenopentathionate," is lost very slowly *in vacuo* over sulfuric acid.

The salts, when pure, may be kept unchanged over sulfuric acid for several months. Eventually selenium or tellurium is liberated. The aqueous solutions gradually decompose into selenium or tellurium and tetrathionate. Thus, 0.064 *M* solutions of "selenopentathionate" become

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red after standing about 10 hours at 25°, and solutions of "telluropentathionate" become gray after standing about 3 hours. The rate of decomposition is more rapid for the selenium compound than for the tellurium compound. Solutions of these salts are stabilized by mineral acids, whereas alkalies accelerate the decomposition. Alkali xanthates and dithiocarbamates react to give xanthates and dithiocarbamates of bivalent selenium and tellurium (synthesis 32).

References

1. Foss: *Acta Chem. Scand.*, **3,** 435 (1949).
2. Norris and Fay: *Am. Chem. J.*, **23,** 119 (1900).
3. Foss: *Acta Chem. Scand.*, **3,** 708 (1949).
4. Norris: *J. Am. Chem. Soc.*, **28,** 1675 (1906).
5. Foss: *Acta Chem. Scand.*, **3,** 1385 (1949).

32. XANTHATES AND DITHIOCARBAMATES OF SELENIUM(II) AND TELLURIUM(II)

$$MS_4O_6^{=} + 2ROCS_2^{-} \rightarrow M(S_2COR)_2 + 2S_2O_3^{=}$$
$$MS_4O_6^{=} + 2R_2NCS_2^{-} \rightarrow M(S_2CNR_2)_2 + 2S_2O_3^{=}$$
$$(M = Se, Te)$$

Submitted by Olav Foss*
Checked by John J. Pitha†

Selenium and tellurium dioxides react with alkali xanthates and dithiocarbamates to give xanthates and dithiocarbamates of selenium(IV) and tellurium(IV).[1,2] Russell[1] states that the product formed by sodium diethyldithiocarbamate and selenium dioxide sometimes appears as an equimolar mixture of selenium(II) dithiocarbamate and the corresponding bis(thiocarbamyl) disulfide, $(R_2NCS)_2S_2$. The commercial selenium dithiocarbamates, prepared by the above-mentioned method, usually consist of such mixtures. The disulfide can, in most cases, be extracted from selenium(II) dithiocarbamate by means of cold benzene or chloroform.

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Xanthates and dithiocarbamates of bivalent selenium and tellurium may be conveniently prepared[3-5] by allowing sodium "selenopentathionate" or sodium "telluropentathionate" to react with alkali xanthates or dithiocarbamates. The reactions are rapid and quantitative, and the products separate from the aqueous reaction mixtures in a high state of purity.

Procedure

A solution of 0.025 mol of sodium or potassium xanthate or dithiocarbamate in 100 ml. of water is added, with stirring, to 3.5 g. of sodium "selenopentathionate" (0.01 mol) or 4.0 g. of sodium "telluropentathionate" (0.01 mol) (synthesis 31) dissolved in 100 ml. of water. The product immediately precipitates, and after being stirred for several minutes, it coagulates, leaving a clear liquid. It is filtered, washed with water and methanol, and dried *in vacuo* over sulfuric acid. Conditions for crystallization of some of these compounds are outlined in Table I. Selenium ethylxanthate, which is an oil, is extracted from the aqueous layer with ether. The ether extract so obtained is dried over anhydrous sodium sulfate, after which the ether is removed by distillation.

Properties

The selenium derivatives of xanthates and dithiocarbamates are greenish yellow; the tellurium compounds are red. In the solid state, the dithiocarbamates are quite stable, while the xanthates decompose after a few days, liberating selenium or tellurium. The compounds are insoluble in and unaffected by water. The decomposition of the selenium compounds into selenium and disulfides is strongly catalyzed by xanthates and dithiocarbamate ions. The uncorrected melting points are summarized in Table I.

TABLE I

Compound	M.p.	Purification	Crystalline form
$Se(S_2COCH_3)_2$	106	Recrystallized from ethyl acetate (5 g. dissolved in 75 ml. at 60°)	Plates or prisms
$Se(S_2COC_2H_5)_2$	....	Extracted with ether and distilled	(An oily liquid)
$Se(S_2CN(CH_3)_2)_2$	182–183	Recrystallized from chloroform (1 g. dissolved in 300 ml. at b.p.)	Microcrystalline powder
$Se(S_2CN(C_2H_5)_2)_2$	116	Recrystallized from benzene (5 g. dissolved in 80 ml. at 60 to 70°)	Plates or leaves
$Te(S_2COCH_3)_2$	89	Recrystallized by dissolving 5 g. in 20 ml. of warm benzene and adding 50 ml. of warm methanol	Flat needles
$Te(S_2COC_2H_5)_2$	94	Recrystallized by dissolving 5 g. in 10 ml. of warm benzene and adding 25 ml. of warm ethanol	Long needles
$Te(S_2CN(CH_3)_2)_2$	Above 250	Too insoluble in ordinary organic solvents to be conveniently recrystallized	
$Te(S_2CN(C_2H_5)_2)_2$	164	Recrystallized by dissolving 5 g. in 15 ml. warm carbon disulfide and adding 25 ml. of ether	

References

1. RUSSELL: U.S. patent 2347128 (Apr. 18, 1944); *cf. Chem. Abstracts*, **38**, 6301[1] (1944).
2. MURRILL: U.S. patent 1921091 (Aug. 8, 1933); *cf. Chem. Abstracts*, **27**, 5218 (1933).
3. FOSS: *Acta Chem. Scand.*, **3**, 435 (1949).
4. FOSS: *ibid.*, 708.
5. FOSS, *ibid.*, 1385.

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CHAPTER VIB

33. ADDITION COMPOUNDS OF CHROMIUM(VI) OXIDE

Submitted by Oliver E. Accountius,* Jack Bush,*
and Harry H. Sisler*
Checked by W. F. Luder†

The ability of certain nitrogen bases to form addition compounds with Lewis acids (electron-pair acceptors) is well known. Reactions of this type in the case of chromium(VI) oxide are complicated by the fact that the oxide is a strong oxidizing agent. Procedures are given here for the preparation of three typical compounds: pyridine–chromium(VI) oxide, $2C_5H_5N{\cdot}CrO_3$; 3(or β)-picoline–chromium(VI) oxide, $2C_6H_7N{\cdot}CrO_3$; and 4(or γ)-picoline–chromium(VI) oxide, $2C_6H_7N{\cdot}CrO_3$.[1]

Procedure

A. PYRIDINE–CHROMIUM(VI) OXIDE

$$2C_5H_5N + CrO_3 \rightarrow 2C_5H_5N{\cdot}CrO_3$$

Four grams of chromium(VI) oxide (0.04 mol) is dried at 110° *in vacuo* for 4 hours and is then cooled in an ice-salt mixture. Fifty milliliters of pyridine (0.63 mol) is also cooled in a 300-ml. Erlenmeyer flask. While the 50 ml. of pyridine is shaken in the flask immersed in an ice-salt-water mixture, the chromium(VI) oxide is slowly added. The flask is stoppered, and the mixture is agitated until all solid particles have dissolved. A larger amount of pyridine may be used to hasten solution, if desired. Cooling is necessary, since the reaction generates enough heat to bring about oxidation of the pyridine unless the temperature is controlled.

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† Northeastern University, Boston, Mass.

The reaction flask is connected to a vacuum pump through a cold finger cooled in an acetone–Dry Ice mixture or in liquid air. The evacuation is continued until all the liquid has evaporated. Since the compound is photosensitive, the reaction flask should be protected from light.

After evaporation of the excess liquid, the reaction flask is disconnected and the product removed. The product will vary from a light yellow cake to dark red crystals depending on the rate of evaporation of the pyridine. Slow evaporation is most favorable to the formation of large crystals. The yield is approximately 10.3 g. (100%). The sample may be stored indefinitely at room temperature in a tightly stoppered bottle in the dark. *Anal.* Calcd. for $2C_5H_5N \cdot CrO_3$: Cr, 20.14. Found: total Cr, 20.48, 20.58; Cr^{6+}, 20.15, 20.35.

B. 3-PICOLINE–CHROMIUM(VI) OXIDE

$$2C_6H_7N + CrO_3 \rightarrow 2C_6H_7N \cdot CrO_3$$

The procedure is the same as for the pyridine compound. The product is a yellow-tan cake. Yields are approximately quantitative. *Anal.* Calcd. for $2C_6H_7N \cdot CrO_3$: Cr, 18.17. Found: total Cr, 18.41, 18.28; Cr^{6+}, 18.34, 18.14.

C. 4-PICOLINE–CHROMIUM(VI) OXIDE

$$2C_6H_7N + CrO_3 \rightarrow 2C_6H_7N \cdot CrO_3$$

The procedure is the same as for the other two compounds. The product is a yellow cake, and yields are approximately quantitative. *Anal.* Calcd. for $2C_6H_7N \cdot CrO_3$: Cr, 18.17. Found: total Cr, 18.21, 18.20; Cr^{6+} 17.92, 18.10.

Analysis

A weighed sample of the product (approximately 1 g.) is dissolved in a 3% perchloric acid solution, with gentle heating in a water bath if necessary. To determine chromium(VI), aliquot portions of the solution are acidified with 10%

sulfuric acid, after which 3 ml. of 80% phosphoric acid and an excess of standard iron(II) ammonium sulfate are added. The solution is then back-titrated with standard potassium dichromate solution, using sodium diphenylamine-*p*-sulfonate as an indicator.

The amount of reduction of the chromium may be determined by oxidizing aliquot portions of the above solution and determining the total chromium content. The oxidation is effected by acidifying the sample with 10% sulfuric acid and heating nearly to boiling. A small crystal of silver nitrate and approximately 2 g. of ammonium peroxydisulfate are added for every 50 ml. of solution. The treated solution is evaporated to one-half its former volume, cooled, and diluted to 50 ml. The remainder of the procedure is the same as that used for hexavalent chromium.

Properties

These compounds are insoluble in carbon tetrachloride, benzene, and ethyl ether but they color ethanol, acetone, and ethylene glycol appreciably. They are slightly photosensitive and somewhat hygroscopic. They decompose only slowly at 100°; however, they tend to ignite at higher temperatures, giving a voluminous, gray-green mass of chromium(III) oxide. They are soluble in the parent nitrogen base, though the picoline compounds are somewhat less so than the pyridine compound. All undergo hydrolysis in water.

Reference

1. Sisler, Bush, and Accountius: *J. Am. Chem. Soc.*, **70,** 3827 (1948).

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34. POTASSIUM PENTACHLOROAQUOMOLYBDATE(III) AND POTASSIUM HEXACHLOROMOLYBDATE(III)

$$MoO_3 + 6H^+ + 6Cl^- + 3e^- \rightarrow [MoCl_6]^{\equiv} + 3H_2O$$
$$[MoCl_6]^{\equiv} + H_2O \rightarrow [MoCl_5H_2O]^{=} + Cl^-$$
$$3K^+ + [MoCl_6]^{\equiv} \rightarrow K_3[MoCl_6]$$
$$2K^+ + [MoCl_5H_2O]^{=} \rightarrow K_2[MoCl_5H_2O]$$

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In 1903, Henderson[1] prepared a compound to which he assigned the formula $3KCl \cdot MoCl_3 \cdot 2H_2O$. It was made by the action of potassium amalgam on a solution of molybdic acid in hydrochloric acid. Several workers[2–14] have studied the electrolytic reduction of solutions of molybdic acid. They observed that the lowest oxidation state attained by molybdenum under these conditions is +3. The addition of alkali chloride to the reduced solutions precipitates red salts represented by the formulas $M_3[MoCl_6]$ and $M_2[MoCl_5H_2O]$. The pentachloro salt is a much darker red than the hexachloro salt. The solubilities of the salts formed decrease as the atomic weights of the alkali ions increase.

Procedure

A. POTASSIUM PENTACHLOROAQUOMOLYBDATE(III)

Twenty-one grams of molybdenum(VI) oxide (0.15 mol) is refluxed with 150 ml. of 12 *N* hydrochloric acid until solution of the oxide is almost complete. Water is added (in small increments so that the solution may be kept hot) until the volume is 350 ml. The mixture is then transferred to the cathode compartment of an electrolytic cell.

The glass cell is cylindrical in shape, 15 cm. in height and 9.5 cm. in diameter. A pool of mercury covering the bottom serves as the cathode, to which the current is conducted

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by a platinum wire sealed inside a glass tube. The cell is closed to the air with a rubber stopper, which is provided with holes for a porous cylindrical cup, an inlet tube for carbon dioxide, which serves both to stir the solution and as an inert atmosphere, and an outlet tube for hydrogen and carbon dioxide. The porous cup is fitted with a rubber stopper which holds a graphite anode and an exit tube for chlorine. This anode chamber is filled with 6 *N* hydrochloric acid to the same height as in the cathode compartment.

The voltage across the cell is maintained at 2.2, and the current, which is 1.4 amp. at the start (about 0.1 amp./sq.cm.), decreases to 0.9 amp. at the end of 3 hours. This decrease continues until a value of about 0.5 amp. is reached, where the current remains approximately constant, at least until the twentieth hour.* The color of the solution changes from light green at the beginning to dark green, then brown, and finally red.

When no further change is noted in the color of the solution, it is transferred to a 1000-ml. flask. Care must be taken to make the transfer, as well as all subsequent transfers, filtrations, and concentrations, under an atmosphere of carbon dioxide or nitrogen. A solution of 34 g. of potassium chloride (0.46 mol) in 300 ml. of water from which the air has been expelled is added to the solution containing the complex molybdenum chloride. The flask is immersed in an ice bath, and hydrogen chloride gas† is passed into the solution until a red salt begins to precipitate. This is contaminated with precipitated potassium chloride. The flask is fitted with a two-hole rubber stopper containing two glass tubes, one of which extends to the bottom of the flask and is connected by rubber tubing to a source of carbon dioxide. The other is connected by rubber tubing to a glass tube in the stopper of a sintered-glass crucible which is connected in turn to a filter flask. A tube and filter-paper thimble

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* These values apply to the particular cell used by the authors.

† Since rather large amounts of hydrogen chloride are required, best results are obtained through the use of a cylinder of the gas.

may be substituted for the sintered-glass crucible. The contents of the flask are transferred to the filtering apparatus by inverting the flask. If preferred, the filtration can be carried out by using a fritted-glass filter stick to siphon the mother liquor from the precipitate.

The solution is next concentrated to one-half its volume at 70° by the use of a water pump, and then cooled in an ice bath. Small rhombic, red crystals of the potassium pentachloroaquomolybdate(III) form. These are subsequently filtered with suction and washed with 12 *N* hydrochloric acid and then with alcohol. The washings are allowed to run into the filtrate in the filter flask. The product is dried in a current of carbon dioxide or *in vacuo*. The yield is 19.0 g. (34.2%).* *Anal.* Calcd. for $K_2[MoCl_5\text{-}H_2O]$: Mo, 26.0; Cl, 48.0. Found: Mo, 25.3; Cl, 48.7. These results imply some contamination with $K_3[MoCl_6]$.

B. POTASSIUM HEXACHLORMOLYBDATE(III)

Further precipitation occurs when the alcohol mixes with the filtrate from the precipitation of the pentachloroaquo salt. This precipitate is a mixture of potassium hexachloromolybdate(III) and potassium pentachloraquomolybdate(III) and is removed by filtration. The filtrate is then concentrated at 70° to 80 ml. by use of the water pump, and more of the mixture of the two salts is precipitated (3.8 g.). This mixture is filtered and washed with 12 *N* hydrochloric acid and with alcohol, the latter causing the second salt, potassium hexachloromolybdate(III), to precipitate in the filtrate in fairly pure form. The yield is 10.0 g. (15.6%).* *Anal.* Calcd. for $K_3[MoCl_6]$: Mo, 22.5; Cl, 50.0. Found: Mo, 22.3; Cl, 50.6. The impurity here is probably potassium chloride.

Properties

In addition to the anions of the two salts described above, there are undoubtedly many other ionic species present in electrolyzed hydrochloric acid solutions of molybdenum(VI)

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* The sum of the percentage yields of the two salts is 49.8.

oxide. The relative abundance of any given species is determined in part by the concentrations of the chloride ion and of the hydrogen ion and by the temperature. These phenomena are discussed by Wardlaw and Wormell[11] and by Foerster and Fricke.[13] The salts are fairly stable in dry air and in hydrochloric acid, but in water they undergo hydrolysis and oxidation, the red color fades, and colloidal substances are formed. In liquid ammonia the water of hydration is replaced by ammonia.

The salts are strong reducing agents. If a solution of iron(III) chloride in hydrochloric acid is added to a solution of either of the salts, the molybdenum is oxidized, as is evidenced by a reversal of the color changes observed during the electrolytic reduction of molybdic acid.

The physical properties of the aqueous solutions were studied by Bucknall and coworkers;[14] Ray and Bhar[15] studied the magnetic susceptibility of the hexachloro complex. Potassium pentachloroaquomolybdate(III) exists as rhombic crystals and is isomorphous with potassium pentachloroaquoferrate(III).[16] Potassium hexachloromolybdate(III) has been used for the preparation of potassium hexathiocyanatomolybdate(III), potassium heptacyanoaquomolybdate(III),[17] and potassium octacyanomolybdate(IV).[18]

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35. BIS(8-QUINOLINOLO)DIOXOURANIUM(VI) AND ITS ADDITION COMPOUND WITH 8-QUINOLINOL

$$UO_2(NO_3)_2 + 3C_9H_6NOH \rightarrow UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH + 2HNO_3$$

$$UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH \rightarrow UO_2(C_9H_6NO)_2 + C_9H_6NOH$$

Submitted by Therald Moeller* and Donald H. Wilkins*
Checked by Lynne L. Merritt, Jr.†

The compound $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ has been prepared by the direct reaction of 8-quinolinol with dioxouranium(VI) (uranyl) salts in nearly neutral aqueous solutions.[1–3] Precipitation is reported, variously, to be complete in the pH ranges 5.71 to 9.81[4] and 4.07 to 8.84.[5] The usual procedure involves treating the acidified uranium(VI) salt solution with 8-quinolinol and adding ammonium acetate or aqueous ammonia or both. These procedures may be improved to yield more uniform products containing larger crystals by combining the reagents in acidic solution and precipitating homogeneously by the thermal hydrolysis of urea. The red product loses its extra mol of 8-quinolinol on being heated[2] to give the normal olive-green chelate, $UO_2(C_9H_6NO)_2$.

Procedure

Five grams of dioxouranium(VI) nitrate 6-hydrate, $UO_2(NO_3)_2 \cdot 6H_2O$, (0.010 mol) is dissolved in 300 ml. of water containing 1 ml. of concentrated nitric acid. A solution of 5 g. of 8-quinolinol (0.034 mol) in 10 ml. of glacial acetic acid is added slowly with stirring. Any precipitate which forms is dissolved as it forms by the dropwise addition of

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8 *N* nitric acid. Only sufficient nitric acid to prevent precipitation should be present. This may be judged by the formation of a deep red solution which appears clear under artificial light. To the resulting solution, 25 g. of urea (0.416 mol) is added. The solution is brought to boiling and then heated on a steam bath for 4 hours. The beaker containing the solution should be suspended so that all the contents are heated. At the end of 4 hours, a brick-red precipitate should have settled out, leaving a clear, light yellow supernatant liquid. If the liquid is reddish, it should be cooled, treated with 5 g. of urea, and reheated until yellow. The suspension is cooled and filtered through a sintered-glass crucible. The precipitate is washed once with ethanol and several times with cold water to remove excess 8-quinolinol. Air is drawn through the crucible for several minutes to remove excess moisture, and the product is dried either over anhydrous magnesium perchlorate for 24 hours or at 110° for 1 hour. The yield is 7.0 g. (quantitative based upon the uranium material used). *Anal.* Calcd. for $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$: C, 46.09; N, 5.97; H, 2.72. Found: C, 46.29; N, 5.99; H, 2.90.

To prepare the normal chelate, $UO_2(C_9H_6NO)_2$, the red product is spread in a thin layer on a watch glass and heated for 48 hours at 210 to 215° with occasional stirring.

Properties

The dioxouranium(VI), or uranyl, ion is peculiar in forming two 8-quinolinol derivatives. Only the red crystalline compound containing an added mol of 8-quinolinol can be prepared by direct precipitation. This material has been recommended for the accurate determination of uranium(VI)[1,3,6,7] because of its insolubility, constancy of composition, ease of drying, and large molecular weight.

Thermogravimetric studies[6,7] show that its composition remains unchanged up to 157°. Between 157 and 252°, the added mol of 8-quinolinol is lost, the normal chelate then remaining unchanged to 346°. Above this temperature, thermal decomposition occurs, with the ultimate formation of U_3O_8.

The normal chelate, $UO_2(C_9H_6NO)_2$, is also stable in contact with air. When treated with 8-quinolinol solutions, it rapidly adds a mol of the reagent to give the red compound.[2]

The two chelates appear to be soluble in organic solvents, but specific data are lacking. Although it is known that they give different x-ray-diffraction patterns, no data on their structures are available. The mode of attachment of the extra mol of 8-quinolinol in the red compound has not been determined.

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CHAPTER VIIA

See also: Cesium iododichloride, synthesis 2
- Iodotrichlorosilane and diiododichlorosilane, synthesis 13
- Nitrosyl chloride, synthesis 16
- Nitryl chloride, synthesis 17
- Nitrosylpentamminecobalt(II) chloride, synthesis 55
- Potassium pentachloroaquomolybdate(III) and hexachloromolybdate(III), synthesis 34
- Alkyl dichlorophosphites, synthesis 21
- 2-Chloroethyl dichlorophosphite, synthesis 22
- Phosphorus(V) sulfochloride, synthesis 24
- *O*-Ethyl dichlorothiophosphate, synthesis 25
- Diethyl monochlorophosphate, synthesis 27
- 2-Chloroethyl chlorosulfonate and (2-chloroethoxy)trichlorosilane, synthesis 30
- Iron(II) bromide 6-ammoniate, synthesis 53
- Potassium tetrabromoaurate(III), synthesis 4

36. ANHYDROUS METAL HALIDES

BY S. Y. TYREE, JR.*

Classification of Anhydrous Metal Halides. The metal halides vary in their properties from the ionic, high-melting, conducting compounds, such as sodium chloride, to the covalent, volatile, nonconducting compounds, such as osmium octafluoride (m.p., 35°). The variations observed admit of some systematization by classification based on the oxidation state of the metal in the compound.

MX		MX_8
Ionic lattice		Molecular compounds
Nonvolatile	intermediate properties	Easily volatile
Very slightly hydrolyzed	$\longrightarrow$	Completely hydrolyzed

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As is illustrated by the data given below for vapor pressures of the fluorides[1] of the second period, variations in the series frequently are quite irregular.

Compound	NaF	MgF_2	AlF_3	SiF_4	PF_5	SF_6
Temp., °K., at which v.p. = 1 atm.	1977	2500	1545	178	189	210

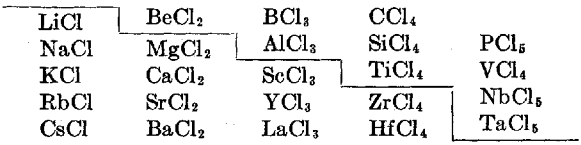
The major discontinuity in boiling points is shifted one position to the left in the chloride series.[1]

Compound	$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5
Temp., °K., at which v.p. = 1 atm.	1738	1691	435	330	439

The variations that are observed within one valence type are illustrated in a series of bivalent chlorides:

Compound	$BeCl_2$	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$
M.p.[1]	405	714	782	872	960
pK of hydrated cation[2]	5	11.4	12.5	....	13.4

A parameter, first defined by G. H. Cartledge,[3] which indicates the effective charge density on the cation, is the ionic potential $\phi = Z/r$, where Z = valence of the cation and r = cationic radius. A line corresponding to $\sqrt{\phi} = 2.2$ coincides with the diagonal line through the periodic table used by Biltz and Klemm[4] to separate the conducting metal chlorides from the nonconducting metal chlorides.



$LiCl$	$BeCl_2$	BCl_3	CCl_4	
$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5
KCl	$CaCl_2$	$ScCl_3$	$TiCl_4$	VCl_4
$RbCl$	$SrCl_2$	YCl_3	$ZrCl_4$	$NbCl_5$
$CsCl$	$BaCl_2$	$LaCl_3$	$HfCl_4$	$TaCl_5$

Compounds above and to the right of the line are easily volatile and extensively hydrolyzed in comparison to those below and to the left of the line. However, differences in crystal structure result in substantial deviations from the expected properties in a number of cases. For example, aluminum fluoride is relatively nonvolatile (sublimation temperature, 1272°), whereas the other three aluminum halides sublime at much lower temperatures: 193°, 257°, and 386° for the chloride, bromide, and iodide, respectively. These last three halides have similar crystal structures, whereas the crystal structure of the fluoride is different as a result of the increased crystal coordination number of aluminum ion in combination with the relatively small fluoride ion. On the other hand, there is a *more regular* decrease in the heat of formation (ΔH per equivalent) in the series AlF_3, . . . , AlI_3. In contrast, the expected progression in properties is observed in a series of halides having identical structures and no great variation in bond type. The tantalum halides typify this.

Compound........	TaF_5	$TaCl_5$	$TaBr_5$	TaI_5
M.p.[1]............	97	208	240	367
Color of solid......	White	Yellow	Orange	Brownish-black

Color gradations are commonly observed when the polarizing power of the cation is great; this is also exemplified by the tantalum(V) halides. The zinc halides, all of which are white, typify the case of cations which have lesser polarizing power. In this respect, 18-electron ions appear to have greater polarizing powers than 8-electron ions of the same size.

Recently Cartledge[5] has found the equivalent heat of formation of metal halides to be a linear function of ϕ (in calculating ϕ in this paper, the effective, univalent, ionic radii for cations with coordination numbers of six, as estimated by Zachariasen, are used). Though properties may generally be estimated qualitatively from charge and radius considerations, the following data illustrate the type of anomaly which necessarily limits the applicability of any such generalization to this field:

Ion..................	Al^{3+}	Ga^{3+}	Cr^{3+}	Fe^{3+}	Sc^{3+}	In^{3+}	Y^{3+}
Radius, Å[1]............	0.52	0.60	0.62	0.64	0.81	0.81	0.96
B.p. of chloride[1].......	193 (sub.)	201	947 (sub.)	304	967	498 (sub.)	1500 (est.)
Heat of formation[1] of chloride, kcal. mol...	167	125	132	96	221	126	235
pK of hydrated ion[2]...	5	3	4	2.2	5	4	9

The volatility of the chlorides decreases as the ionic radii increase; however, there is one anomaly at chromium and a second at indium. The heats of formation and the hydrolysis data given above are even less consistent. It should be pointed out that in some cases the hydrolysis of halides is influenced greatly by the presence of excess halide ions. For example, antimony(III) chloride hydrolyzes only slightly in solutions containing appreciable concentrations of chloride ion, whereas its hydrolysis is extensive in *pure* water. Also, a cation may form a very stable fluoride complex but much less stable complexes with the other halides; the hydrolysis will be much greater in the latter cases. In recent years hydrolysis constants have been determined, whenever possible, in the presence of perchlorate supporting electrolyte, to minimize interaction between the supporting electrolyte and the cation. Nearly all halides of elements of valence numbers +5, +6, or higher are extensively hydrolyzed, except in those cases where complex ions are formed.

No parameter has yet been described which permits good correlation of a substantial number of the properties of metal halides. For a reasonably complete compilation of the thermochemical properties of the halides of all the elements, the reader is referred to reference 1.

Preparation of Anhydrous Metal Halides. The methods used to prepare high-purity samples of anhydrous metal halides may be divided into four distinct classes plus a fifth class of special cases.

1. Dehydration of Hydrated Salts. The alkali and alkaline-earth halides may be crystallized from aqueous solution and dehydrated thermally. With many less basic metal halides the same process may be used with modifications to prevent hydrolysis. For example, the hydrated chlorides of magnesium[6] and the lanthanides[7] may be dehydrated thermally in a stream of hydrogen chloride. Hecht[8] states that chlorides of magnesium, strontium, barium, tin(II), tin(IV), copper, iron(III), cobalt, nickel, and titanium(III) may be dehydrated by heating in a stream of carbonyl chloride or thionyl chloride. Hydrated chromium(III) chloride is converted to the anhydrous halide by heating in an atmosphere of carbon tetrachloride.[9] The method appears to be of wide application where the metal halide is sufficiently basic to permit crystallization as a hydrate.

2. Direct Synthesis. Most metals react readily with halogens, and if the metal is available in the pure state, techniques based on direct reaction of the elements are applicable. In particular, such techniques are of value in the preparation of iodides, which are the most difficult to prepare by other methods. This method has been widely used to provide the materials for recent studies of the physical properties of polyvalent metal halides. The pentavalent chlorides, bromides, and iodides of niobium and tantalum have been prepared by direct synthesis.[10,11] From the few cases studied, it is evident that a knowledge of the tendency of higher halides to dissociate thermally to lower halides and free halogen is needed. Titanium(IV) iodide may be prepared by direct synthesis between 175 and 525°; however, it decomposes at higher temperatures, as illustrated by the well-known De Boer process.[12] Gregory and Thackrey[13] have shown that iron(III) bromide has a measurable dissociation pressure below 100°. The author's experience indicates that the chlorination of metals is difficult to control. In some cases this difficulty may be overcome by dissolving the halogen in an inert solvent and refluxing with fine metal powder.[14,15]

3. Decomposition of oxide. Because of the availability of most metal oxides, methods of converting oxides to halides have been studied extensively. In general, they are limited to the preparation of chlorides and bromides. The action of free bromine on an intimate mixture of an oxide and pure sugar carbon has been used to prepare tantalum(V) bromide,[16] the tetrabromides of all of the group IVA metals[17–19] and thorium(IV) bromide.[20] More recently, natural lanthanide phosphates have been made to react with carbon and chlorine to yield the anhydrous halides.[21] Camboulives[22] studied the reaction of carbon tetrachloride with 33 oxides and found that only nonmetal oxides such as B_2O_3 and SiO_2 are not converted to the halide in this manner. The alkaline-earth and rare-earth oxides are converted to chlorides at 250 to 330°, whereas oxides of titanium, zirconium, aluminum, beryllium, etc., require temperatures in the vicinity of 400°. If an element forms volatile oxychlorides, passing carbon tetrachloride vapor over the heated oxide results in mixed products. The author has found that, when such substances are allowed to react with carbon tetrachloride in a sealed tube, so that a liberal excess of carbon tetrachloride can be maintained, no oxychloride formation is observed. Carbonyl chloride (phosgene),[23] carbon monoxide and chlorine,[24] thionyl chloride,[25] sulfur monochloride and chlorine,[26] and phosphorus(V) chloride[27] have been used to convert metal oxides to chlorides. The trivalent rare-earth oxides are converted to chlorides and bromides by reaction with ammonium halides.[28] Recently it has been shown that niobium and tantalum oxides are converted to the pentachlorides when refluxed with octachloropropane or other chlorocarbons.[29] Similarly, uranium(IV) chloride has been prepared by the action of trichloroacetyl chloride on UO_2, UO_3, or U_3O_8.[30]

4. Displacement Reaction. The action of fluorine on metal chlorides has been used to prepare several anhydrous metal fluorides.[31] Van Haagen[16] distilled tantalum(V) bromide through granular silver iodide to produce the pentaiodide. He obtained the same product by distilling tantalum(V) bromide in a steady stream of hydrogen iodide. The action of sulfur monochloride and hydrogen bromide on thorium oxide results in the formation of thorium(IV) bromide in a combination decomposition and displacement reaction.[32] Emeléus and Gutmann[33] showed that hydrogen fluoride reacts with molybdenum(III) bromide at 600° to give the trifluoride. Vanadium(III) fluoride may be prepared from the trichloride under similar conditions. Mercury(II) chloride may be distilled from a reaction mixture of mercury(II) sulfate and sodium chloride. Antimony, aluminum, magnesium, iron, tin, bismuth, and mercury salts react with boiling thionyl chloride to produce metal chlorides in interesting displacement reactions which are catalyzed by aluminum chloride, iron(III) chloride, and tin(IV) chloride.[34]

5. Special Preparations. The Sainte-Claire Deville hot-cold tube is used to prepare the lower halides of many transition elements.[35] Gutmann[36] has prepared vanadium(III) chloride by refluxing vanadium powder with iodine monochloride. Several authors report that zirconium oxychloride may be decomposed thermally to give the oxide and the tetrachloride, although the yield is not high.[37–39] Rare-earth chlorides have been prepared by extracting the benzoates with ether saturated with hydrogen chloride.[40] These are only examples of the many special methods reported for the preparation of specific anhydrous metal chlorides.

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37. GALLIUM(II) CHLORIDE

$$Ga_2Cl_6 + Ga \rightarrow 3GaCl_2$$

SUBMITTED BY LAURENCE S. FOSTER*
CHECKED BY HAROLD L. FRIEDMAN† AND HENRY TAUBE†

When gallium(III) chloride is heated at 200° under anhydrous conditions with slightly more than an equivalent

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quantity of gallium, gallium(II) chloride is produced.[1–3] Gallium(II) chloride is also obtained when gallium metal is heated at 170 to 180° in a stream of dry hydrogen chloride.[4] The first of these procedures is the better for preparation of the substance in reasonable quantities.

Procedure

A lump of solid gallium weighing about 10 g. (0.14 mol) is placed in reaction tube *C*, which is then sealed to the glass apparatus shown in Fig. 10. A constriction *A* is provided to facilitate subsequent sealing of the tube under vacuum. A sample tube containing not more than 50 g. of gallium(III) chloride[5] (0.28 mol) is opened and inserted through the open end *B*. This end is then closed quickly by fusion. The system is evacuated, and the gallium(III) chloride is transferred by sublimation into the enlargement *D* above the tube containing the metal. The sublimed gallium(III) chloride is melted by rapid heating with a flame and flows into the reaction tube *C*, which is surrounded by ice water during this operation. The reaction tube is removed by fusing at the constriction *A* and is placed in a furnace, which is heated initially to 150°; the temperature is then gradually raised to 200°. Reaction is judged com-

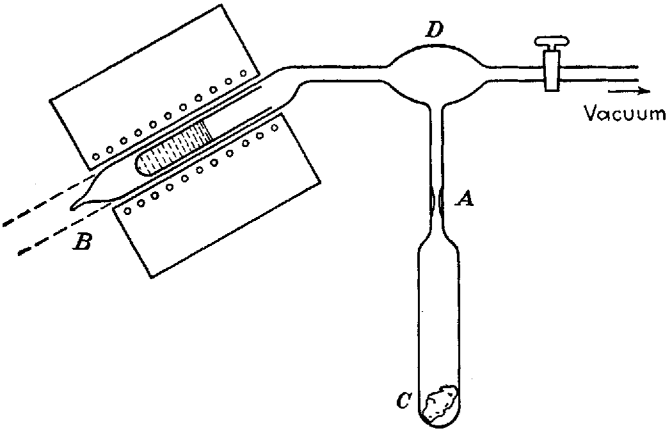

Fig. 10. Apparatus for the preparation of gallium(II) chloride.

plete when, after being heated for several hours, the contents remain solid at 165°.

In order to purify the gallium(II) chloride, the container is opened and immediately sealed to one of the legs of a three-legged glass tube. The tube is evacuated, and the sample is heated. The relatively more volatile gallium(III) chloride is removed first and is condensed in one of the other legs. Gallium(II) chloride is then volatilized away from the remaining gallium and is condensed into the third leg. The yield is almost 60 g., which is essentially quantitative.

Properties

Gallium(II) chloride is a white crystalline solid which melts[3] at 170.5° to a colorless, strongly refracting liquid[2] which does not wet glass. The liquid, when pure, is readily supercooled, and samples may remain liquid at room temperature for years. The density of the liquid is somewhat greater than that of pyrex glass. The boiling point has been listed as 535°, but at temperatures above 200° decomposition to gallium and gallium(III) chloride is appreciable. Vapor-density studies[3] show the presence of some monomeric $GaCl_2$ molecules in the range 400 to 470°. The solid is diamagnetic[5] and therefore cannot contain simple $GaCl_2$ molecules.

Gallium(II) chloride is a strong reducing agent which deliquesces in moist air, with slight hydrogen evolution, to form a clear, colorless, strongly refracting sirup. When stirred with water, gallium(II) chloride is converted to brown, solid gallium(II) hydroxide, which in turn is changed slowly to white gallium(III) hydroxide or hydroxychloride with hydrogen evolution. Gallium(II) chloride decolorizes dilute acidified potassium permanganate solution instantly. The compound is soluble without reaction in benzene (4.60 g./100 g. of benzene[4]) and may be recrystallized from that solvent. It reacts vigorously with carbon tetrachloride, ether, and nitric acid.

Gallium metal is soluble in liquid gallium(II) chloride.

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The composition of the saturated solution at 200 to 250° corresponds to 3.99 mols of gallium(I) chloride in 100 mols of gallium(II) chloride.[6] It is very probable that gallium(I) chloride is formed in accordance with the equation

$$Ga + GaCl_2 \rightarrow 2GaCl$$

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38. BISMUTH(III) IODIDE

(Bismuth Triiodide)

$$2Bi + 3I_2 \rightarrow 2BiI_3$$

Submitted by George W. Watt,* Wafai W. Hakki,* and Gregory R. Choppin*
Checked by M. Tamres† and Daryle H. Busch†

Bismuth(III) iodide has been prepared in the absence of solvents by the reaction of iodine with elemental bismuth[1,2] or with bismuth(III) sulfide.[3] Alternative methods involve precipitation of bismuth(III) iodide from aqueous solutions of bismuth salts by adding alkali-metal iodides,[4] and the addition of bismuth(III) oxide to a solution of iodine and tin(II) chloride in saturated hydrogen chloride.[5] In either case the initial product is purified by sublimation, usually in an atmosphere of carbon dioxide. The product obtained by precipitation requires several resublimations for complete purification.[6]

In the procedure described below, bismuth(III) iodide of high purity is formed by the direct union of bismuth and

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iodine, followed by sublimation at low pressure in an atmosphere of nitrogen.

Procedure

The reaction vessel consists of a pyrex glass tube 50 cm. in length and of 35 mm. i.d., with a 6-mm. gas inlet tube sealed to one end. The tube is supported in an upright position, and the gas inlet tube is covered with a loose plug of glass wool. Forty-eight and one-half grams of resublimed iodine crystals (0.191 mol) is placed in the tube; this is followed by 26.4 g. of c.p. bismuth (0.126 mol) (−200 mesh) intimately mixed with asbestos fiber. A second glass-wool plug is inserted, and the tube is constricted immediately beyond the glass wool to i.d. 15 to 20 mm.* The tube is supported in a horizontal position, the open section is wiped clean, and a thermometer is inserted into the bismuth-asbestos mixture.

A slow stream of nitrogen gas, dried by scrubbing with concentrated sulfuric acid, is admitted while the bismuth-asbestos mixture is heated to 150° by means of a Tirrill burner equipped with a 6-in. flame spreader. While the temperature of this mixture is maintained within the range 150 to 180°, sublimation of the iodine is initiated by heating with another Tirrill burner adjusted to low heat. When the first iodine vapor appears at the constriction in the tube, the spread flame is moved so that it heats both the iodine and the bismuth-asbestos mixture. The tube is rotated slowly to improve the uniformity of heating, and both the temperature and the nitrogen flow rate are regulated so that 1.5 to 2.0 hours are required to transfer the iodine into the bismuth-asbestos mixture and to remove the excess iodine, which is vented to a hood or condensed under concentrated sulfuric acid. When there is no visible evidence of iodine vapor, heating is stopped, the thermometer is removed, and the empty end of the tube is again wiped clean.

* The total volume occupied by the charge should be such that the constriction is approximately at the mid-point of the reaction tube.

The open end of the reaction tube is attached to an oil pump through a dust trap, and dry nitrogen is admitted at a rate such that the pressure is maintained at or below 25 mm.* The bismuth(III) iodide is sublimed into the receiver end of the tube by heating with the spread burner flame and with an auxiliary Tirrill burner adjusted to maximum heat. Satisfactory progress of the sublimation is indicated by the persistence of yellowish-brown bismuth(III) iodide vapors and by the absence of the violet color of iodine vapor. When the sublimation is complete, the tube is allowed to cool to room temperature in nitrogen at atmospheric pressure. The product is scraped from the receiver section of the tube and stored out of contact with the atmosphere. The yield is 72% based on bismuth. *Anal.* Calcd. for BiI_3: Bi, 35.44. Found: Bi, 35.42. The same result is found upon analysis of a resublimed sample of this product.

Properties

Bismuth(III) iodide prepared as described above consists of very small, black, hexagonal crystals having specific gravity 5.64. At atmospheric pressure this compound sublimes at 439° and decomposes at 500°. It is soluble in liquid ammonia and in absolute ethanol. It is insoluble in cold water but decomposes slowly in hot water. Bismuth(III) iodide is slowly converted to bismuth(III) oxyiodide upon extended exposure to the atmosphere.

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* At higher pressures the iodide undergoes partial decomposition during the sublimation process.

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39. ALUMINUM IODIDE

$$2Al + 3I_2 \rightarrow Al_2I_6$$

SUBMITTED BY GEORGE W. WATT* AND JAMES L. HALL*
CHECKED BY WILLIAM LLOYD TAYLOR† AND JACOB KLEINBERG†

The preparation of anhydrous aluminum iodide by methods described previously[1,2] involves direct union under conditions that invariably yield products contaminated with elemental iodine. Attempts to purify these products by sublimation under a variety of conditions (including sublimation *in vacuo* or in an atmosphere of carbon dioxide or helium) result in at least partial decomposition of the iodide and a final product that is colored, owing to the presence of iodine. The method described below also provides for direct union of the elements, but under conditions that eliminate contamination with elemental iodine and yield an initial product of exceptionally high purity.

Procedure

The apparatus consists of a pyrex glass tube 55 cm. in length and of 2.4 cm. i.d. (Fig. 11) provided with a receiver tube *R* (length, 20 cm.; i.d., 1.5 cm.), a stopcock *S* for attachment to a vacuum line, and a 100-ml. flask *F* attached by a ground-glass joint *J* (standard taper 19/38). Before the receiver tube is attached, the section between the glass-wool plugs *P* and *P′* (33 cm.) is filled with approximately

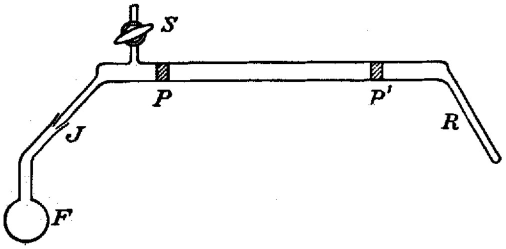

FIG. 11. Apparatus for the preparation of aluminum iodide.

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300 g. (11 mols) of granular aluminum (8 to 16 mesh). The tube is placed in a Lindberg furnace, the receiver tube is sealed on, and the inlet end of the furnace is raised about 5 cm. and blocked in this position. Ninety grams of iodine (0.35 mol) is placed in flask *F*, which is cooled in an ice bath to prevent premature sublimation of the iodine.

The system is evacuated for 1 hour at 1 to 2 mm., while the furnace is heated to 500° and maintained within the range 500 to 525°. The ice bath is removed, and *slow* sublimation of the iodine into the aluminum is initiated by means of a Bunsen burner flame. Thereafter the rate of sublimation of the iodine is increased, and a Fisher burner is used during the latter stages of the transfer; the total time for introduction of the iodine onto the aluminum is approximately 1 hour.

As the temperature of the furnace is raised to 600°, most of the aluminum iodide sublimes into the receiver.* Any salt that condenses between *P′* and *R* may be transferred to *R* by heating with a burner flame. Finally, the receiver is sealed off; the white crystalline product must be protected from exposure to the atmosphere.

The yield is 72 g., or 75% based on iodine. *Anal.* Calcd. for AlI_3: Al, 6.6; I, 93.4. Found: Al, 6.5; I, 93.2.

Properties

Aluminum iodide is dimeric in both the solid and gaseous states and in solution. The melting point of the product prepared as described above depends upon the technique employed. Samples contained in pyrex capillary tubes sealed with soft wax begin to decompose at 179°; melting is complete and a meniscus is formed at 189.9° (corr.). In sealed capillaries, decomposition is first detectable at 178 to 179°, and melting is complete at 184° (corr.). Aluminum iodide is best characterized by its x-ray-diffraction pattern, which includes five quite distinct max-

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* If any of the iodide collects in flask *F*, the salt may be distilled back into the reaction tube and thence to the receiver.

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ima. The interplanar spacings and the corresponding relative intensities (in parentheses) are:[3] $d = 3.50$ Å (1.00), 3.08 Å (0.50), 2.98 Å (0.50), 2.14 Å (0.50), and 1.84 Å (0.38). This compound hydrolyzes upon contact with the atmosphere, and its reaction with liquid water is strongly exothermic. It is readily soluble in liquid ammonia,[4] in which it forms a 20-ammoniate at −33°. A 6-ammoniate is stable at 8 to 13°.

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40. TIN(IV) IODIDE

(Stannic Iodide)

$$Sn + 2I_2 \rightarrow SnI_4$$

Submitted by Therald Moeller* and Delwin C. Edwards*
Checked by Robert L. Brandt† and Jacob Kleinberg†

Tin(IV) iodide has been prepared by heating tin with iodine,[1,2] by heating a concentrated aqueous tin(II) chloride solution with iodine,[3] by treating a saturated aqueous solution of tin(IV) chloride with a soluble iodide,[4] and by allowing tin to react with iodine in the presence of a nonaqueous solvent. The last-named procedure has the advantages of giving pure, crystalline products and avoiding all hydrolytic decompositions. Carbon disulfide is an excellent medium for the reaction,[5] but carbon tetrachloride is preferred[6] because of its nonflammability and lower volatility. Because tin(IV) iodide is much less soluble in carbon tetrachloride at room temperature than at the boiling point, the product is easily recovered. An excess of tin prevents contamination of the product with iodine.

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Procedure

Twelve grams of granulated tin (0.101 mol) and 40 g. of iodine (0.157 mol) are placed in a dry Kjeldahl flask. Seventy-five milliliters of carbon tetrachloride is added, and a reflux condenser is attached. The flask and its contents are heated gently until the reaction begins, after which heating is no longer necessary. When the solution ceases to boil, the flask is heated until all the iodine has disappeared. This is readily determined by the change in color of the liquid from violet to orange-red and by the absence of colored vapors in the flask and of colored liquid dripping from the reflux condenser. The condenser is removed, and the solution in the flask is heated to vigorous boiling. The hot solution is filtered quickly, using a steam-jacketed funnel, to remove unreacted tin. The residue on the filter is washed with 10 ml. of boiling carbon tetrachloride. The filtrate and washings are cooled in an ice bath, and the crystallized product is removed by filtration. The solution remaining is evaporated and cooled to give a second crop of crystals. The combined yield is about 44 g. (90%). The product may be recrystallized from carbon tetrachloride.

Properties

Tin(IV) iodide is a red-orange, crystalline material, which melts at 143.5° and boils at 348° (extrapolated). It begins to sublime at about 180°. The compound is readily soluble in carbon tetrachloride (8.35 g./100 ml. of solution at 22.4°; 20.47 g./100 ml. at 50°),[6] chloroform (12.32 g./100 ml. of solution at 28.0°),[6] benzene (12.02 g./100 ml. of solution at 20.2°),[6] carbon disulfide, alcohol, and ether. It is completely hydrolyzed by water. The vapor is monomeric and is made up of tetrahedral SnI_4 molecules (Sn-I bond distance, 2.65 Å). These discrete groups are also found in the solid. The lack of association is indicated by the value of Trouton's constant, 22.1.

In alcoholic solution containing hydrogen iodide, tin(IV)

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iodide reacts with alkali-metal iodides to give black, crystalline compounds of the type $M_2^{1+}[SnI_6]$. These contain the octahedral $[SnI_6]^{=}$ ion.[7] The increase in color in the series tin(IV) chloride, tin(IV) bromide, tin(IV) iodide parallels the increase in covalence.[8]

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41. ZIRCONIUM AND HAFNIUM TETRACHLORIDES

$$MO_2 + 2CCl_4 \rightarrow MCl_4 + 2COCl_2$$

Submitted by W. S. Hummers,* S. Y. Tyree, Jr.,* and Seymour Yolles*
Checked by F. Basolo† and L. Bauer†

Zirconium tetrachloride is produced on a large scale by a method developed by Kroll *et al.*[1] in which the ultimate product is ductile zirconium. Zirconium oxide is converted to the carbide, which is chlorinated to yield the tetrachloride. This procedure is not easily adaptable to laboratory use, since an arc furnace is used to produce zirconium carbide. Furthermore, the chlorination of zirconium carbide is a strongly exothermic reaction requiring apparatus that will withstand temperatures of at least 1000°.

The laboratory-scale preparation of zirconium tetrachloride has been accomplished through the use of a variety of techniques. Several authors[2-4] report that dry zirconium oxychloride may be thermally decomposed to yield zirconium oxide and zirconium tetrachloride. These authors

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† Northwestern University, Evanston, Ill.

do not agree on the temperature at which the reaction is workable nor on the practical yields. Picon[5] reports a preparation utilizing the chlorination of Zr_2S_3. It has been reported[6] that phosphorus(V) chloride will convert zirconium oxide to the tetrachloride in a sealed tube at 190°. The conversion may be obtained at much higher temperatures by the action of sulfur monochloride,[7] thionyl chloride,[8] carbonyl chloride,[9] or carbon tetrachloride[9] on zirconium oxide. The chlorination of a mixture of carbon and zirconium oxide at 500° has also been used.[10] Since zirconium wire is now available, zirconium tetrachloride has been prepared by direct synthesis by one of the authors (Yolles). The reaction was difficult to control and was discarded in favor of the following one, which proceeds at a desirable rate and involves easily constructed pyrex apparatus. This apparatus may be used without modification for the preparation of hafnium tetrachloride.

Because of the relatively recent discovery of hafnium and the great cost of reasonably pure hafnium compounds, fewer authors report attempted syntheses of hafnium tetrachloride than for its congener, zirconium. De Boer and Fast[11] report that the action of chlorine and carbon tetrachloride converts hafnium oxide to the tetrachloride. Fischer *et al.*[12] prepared the tetrachloride by chlorinating a mixture of the oxide and carbon.

Procedure

The apparatus* is shown in Fig. 12. A reaction tube is fabricated of 18-mm. pyrex tubing, 50 cm. long, by sealing the inner part of a 19/36 ground-glass joint to one end and drawing down as shown at *J*. About 2.5 cm. of pyrex glass wool is introduced at *J*. Between 5.0 and 15.0 g. of metal oxide is placed in the tube so as to be in the center of the sleeve heating unit *I* (20 cm. long) when the reaction tube is inserted. The loaded tube is then inserted through *I* and

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* The checkers have found that satisfactory results can be obtained with simplified apparatus, in which rubber connections and stoppers were substituted for some of the glass seals and ground-glass joints.

a seal made at *H*. Fifty to one hundred milliliters of dry carbon tetrachloride is introduced into the 300-ml. flask *E* through tube *F*, after which *F* is sealed off. With stopcock *D* closed and stopcock *G* in the proper position, tank nitrogen is admitted through phosphorus(V) oxide towers *A* and *B* and safety trap *C* into the reaction tube. The furnace *I* is heated to between 300 and 400°. Moisture collects between *I* and *J* and is driven out through the end of the reaction tube with a free flame. A drying tube is sealed to the outer part of a 19/36 ground-glass joint; pyrex wool is inserted at *L*, followed by calcium chloride. The ground-glass joint is lubricated with Dow-Corning silicone. A constriction may be desired between *K* and *L* to simplify the subsequent seal at this point. The drying tube is connected at *K* and the sample heated in dry nitrogen overnight. Before starting the preparation, a trap of concentrated aqueous caustic soda is connected to the drying tube at *M*. The gases from *N* should be exhausted through a well-ventilated hood, since carbonyl chloride is the principal by-product. To start the preparation, the furnace *I* is heated to 450 to 500°; stopcock *G* is reversed, and stopcock *D* is opened. The rate of flow of nitrogen through the carbon tetrachloride is adjusted to about 60 to 80 bubbles/min. Metal tetrachloride begins to collect between *I* and *J*. It is sublimed through the pyrex wool into the final receiver between *J* and *K* with a free flame. Wrapping the reaction tube, between *I* and *J*, with ordinary copper screening makes it possible to obtain much more uniform heating. Overheating of the product probably results in some reaction with the pyrex wool.[10] About 1 to 2 g. of metal chloride is produced per hour. This product is allowed to build

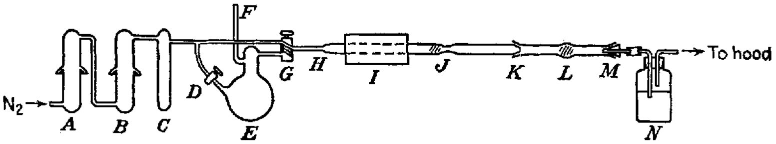

FIG. 12. Apparatus for the preparation of zirconium and hafnium tetrachlorides.

up between *J* and *K*, the size of this receiver fixing the limit on the yield. The reaction at *I* gradually slows down; the last few tenths of a gram of oxide are rarely converted. Stopcock *D* is closed and *G* reversed. The temperature of *I* is reduced into the range 300 to 400°, and dry nitrogen is again allowed to flow through the system overnight. This procedure is found to be desirable since it removes any hexachloroethane between *J* and *K*. After the overnight "soaking," the nitrogen is shut off, and a seal is made between *K* and *L*, followed by a seal at *J*.

Two impurities are apparent in the product, iron(III) chloride and hexachloroethane. Both are more volatile than zirconium tetrachloride. Nevertheless, if both are to be removed from the product, considerable product inevitably sublimes beyond *K*. The amount of hexachloroethane impurity is roughly a function of temperature, since runs made at 450° yield virtually none, whereas if the furnace is allowed to go much above 500°, appreciable quantities are formed. The amount of iron(III) chloride impurity depends on the purity of starting materials.*

In a typical preparation, the zirconium oxide starting material was found to have a Hf:Zr ratio of 0.026 ± 0.002 by spectroscopic analysis.[13] This ratio gives an average atomic weight of metal (zirconium and hafnium) of 92.35 ± 0.10. *Anal.* Calcd. for $Zr(Hf)Cl_4$: Zr(Hf), 39.44 ± 0.10; Cl, 60.56. Found: Zr(Hf), 39.52, 39.61, 39.56, 39.61; Cl, 60.62, 60.56, 60.60, 60.65.

In a typical preparation, 5.0 g. of hafnium oxide (0.025 mol) gave a yield of 6.7 g. of the tetrachloride (88%). Six-tenths of a gram of unreacted oxide was recovered. Small

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* The checkers report that it is possible to effect partial removal of iron(III) chloride in the following manner: A plug of clean steel wool is located near the end of the receiving tube. The product is allowed to form in front of this plug. The system is then swept free of carbon tetrachloride, and with dry nitrogen passing through the system, the furnace is gradually moved so as to cause the solid to sublime through the steel wool. Under these conditions most of the iron(III) chloride is reduced to iron(II) chloride and is held on the steel wool.

losses are incurred in transferring the product from the sample tube to a weighing bottle within the dry box. The Zr:Hf ratio in this sample was found to be 0.017 by spectroscopic analysis.[13] This ratio gives an average atomic weight of metal (hafnium and zirconium) of 175.7. *Anal.* Calcd. for Hf(Zr)Cl_4: Hf(Zr), 55.3; Cl, 44.7. Found: Hf(Zr), 55.48, 55.49; Cl, 44.76, 44.72, 44.74, 44.75. Samples for analysis were prepared in a dry box.

It should be noted that a partial fractionation of zirconium and hafnium may be obtained in the sublimation of the tetrachlorides.[11,14]

Properties

Zirconium tetrachloride is a white crystalline solid with specific gravity 2.803.[4] The solid sublimes under atmospheric pressure at 331° [$\log p_{\text{mm.}} = -(26{,}000/4.57T) + 12.30$] but melts at 437° under its own pressure, which is about 25 atm. at this temperature.[15] The vapor density shows normal behavior up to 500°, at which point dissociation is suspected.[16] Electron-diffraction results show tetrahedral symmetry with the Zr-Cl distance 2.33 Å.[17] Todd[18] has recently determined the heat capacity of zirconium tetrachloride at low temperatures (extrapolated below −222°) and calculated the usual thermodynamic constants for the compound. The melting point of hafnium tetrachloride has been estimated as 432° under its own pressure, but the solid sublimes under atmospheric pressure at 317°.[12] Both metal chlorides are extremely hygroscopic. They are easily soluble in water, although extensively hydrolyzed. All high-purity samples should be desiccated as well as possible.

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42. VANADIUM(II) CHLORIDE

(Vanadium Dichloride)

$$2VCl_3 + H_2 \rightarrow 2VCl_2 + 2HCl$$

Submitted by Ralph C. Young* and Maynard E. Smith†
Checked by Therald Moeller,‡ Paul G. Gordon,‡ and Fred McCullough, Jr.‡

Vanadium(II) chloride is formed when a mixture of vanadium(IV) chloride and hydrogen is passed through a hot tube[1] and by the reduction of vanadium(III) chloride with hydrogen.[2] It is also produced by the thermal disproportionation of vanadium(III) chloride[3,4] into the nonvolatile dichloride and the volatile tetrachloride.

The method adopted for the preparation of vanadium(II) chloride is the reduction of the trichloride by hydrogen at temperatures not exceeding 675°.

Procedure

About 30 g. of vanadium(III) chloride (0.19 mol) is placed at the middle of a pyrex tube 60 cm. long and 25 mm. in diameter, through which dry nitrogen is passing. This operation can be performed without moisture coming in contact with the salt with the apparatus described in syn-

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thesis 43. The reaction tube, which is held horizontally in an electric furnace approximately 35 cm. long, is fitted at the outer end with a tube containing calcium chloride, as a protection against back-diffusion of moisture. Hydrogen from which the oxygen has been removed and which is subsequently passed through a tube containing phosphorus(V) oxide is substituted for the nitrogen. The temperature of the furnace (registered by means of a thermocouple) is raised to around 400°, whereupon hydrogen chloride begins to evolve. The temperature is gradually increased to 675°, and at the end of about 40 hours of heating the evolution of hydrogen chloride will have ceased. Above 700°, reduction to the metal takes place; consequently, such temperatures must be avoided. When the reaction is complete, the tube is cooled to room temperature; dry carbon dioxide is substituted for the hydrogen, and the contents of the tube are removed, proper precautions being taken to avoid contact with moist air. The apparatus used in transferring vanadium(III) chloride (synthesis 43) is applicable here. The yield of about 20 g. is nearly 90% of the theoretical.

Properties

Vanadium(II) chloride forms apple-green leaflets which behave toward water somewhat like chromium(II) chloride.[5] They may be wetted slowly by water. The salt is soluble in water, forming the violet hydrated vanadium(II) ion. This ion is readily oxidized by the oxygen of the air and by hydrogen ion. The salt dissolves in alcohol and ether, the resulting solutions being respectively blue and greenish yellow.[3]

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43. VANADIUM(III) CHLORIDE

(Vanadium Trichloride)

$$2VCl_4 \rightarrow 2VCl_3 + Cl_2$$

Submitted by Ralph C. Young* and Maynard E. Smith†
Checked by Therald Moeller,‡ Paul G. Gordon,‡ and Fred McCullough, Jr.‡

Vanadium(III) chloride is formed by the decomposition of vanadium(IV) chloride[1–4] and by the reaction of vanadium(IV) chloride or vanadium(V) oxychloride with sulfur.[3] It may also be produced by the chlorination of vanadium(III) sulfide,[5] by the action of carbon tetrachloride on vanadium(III) oxide[6] and of hydrogen chloride on powdered vanadium,[2] and by the reaction of liquid chlorine with vanadium metal in a sealed tube.[7] The method described here is essentially that of Meyer and Backa,[2] who decomposed vanadium(IV) chloride into vanadium(III) chloride and chlorine and removed the latter with carbon dioxide.

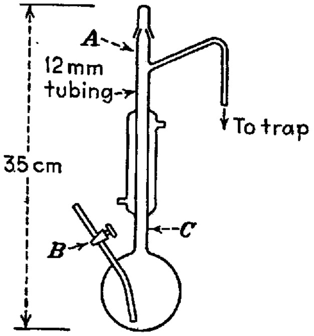

Fig. 13. Apparatus for the preparation of vanadium(III) chloride.

Procedure

Thirty milliliters of vanadium(IV) chloride (0.28 mol) is introduced into a 50-ml. round-bottomed flask to which is sealed a small water-cooled condenser (Fig. 13). This operation is carried out in a dry box since the tetrachloride must be protected from contact with moist air. The top of the condenser is sealed to a tube which is connected to a trap cooled with ice. The trap is joined by rubber tubing to a tube containing anhydrous calcium chloride. Dry carbon dioxide is passed through an inlet

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tube (8 mm. i.d.) provided with a stopcock and sealed in near the neck of the flask. The inlet tube extends to within 2 cm. of the bottom of the flask.

The flask and its contents are heated in an oil bath or mantle kept at about 160 to 170°. In approximately 50 hours the conversion of the tetrachloride to the trichloride is nearly complete, and any of the former remaining can be removed by means of a vacuum pump. The tube containing calcium chloride is removed, and the pump, suitably protected with traps cooled with Dry Ice, is connected at this point. The flow of carbon dioxide is discontinued, and the stopcock through which it passed is closed. The pump is then operated until the undecomposed vanadium(IV) chloride has been eliminated completely from the trichloride. The oil bath is removed, and carbon dioxide is again passed through the system while the flask is cracked off at *C* (Fig. 13). The product is loosened from the bottom of the flask with a glass rod and transferred to the apparatus shown in Fig. 14 while dry carbon dioxide or nitrogen is admitted through tube *D*. This is accomplished by inserting the neck of the flask at *E*.

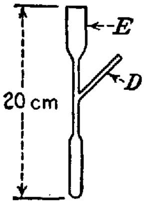

FIG. 14. Apparatus for transferring vanadium(III) chloride.

If the vanadium(III) chloride is to be stored, the apparatus (Fig. 14) is sealed below the delivery tube *D*, but if the salt is to be used immediately, it can be transferred in a stream of dry inert gas after the tube is cracked off above tube *D*. The yield is about 40 g., or approximately 90% of the theoretical.

Properties

Vanadium(III) chloride is a violet solid which undergoes disproportionation into the dichloride and tetrachloride when heated in a vacuum to a sufficiently high temperature. The trichloride is very soluble in water and behaves like iron(III) chloride and aluminum chloride with respect to

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ionization and hydrolysis. A 6-hydrate, $VCl_3 \cdot 6H_2O$,[8] can be crystallized from water, and hydrated complex chlorides can be formed in the presence of excess chloride ion. The hydrated vanadium(III) ion is green. An ammine, $[V(NH_3)_6]Cl_3$, is produced with liquid ammonia; however, it cannot be formed in the presence of water; with gaseous ammonia, the nitride, VN, forms. Coordination compounds can be made with amines[6] and other organic compounds.[9] Vanadium(III) chloride is soluble in alcohol and acetic acid but insoluble in ether, benzene, chloroform, toluene, and carbon disulfide.

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44. TANTALUM(V) BROMIDE

(Tantalum Pentabromide)

$$2Ta + 5Br_2 \rightarrow 2TaBr_5$$

Submitted by D. H. Nowicki* and I. E. Campbell*
Checked by W. C. Schumb† and C. H. Brubaker†

Tantalum(V) bromide may be prepared by bromination of tantalum carbide or of mixtures of tantalum(V) oxide and carbon. It is most conveniently prepared by reaction between the elements,[1] either at atmospheric pressure, using an inert carrier gas, or *in vacuo*. The reaction of bromine vapor with tantalum powder in a nitrogen atmosphere forms the basis of the procedure outlined below.

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Procedure

The apparatus is constructed of pyrex glass and is assembled as shown in Fig. 15. Reaction tube *A* (1.6 by 41 cm.) is inserted in tube *B* (5 by 53 cm.), which leads to the condensing chamber *C* (6 by 35 cm.). A 35/25 standard-taper joint *E* connects the condensing chamber to the collection bottle *D*. A plunger *F*, made of Transite and connected to a pyrex rod, is used to dislodge any bromide which may adhere to the walls of the condensing chamber. The reaction tube is heated by a resistance furnace *G*.*

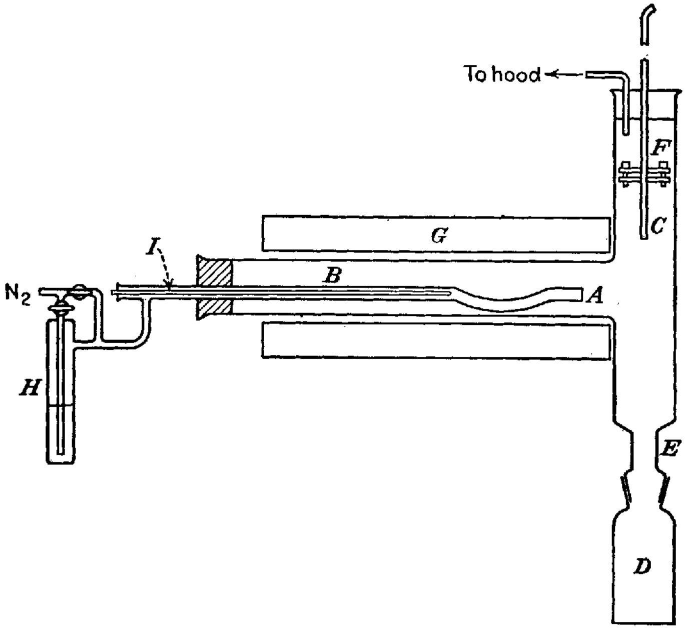

FIG. 15. Apparatus for the preparation of tantalum(V) bromide.

The nitrogen is purified by passing through a tube containing copper turnings heated at 600 to 800° in a tube furnace, to remove oxygen, and then through two towers packed with magnesium perchlorate, to remove moisture.

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* Care must be taken to heat the entire reaction tube in order to prevent clogging.

Forty-one grams of tantalum metal (0.227 mol), either powder or sheet trimmings, is placed in reaction tube *A*, which is then inserted in tube *B*, and seventy milliliters of bromine (1.37 mols) is placed in trap *H*. Nitrogen (250 ml./min.) is passed through the system (by-passing the bromine in trap *H*), and the reaction tube is heated slowly to 500°, the temperature being measured by a thermocouple placed in tube *I*. After the furnace has been at 500° for 10 minutes, the nitrogen is routed through the bromine. The flow of the nitrogen is continued for 10 minutes after all the bromine has been volatilized, after which the rate of flow is reduced to about 10 ml./min. while the furnace is cooled to room temperature. The tantalum is completely converted to the bromide when the bromine is transferred over an 8-hour period, but the tantalum(V) bromide is not completely recovered, the yield being 106 g., corresponding to an 80.4% efficiency in the recovery of tantalum as bromide, and a 33.4% efficiency in the recovery of bromine as bromide. Higher efficiencies in the conversion of bromine can be obtained by reducing the rate of vaporization of the bromine, but this, of course, increases the length of time required for the preparation.

Since the bromide is collected as a fine powder which is extremely hygroscopic, it is desirable, wherever possible, to modify the apparatus so that the product can be sublimed (preferably in hydrogen) directly into the equipment in which it is to be used. This will also reduce loss of material in handling.

Properties

Tantalum(V) bromide forms pale yellow, tabular crystals of specific gravity 4.67. It is extremely hygroscopic and is decomposed in cold or hot water. It dissolves with reaction in methanol and ethanol, with the evolution of heat, forming clear solutions which give no precipitate upon dilution with water.[2] Its solubility in carbon tetrachloride is 0.3921 and 1.4651 g./100 ml. of solution at 20° and 30°,

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respectively; in ethyl bromide its solubility is 0.2560, 0.3985, and 0.4277 g./100 ml. of solution at 0°, 20°, and 25°.[3] It is soluble in and reacts with aniline, acetonitrile, acetamide, and liquid ammonia, in which it undergoes ammonolysis. Its melting point is 280.0°, and the normal boiling point is 348.8°. Equations[4] for the vapor pressure of the solid and the liquid follow:

Solid, 240 to 280°,

$$\log p_{mm.} = \frac{-5550}{T} + 12.27$$

Liquid, 280 to 350°,

$$\log p_{mm.} = -\frac{3290}{T} + 8.17$$

The molten salt is a nonconductor.

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45. FLUORINATION OF VOLATILE INORGANIC COMPOUNDS

By Donald Ray Martin*

The selection of a method for the fluorination of volatile inorganic compounds is dependent upon several factors, among which are:

The desired extent of fluorination of the starting material may dictate the fluorinating agent to be used. For example, fluorine converts silicon tetrachloride to silicon tetrafluoride, whereas antimony(III) fluoride promotes the reactions which produce the chlorofluorides, $SiCl_3F$, $SiCl_2F_2$, and $SiClF_3$.

The ease of replacing halogens by fluorine increases from

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chlorine to iodine. There is a greater possibility of reduced yields of the desired product with iodine compounds because of the increased tendency for side reactions to occur. Halofluoride derivatives of some halides have not been prepared, either because the halofluorides are too unstable to be prepared or because the necessary reagents and conditions for fluorination have not yet been ascertained. Numerous unsuccessful attempts have been made to prepare the chlorofluorides of boron by fluorinating boron trichloride and by chlorinating boron trifluoride.

A given fluorinating agent may be preferred for a laboratory synthesis, but the yield of the desired product may be too low to permit the economical use of this agent in a commercial process.

If two fluorinating agents are equally satisfactory as far as their role in a synthesis is concerned, the cost of the available fluorine merits consideration. For example, although hydrofluoric acid is more expensive per pound than sodium fluoride, it yields more fluorine per dollar.

The starting material may be selected on the basis of the type of equipment available. A bromide might be used as a starting material in ordinary reactors, whereas a chloride might require pressure equipment. The fluorinating agent also may dictate the type of equipment to be used. Thus, calcium fluoride may be used in glass equipment, whereas hydrofluoric acid requires metal apparatus.

Other considerations being equal, the synthesis involving the more easily handled materials is preferred. Therefore, hydrofluoric acid is frequently replaced by one of its more easily handled salts.

Methods Employed. 1. Antimony(III) Fluoride (Swarts Reaction). Many years ago, Swarts[1] discovered that antimony(III) fluoride affords an excellent reagent for introducing fluorine into organic molecules. Henne[2] has summarized the advantages and disadvantages of the Swarts reaction when employed in the fluorination of organic molecules. The first application of the Swarts reaction in the fluorination of volatile, inorganic, nonpolar halides was reported by Booth and Swinehart in 1932.[3] In the ensuing 18 years, many fluoride and halofluoride derivatives of volatile inorganic halides were prepared and characterized by Booth and his students.

Halogen atoms in certain inorganic compounds may be replaced by fluorine by the use of antimony(III) fluoride without a catalyst. In other cases, varying amounts of different kinds of catalysts are required. For example, sometimes the addition of chlorine in the amount of 1% of the antimony(III) fluoride will suffice. Molecules which are more difficult to fluorinate may require chlorine, bromine, or antimony(V) chloride in quantities amounting to as much as 5% of the weight of antimony(III) fluoride used.

The generally accepted mechanism of the Swarts reaction assumes the formation of an antimony(V) halofluoride. The following reactions are postulated in connection with the catalysts mentioned above:

$$SbCl_5 + SbF_3 \rightarrow SbF_3Cl_2 + SbCl_3$$
$$Cl_2 + SbF_3 \rightarrow SbF_3Cl_2$$
$$Br_2 + SbF_3 \rightarrow SbF_3Br_2$$

Fluorination of the inorganic halide probably occurs in accordance with the following equation (*e.g.*, with silicon tetrachloride):

$$3SiCl_4 + SbF_3Cl_2 \rightarrow 3SiCl_3F + SbCl_5$$

the catalyst being liberated for further reaction.

It has been observed that a definite threshold temperature exists below which the Swarts reaction will not proceed. The best results are obtained if the desired product is removed as fast as it is formed. More highly fluorinated products may be obtained if the reaction products are refluxed in the reactor.

Hydrogen fluoride is used in the Swarts reaction on a commercial scale to regenerate the antimony(III) fluoride. The compound to be fluorinated and anhydrous hydrogen fluoride are introduced together into the reactor which contains antimony(V) chloride or bromide.

2. Mercury Fluorides. The fluorides of mercury are among the most useful fluorinating agents. Mercury(II) fluoride can be generated in a reactor by adding mercury(II) oxide and hydrofluoric acid to the reaction mixture. It can replace antimony(III) fluoride in the Swarts reaction; accordingly it has been used to fluorinate organic polyiodides and polybromides.

Mercury(I) fluoride may be oxidized during a fluorination; hence it cannot be used to fluorinate materials susceptible to reduction if the fluoride of the element in the higher oxidation state is desired.

3. Silver(I) Fluoride. Silver(I) fluoride, like the mercury fluorides, has been used as a fluorinating agent for many years. It can be used in most of the reactions for which other inorganic fluorides are used. Its use has declined in recent years, primarily because it is deliquescent, light-sensitive, and easily reduced. Only one-half of its fluorine is available for fluorination because it forms the compound AgCl·AgF, which has very little fluorinating power.

4. Hydrogen Fluoride. Hydrogen fluoride is designated by some chemists as *the* fluorinating agent. It is widely used in industry and in the laboratory. Compounds containing fluorine are frequently mixed with sulfuric acid to generate hydrogen fluoride *in situ.* The alkali-metal hydrogen fluorides (bifluorides) and ammonium hydrogen fluoride have long been used as fluorinating agents. Frequently, the fluorination reaction must be promoted by heating. Sometimes the alkali fluorides are used with a nonvolatile acid; this produces hydrogen fluoride, which effects the fluorination. Fluorosilicates and fluoroaluminates have been used to a limited extent as fluorinating agents. Usually they, too, are used with a nonvolatile acid to generate hydrogen fluoride *in situ.*

Many elements react with hydrogen fluoride to yield fluorides; practically all the nonmetallic elements yield gaseous fluorides. Oxides and halides are fluorinated easily by this reagent. The yield of the halofluorides is usually lower than that obtained with the Swarts reaction.

A disadvantage of the use of hydrogen fluoride on a laboratory scale is the fact that glass equipment must be replaced by plastic or metal equipment.

5. Other Fluorides. Calcium fluoride is one of the oldest fluorinating agents. Ordinarily, it is used with sulfuric acid, which generates hydrogen fluoride. On a laboratory scale, this reagent is not very satisfactory because the solid cake of calcium sulfate is difficult to remove from the reactor flask.

Calcium fluoride has also been used in metathetical reactions. Usually, heat is required to promote reactions of this type. Booth and Dutton[4] passed vapors of a volatile halide [phosphorus(V) oxychloride] over a bed of heated calcium fluoride to produce the chlorofluoride and fluoride derivatives. Sodium fluoride, potassium fluoride, titanium(IV) fluoride, and zinc fluoride have been used in similar metathetical fluorination reactions.

Lead fluoride was frequently used by the early chemists; however, it is a poor fluorinating agent and is little used today.

Arsenic(III) fluoride would no doubt be more generally used as a fluorinating agent if it were not toxic. The fact that it is a liquid gives it an advantage over solid agents because better control may be exercised over the rate of its introduction into the reactor.

6. Fluorine. Fluorine reacts too violently for use with most compounds, and for many compounds, other fluorinating agents which are more easily handled may be used in less elaborate apparatus. Reactions with fluorine are generally so rapid that it is not possible to isolate the halofluorides, and only the completely fluorinated products are obtained. Fluorine reacts directly with all elements except nitrogen, oxygen, and the inert gases. Compounds of oxygen and nitrogen with fluorine have been prepared by other procedures. Fluorine reacts with most compounds, especially halides, hydrides, and carbides. Its use with hydrides is inefficient because half of the fluorine is lost as hydrogen fluoride.

Fluorine is the best agent for the preparation of fluorides of elements in their higher oxidation states, *e.g.*, BrF_3, CeF_4, CoF_3, PbF_4, MnF_3, AgF_2, SnF_4, PF_5.

An Apparatus for the Fluorination of Halides of Nonmetals. The discussion which follows is representative of the adaptation, by Prof. Harold S. Booth[3] and his students, of the Swarts[1] reaction to the fluorination of halides.

The reaction involves the replacement of the halogen atoms in nonpolar halide molecules by fluorine atoms. The fluorinating agent is usually resublimed antimony(III) fluoride. If necessary, a catalyst, such as antimony(V) chloride, chlorine, or bromine, may be used.

The type of apparatus and the details of the procedure for a given synthesis necessarily will vary with properties of the reactants. Consequently, the apparatus depicted in Fig. 16 is a general type which may be modified as directed in specific syntheses.

The reactor *R*, in which fluorination is effected, is a 1-l. Claisen flask, modified as shown.[5] The solid fluorinating agent is placed in the vertical glass tube (25 mm. o.d.), which is sealed to the glass tube *F* (25 mm. o.d.). A $^{15}\!/_{16}$-in. wood-auger bit serves as a screw feed for the solid within tube *F*. A $^{1}\!/_{8}$-in. steel drill rod brazed to the shank of the bit connects the handle through a vacuum-tight packing gland *PG*. Ideally, the packing gland should fit a standard-taper joint on tube *F*. If such a gland is not available, a rubber stopper (shaded area in Fig. 16) may be slit longitudinally to accommodate the gland. The stopper and gland may be secured to tube *F* with laboratory cement.[6] Similarly, another packing-gland assembly may be used for the stirrer. Inasmuch as the reaction mixture frequently is lumpy and viscous, it is recommended that a bicycle sprocket chain be used for a stirrer blade and that the motor-driver stirrer be rotated at the rate of 1 r.p.m. A 500-ml. dropping funnel is sealed to the original side arm of the Claisen flask to facilitate the addition of the liquid reactants. A constriction in the delivery tube of the funnel is desirable to facilitate sealing off the funnel after all liquids have been added. This procedure is advisable since the grease on the stopcock is usually attacked by the reactants with the result that air leaks into the system at the stopcock.

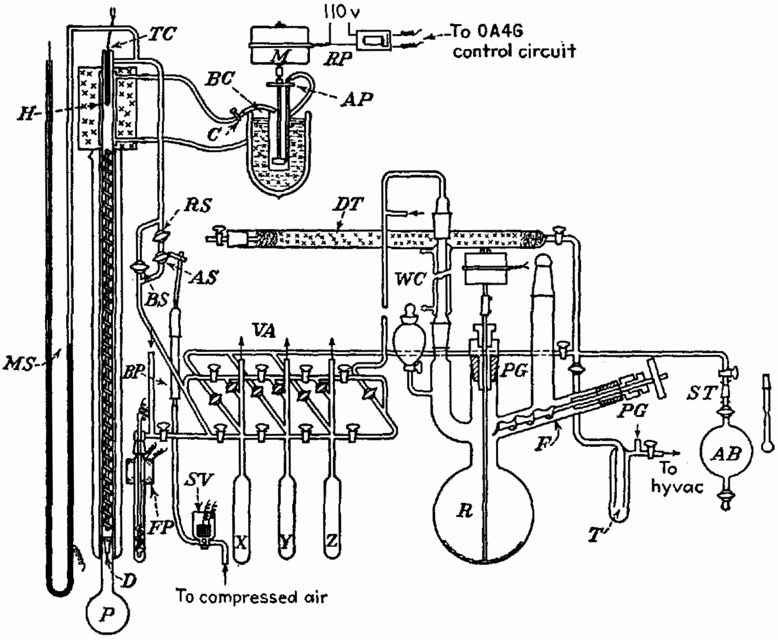

FIG. 16. Apparatus for the fluorination of the halides of nonmetals.

In a typical fluorination, the solid feed assembly *F* is filled with resublimed antimony(III) fluoride. The apparatus is evacuated by a vacuum pump connected through the trap *T*, which is immersed in liquid nitrogen. After the system is evacuated, dry air is admitted through drying tube *DT* containing barium oxide. This procedure of evacuating and rinsing with dry air is repeated ten times, and then the system is finally retained *in vacuo*. The liquid reactants (including the catalyst) are added through the dropping funnel, after which the contents of reactor *R* are cooled to $-78°$ and the funnel is sealed off.

Fluorination is carried out as directed in the specific synthesis. Depending upon the volatility of the reactants and products, the condenser *WC* may be cooled with air, water, or an acetone–Dry Ice bath. The reaction products are condensed in the still pot *P*, which is immersed in liquid nitrogen.

When the fluorination has been completed, stopcocks *BS* and *RS* are closed, and the entire manifold is evacuated and rinsed with dry air ten times and then retained under diminished pressure.[7] The condenser of the fractionating column *H* is precooled to the boiling temperature of the most volatile reaction product. This is achieved by manually closing relay *RP* of an electronic control circuit. The control leads of this circuit are connected to manometer *MS* in such a way as to be actuated at the pressure desired for distillation.

When the thermocouple *TC* indicates that the condenser H is at the desired temperature, the reaction products in the still pot are warmed slowly. When the pressure within the fractionating column reaches the pressure at which the controls are set, the cooling system is actuated. This is achieved by energizing relay *RP*; this causes the motor *M* to drive the centrifugal pump, which is immersed in acetone contained in a brass cylinder packed in Dry Ice.[8] The rate of cooling is controlled by regulating the flow of acetone with pinch clamp *C*. By controlling the heat input to the still pot *P* and the rate of cooling of the condenser *H*, a satisfactory reflux ratio is established and maintained in the fractionating column. The amount of gas removed as distillate is controlled by stopcocks *RS* and *AS*. The pressure under which the gas is to be removed is determined by the position of a second contact wire in the manometer *MS*. When the desired pressure is attained, contact is made; this actuates a relay in the electronic control system. This

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relay in turn energizes the solenoid valve *SV* and allows compressed air to move the piston in bicycle pump *BP*, thus opening the stopcock *AS*. The rate of removal of distillate is controlled by stopcock *RS*.

The purified reaction products are condensed with liquid nitrogen as fractions in the ampoules *X*, *Y*, and *Z*. These are attached, through the tubes leading vertically from them, to manometers, which are not shown in the figure. Samples for analyses and determinations of properties are collected by attaching the appropriate vessels to the standard-taper joint *ST*. Freezing points are determined in the cell *FP*.[9]

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46. METHYL CHLOROFLUOROPHOSPHITE AND METHYL DIFLUOROPHOSPHITE

(Phosphorus(III) Methoxychlorofluoride and Phosphorus(III) Methoxydifluoride)

$$3CH_3OPCl_2 + SbF_3 \rightarrow 3CH_3OPClF + SbCl_3$$
$$3CH_3OPCl_2 + 2SbF_3 \rightarrow 3CH_3OPF_2 + 2SbCl_3$$

Submitted by Donald Ray Martin* and Philip J. Pizzolato*
Checked by Paul W. Trott†

The method used in the preparation of methyl chlorofluorophosphite and the corresponding difluoro ester is

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essentially the same as that described in synthesis 45, except that a catalyst is not required in this case.

Methyl difluorophosphite is very readily obtained by the action of antimony(III) fluoride on the dichloro ester. The intermediate, partially fluorinated chlorofluoro ester is produced in appreciable yields only under carefully controlled conditions. Although the conditions outlined below, *i.e.*, low temperature, low pressure, and slow rate of addition of fluorinating agent, favor the formation of the chlorofluoro ester, a mixture results, and the yield of the chlorofluoro ester is low compared to that of the difluoro.[1]

Procedure

After the Swarts generating system (synthesis 45) is found to be gastight, it is rinsed with dry air ten times. The vertical tube sealed to the upper side of the solid-feed side arm *F* (Fig. 16) is charged with 179 g. of resublimed antimony(III) fluoride (1.0 mol), and the standard-taper cap is replaced. Two hundred fifty-two milliliters of methyl dichlorophosphite (3.0 mols) is admitted to the generator through the attached dropping funnel. After the reactor *R* and its contents have been cooled to −78° with a Dry Ice–acetone mixture, the side-arm connection to the funnel is sealed off at the constriction. Then the pressure within the generator *R* is reduced to below 50 mm. to favor formation of the intermediate, partially fluorinated chlorofluorophosphite. With the liquid in the flask now warmed to slightly below 10°, with water circulating through condenser *WC*, and with the stirrer operating, the reaction is begun by the addition of a small amount of antimony(III) fluoride.*

The volatile products of the reaction are collected in the still pot *P*, which is surrounded by liquid nitrogen. The

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* In order to correct the difficulty associated with clogging of the reservoir by antimony(III) fluoride, the checker installed a stiff spiral wire to scrape the walls of the reservoir. It was fastened in the ground-glass joint cap by a rubber stopper. By rotating the ground-glass joint the wire spiral could easily be turned. No air leaks were encountered with this modification.

fluorinating agent is added in small portions at a rate of between 50 and 80 g./hr. The temperature of the reaction mixture must be maintained below 10° and the pressure below 50 mm. during the synthesis.

The mixture of reaction products is fractionally distilled in a modified Dufton column as described in synthesis 45. The yields based on methyl dichlorophosphite are chlorofluorophosphite, about 8%, and difluorophosphite, about 40%.

Analysis

Samples of the chlorofluorophosphite are collected in glass ampoules of approximately 1 ml. capacity, which are then sealed and weighed.[2] These samples are hydrolyzed in 125 ml. of solution containing sodium hydroxide in slight excess. The difluorophosphite is most conveniently sampled as a gas in a weighing bulb of 500 ml. capacity (*AB*, Fig. 16, synthesis 45).[3]

Chlorine is determined by a modified Volhard procedure.[3] At the beginning of the analysis, the aliquot is made strongly acid with about 10 ml. of freshly boiled concentrated nitric acid. This excess nitric acid prevents the phosphite from reducing the silver ion.

Phosphorus may be determined gravimetrically as magnesium pyrophosphate after oxidation of the phosphite to phosphate by bromine and nitric acid. A sample is hydrolyzed in sodium hydroxide solution and diluted to 500 ml. in a volumetric flask. The analyses are run with 50-ml. aliquots. Each aliquot is acidified with 5 ml. of concentrated, 16 *M* nitric acid, and ¼ ml. (5 drops) of bromine is added (a slight excess over the amount required for complete oxidation of an aliquot containing 0.2 g. of methyl chlorofluorophosphite). The solution is swirled for a few seconds and allowed to stand for 15 minutes, with swirling at intervals. It is then heated on a steam cone until the color of the bromine disappears (the volume is usually reduced considerably during this process). The solution is then cooled to room temperature, the inside walls of the flask are rinsed with distilled water, and 2 drops of bromine is added, after which the solution is treated as above. The solution is then cooled, more bromine is added, and the procedure is repeated a third time. From this point, the usual method of determining phosphorus as magnesium pyrophosphate is followed.

Methoxyl analyses are most conveniently carried out with large samples (2 to 3 g.). The sample is hydrolyzed in a sodium hydroxide solution, and the methanol is fractionally distilled into a tared receiver.[4] From the weight and specific gravity of the distillate the percentage of methoxyl group may be calculated.[5,6]

Anal. Calcd. for CH_3OPClF: C, 10.31; H, 2.60; P, 26.60; Cl, 30.44. Found: C, 10.14; H, 2.73; P, 26.82; Cl, 30.24. Calcd. for CH_3OPF_2: C, 12.01; H, 3.02; P, 30.98; CH_3O, 31.05. Found: C, 11.04; H, 2.98; P, 31.3; CH_3O, 30.9.

Properties

Methyl chlorofluorophosphite is a colorless liquid having the following characteristics: sp. gr. 1.318^0_4; b.p. 38.9° (760 mm.); and a vapor pressure which may be expressed by the equation

$$\log p_{mm.} = 7.8362 - \frac{1546.5}{T}$$

It shows no sharp freezing point, but on cooling it forms a glass at some temperature below $-79°$.

Methyl difluorophosphite is a colorless gas having the following characteristics: b.p. $-15.5°$ (760 mm.); f.p. $-117.3 \pm 0.4°$; and a vapor pressure which may be expressed by the equation

$$\log p_{mm.} = 7.7335 - \frac{1250.5}{T}$$

Both of these compounds hydrolyze readily and fume on contact with moist air.

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47. SILICON TETRAFLUORIDE

$$BaCl_2 + H_2SiF_6 \rightarrow BaSiF_6 + 2HCl$$
$$BaSiF_6 \xrightarrow{\Delta} SiF_4 + BaF_2$$

Submitted by C. J. Hoffman* and H. S. Gutowsky*
Checked by W. C. Schumb† and D. W. Breck†

Silicon tetrafluoride has been prepared by the reaction[1] of concentrated sulfuric acid with a mixture of sand and calcium fluoride, at room temperature or upon mild heating. However, the product is contaminated by hydrofluoric and fluorosilicic acids.‡ The thermal decomposition of barium hexafluorosilicate[2] is a convenient method, requiring simple apparatus and capable of producing silicon tetrafluoride of high purity.

Procedure

Preparation of Barium Hexafluorosilicate, $BaSiF_6$. Twenty-five grams of barium chloride 2-hydrate (0.10 mol) is dissolved in 70 ml. of water. Aqueous fluorosilicic acid (30%) is added until precipitation is complete; this requires about 40 ml. of the solution. The freshly precipitated barium hexafluorosilicate is filtered and washed until free from chloride. The product is dried in an oven at 110 to 120° and then dried further in a desiccator over phosphorus(V) oxide or porous barium oxide. The yield is nearly quantitative.

Thermal Decomposition of $BaSiF_6$. The apparatus is dried thoroughly. The barium hexafluorosilicate is placed

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‡ Booth and Swinehart[5] discuss the difficulties encountered in this reaction and describe two additional methods of preparation.

in a reaction tube, which consists of a 20-cm. length of pyrex tubing of 30 mm. diameter, one end of which is sealed and the other end joined to a length of tubing of smaller diameter. This tube is connected by standard ground-glass joints and stopcocks to two traps in series and ultimately to a vacuum system. The reaction tube is heated by an electric combustion furnace regulated with a Variac. The assembled apparatus containing the barium hexafluorosilicate is dried further by evacuation and by raising the furnace temperature to 200°. The first trap is then immersed in an acetone–solid carbon dioxide bath to remove any hydrofluoric or fluorosilicic acid that may be formed. The second trap is cooled with liquid air to collect the product. At about 300° the evolution of silicon tetrafluoride commences; decomposition proceeds readily at 500°. The product condenses to a white solid in the collection trap. The first portion of the gas contains most of the impurities and should be discarded. The yield is about 75%. If desired, the gas may be transferred for storage to a steel cylinder by the method described in the synthesis for sulfur(VI) fluoride.[4] Spectroscopic examination indicates that the product is at least 98% pure.

Properties

Silicon tetrafluoride is a colorless, pungent, fuming gas at room temperature. The triple point is at −90.2° and 1318 mm.[3] The critical temperature and pressure are −14.5° and 36.66 atm., respectively.[5] The sublimation temperature[3] at 1 atm. is −95.7°. The gas liquefies under pressure to form a colorless, mobile liquid. Distillation of the liquid can be used for purification.[1,5] In the absence of moisture, pure silicon tetrafluoride does not attack glass, mercury, stopcock grease, or rubber.

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48. GERMANIUM(IV) FLUORIDE

(Germanium Tetrafluoride)

$$GeO_2 + 6HF \rightarrow H_2GeF_6 + 2H_2O$$
$$H_2GeF_6 + BaCl_2 \rightarrow BaGeF_6 + 2HCl$$
$$BaGeF_6 \xrightarrow{\Delta} GeF_4 + BaF_2$$

Submitted by C. J. Hoffman* and H. S. Gutowsky*
Checked by W. C. Schumb† and D. W. Breck†

There appears to be only one really satisfactory method for preparing pure germanium(IV) fluoride. This method involves the thermal decomposition of barium hexafluorogermanate[1] in a quartz or Vycor tube, a method analogous to that described for the preparation of silicon tetrafluoride (synthesis 47). Germanium(IV) fluoride has also been produced by the fluorination of germanium(IV) chloride with antimony(III) fluoride;[2] however, it is necessary to distill fractionally the mixture of chlorofluorides resulting from the reaction.

Procedure

Preparation of Barium Hexafluorogermanate, $BaGeF_6$. Five and twenty-three hundredths grams of germanium(IV) oxide (0.05 mol) is dissolved in 15 ml. of a concentrated aqueous solution of hydrofluoric acid (47%). A platinum evaporating dish or a polyethylene plastic beaker is used to keep silicon contamination to a minimum. A solution of 10.5 g. of barium chloride (0.05 mol) in 50 ml. of water is added. Barium hexafluorogermanate forms as a white, granular precipitate, which is filtered and washed free of chloride. The product is dried by heating to 300° *in vacuo* and is stored in a desiccator over phosphorus(V) oxide. The yield is 15.24 g. (94%).

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Thermal Decomposition of $BaGeF_6$. The general procedure and precautions are similar to those for silicon tetrafluoride (synthesis 47). However, the thermal decomposition of barium hexafluorogermanate requires a higher temperature, about 700°. The compound is placed in a quartz or Vycor tube, 20 cm. long and 10 mm. in diameter, sealed at one end. This tube is connected by a short length of heavy-walled rubber tubing to a collection train and vacuum system. The main source of impurities is water which may be adsorbed on the walls of the apparatus or contained in the solid barium hexafluorogermanate. When germanium(IV) fluoride is formed, it reacts with the water to produce germanium(IV) oxide and hydrofluoric acid, which in turn attacks the silica, producing volatile silicon fluorides. Such contamination is decreased if the assembled apparatus, containing the barium hexafluorogermanate, is dried by evacuation and then by heating the reaction tube at 200 to 300° in an electric furnace. At 500° there is slight evolution of germanium(IV) fluoride, and at 700° the decomposition proceeds readily. Toward the end, however, it becomes quite slow again. If high purity is desired, the first portion of the product is discarded. The product is collected as a white solid in a trap cooled by liquid air.

The yield will depend on how long the decomposition is allowed to proceed. A yield of approximately 50%, based on $BaGeF_6$, is normally obtained. Spectroscopic examination indicates that the product is at least 98% pure.

Properties

At room temperature germanium(IV) fluoride is a colorless, fuming, pungent gas with an odor somewhat like that of garlic. At elevated temperatures it is reduced by copper.[1,2] The vapor pressure of the solid is appreciable at temperatures as low as $-111.7°$ and becomes approximately equal to atmospheric pressure at $-36.5°$.[1] The liquid which forms under increased pressure is clear, colorless, and mobile. The triple point is at $-15°$ and 3032 mm. pressure.

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49. PHOSPHORUS(III) FLUORIDE

(Phosphorus Trifluoride)

$$PCl_3 + AsF_3 \xrightarrow{SbCl_5} PF_3 + AsCl_3$$

Submitted by C. J. Hoffman*
Checked by James M. Lutton† and Robert W. Parry†

Phosphorus(III) fluoride can be prepared by the reaction of antimony(III) fluoride with phosphorus(III) chloride, using antimony(V) chloride as a catalyst,[1] or by heating copper phosphide with lead fluoride.[2] The procedure described here involves the reaction of arsenic(III) fluoride with phosphorus(III) chloride, using antimony(V) chloride as a catalyst.[3,4]

Procedure

The apparatus consists of a glass reaction flask fitted with a side arm and dropping funnel. The side arm is connected to two glass traps in series by means of standard ground-glass joints and stopcocks.

After the apparatus is assembled and thoroughly dried, 13.7 g. of freshly distilled phosphorus(III) chloride (0.10 mol) is introduced into the reaction flask, and 13.2 g. of arsenic(III) fluoride (0.10 mol) (synthesis 50) containing a few drops of antimony(V) chloride‡ is placed in the dropping funnel. The phosphorus(III) fluoride is readily generated by allowing the arsenic(III) fluoride to drop slowly into the phosphorus(III) chloride; the reaction proceeds smoothly at room temperature and becomes more rapid with time. The gases formed by the reaction are led from the reaction flask through a trap cooled by an acetone–Dry Ice bath, to

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‡ The checkers report that satisfactory results may be obtained without the antimony(V) chloride catalyst.

remove any of the reactants that may be entrained. Phosphorus(III) fluoride is condensed as a white solid in the second trap, which is cooled by liquid nitrogen. Yield, 85%. As a further purification, the trifluoride can be distilled slowly through a trap immersed in a bath of acetone and Dry Ice. The initial and final fractions of the distillate should be discarded.

Properties

Phosphorus(III) fluoride is a fairly stable, colorless gas which is decomposed slowly by water, forming phosphorous acid and hydrogen fluoride. At elevated temperatures, in the presence of silica, it quickly decomposes. It condenses at −101.1° to form a colorless, mobile liquid and solidifies at −151.5° to a white solid.

When pure, phosphorus(III) fluoride is odorless in concentrations which are great enough to cause the substance to be toxic. It is readily absorbed by sodium hydroxide with evolution of heat.

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50. ARSENIC(III) FLUORIDE

(Arsenic Trifluoride)

$$As_2O_3 + 3CaF_2 + 3H_2SO_4 \rightarrow 2AsF_3 + 3CaSO_4 + 3H_2O$$

Submitted by C. J. Hoffman*
Checked by James M. Lutton† and Robert W. Parry†

Although Moissan prepared arsenic(III) fluoride by the action of fluorine on arsenic and on arsenic(III) chloride,[1] the only convenient laboratory procedure involves distillation of a mixture of arsenic(III) oxide, calcium fluoride, and concentrated sulfuric acid.[2]

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Procedure

The reaction can be carried out in a round-bottomed glass flask fitted with a still head, the arm of which is attached to a trap immersed in a cooling bath of ice. Owing to the reactivity of arsenic(III) fluoride, the apparatus should be well dried, and the use of rubber or cork stoppers must be avoided. A thermometer can be inserted into the still head by means of a ground-glass joint lightly lubricated with Apiezon* grease L, which reacts only very slowly with the vapor.[3]

A dried intimate mixture of 23.4 g. of reagent-grade calcium fluoride (0.30 mol) and 19.8 g. of arsenic(III) oxide (0.10 mol) is introduced into the reaction flask.† To this, 98.1 g. of reagent-grade concentrated sulfuric acid (0.95 mol) is added. The apparatus is then assembled, and the mixture is heated slowly on a water bath to distill the product as it is formed.

The portion of the distillate boiling at 63° comprises the product. The yield is 11.2 g. (85%). Arsenic(III) fluoride obtained in this manner is of sufficient purity to be used for the preparation of phosphorus(III) fluoride (synthesis 49); however, if desired, it can be further purified by distillation at atmospheric pressure in an all-glass system using a column packed with glass helices.[3]

Properties

At ordinary temperatures, arsenic(III) fluoride is a clear, colorless, mobile liquid which hydrolyzes slowly when

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* The checkers report that ordinary Lubriseal mixed with graphite is a suitable substitute for the Apiezon grease.

† The checkers found that, if large quantities of arsenic(III) fluoride are to be prepared, it is expedient to add the dry mixture to the acid in rather small amounts, to prevent the reaction from becoming too vigorous. This can be accomplished by storing the dry mixture in a retort-shaped container connected to the side of the reaction flask by means of a ground-glass joint. Additions of the mixture can easily be made by rotating the storage flask so that the bulb is moved upward, thus spilling portions of the mixture into the reaction flask.

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exposed to the atmosphere. It boils at 57.13° under a pressure of 742.5 mm. and solidifies at $-5.95°$.[3]

Arsenic(III) fluoride readily attacks glass when moist; however, the reaction is very slow when moisture is excluded. When stored in glass under anhydrous conditions, the liquid slowly becomes turbid after 2 or 3 days.

Care should be exercised when handling arsenic(III) fluoride, as it produces skin burns similar to those produced by hydrogen fluoride.

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51. CHLORINE(IV) OXIDE

(Chlorine Dioxide)

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl$$

Submitted by R. I. Derby* and W. S. Hutchinson*
Checked by T. H. Dexter† and J. M. Naughton†

Chlorine(IV) oxide has been produced electrolytically[1] and by a chlorinated-brine process[2] in which chlorine gas diluted with air is metered into a solution of sodium chlorite. These methods entail control difficulties, which are greatly minimized by a procedure based on allowing dry chlorine, obtained from a cylinder, to react with substantially dry powdered sodium chlorite,[3] as indicated in the equation above.

For uses where a small amount of chlorine will not be harmful, up to 0.1 g. of chlorine(IV) oxide may be produced in admixture with inert gas and chlorine by allowing a weighed amount of chlorite to react with an excess of chlorine in a closed system of 1 l. capacity. This produces the chlorine(IV) oxide at a partial pressure of about 26 mm. (0.1 g. of ClO_2 in 1 l.) at room temperature and 1 atm. The

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maximum concentration which may be handled safely is represented by a partial pressure of 36 mm. A procedure for obtaining greater amounts of the gas free from chlorine is also given.

Procedure

Caution. *Chlorine*(IV) *oxide reacts violently with organic materials. In concentrations in excess of* 10% *at atmospheric pressure, it is easily detonated by sources of initiation such as sunlight, heat, or electric discharge.*

Sodium chlorite must be kept out of contact with heat, open flame, acid, organic materials, including paper, and materials containing sulfur, such as rubber. It ignites upon contact with these substances and burns with an intensely hot flame. The flame of burning sodium chlorite may be extinguished by flooding with water.

A. Small-scale Preparation of Chlorine(IV) Oxide Admixed with Inert Gas and Chlorine[5]

The exact amount of sodium chlorite required to produce 0.1 g. of chlorine(IV) oxide is determined by analysis. The required amount (about 1.3 g.) of nearly pure, dry, powdered sodium chlorite is placed in a 1-l. flask.* The flask is fitted with a chlorine-treated stopper† having inlet and outlet tubes equipped with stopcocks. The inlet tube should extend to the bottom of the flask. The flask is partially evacuated by means of a water pump. The resulting vacuum is partially released with chlorine which is metered by using a chlorine-saturated sodium chloride solution as a metering fluid. Chlorine is used in an amount approximately 100% in excess of the theoretical requirements. The system is then returned to atmospheric pressure by

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* It is advisable to wrap this flask with tape as a safety precaution.

† A "chlorine-treated stopper" is a rubber stopper which has been retained in a chlorine-gas atmosphere or painted with chlorinated rubber paint before use. This is probably not necessary where relatively large gas flows are encountered; however, fresh rubber stoppers and also tubing sometimes react with the gas.

admitting air, after which the flask is placed in the dark for 3 hours; during this time the reaction goes to completion. The gaseous mixture can then be stripped by a stream of air flowing at the rate of approximately 300 ml./min. The reaction is about 94% efficient and can be checked in the manner described in the second paragraph of the section on analysis.

B. PREPARATION OF CHLORINE(IV) OXIDE FREE FROM CHLORINE[5]

Using a solution saturated with sodium chloride and chlorine as a metering fluid, the required amount of chlorine is metered into a buret and then slowly conducted into a mixing chamber. From there it is swept by a continuous stream of air, flowing at the rate of about 200 ml./min., through a column packed with dry flaked (not powdered) sodium chlorite.* The diameter of the column is 1.9 cm.; the length, about 41 cm. (Fig. 17). After the chlorine is displaced from the buret, the air flow is directed through the three-way stopcocks, and the screw clamp is closed. The effluent gases from the reaction tube are conducted to the point of application.

The product can be checked for the presence of chlorine by testing the output stream with the fumes from ammonium hydroxide; chlorine produces the typical white cloud of ammonium chloride, while chlorine(IV) oxide does not. No chlorine is present in the effluent gas until two-thirds or more of the sodium chlorite has reacted, at which time chlorine may escape through channels in the remaining sodium chlorite without reacting.

The partial pressure of the effluent gas mixture must be held below 30 mm. An example of the manner of calculating the flow rates necessary to give a desired partial pressure of chlorine(IV) oxide is outlined below. If 5 ml. of chlorine is used per minute, chlorine(IV) oxide will be pro-

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* It is advisable to wrap this sodium chlorite tube with tape as a safety precaution.

duced at the rate of 10 ml./min. The amount of air that must be used in diluting the chlorine at barometric pressure of 740 mm. in order to obtain chlorine(IV) oxide at a partial pressure of 30 mm. is calculated from the following equation:

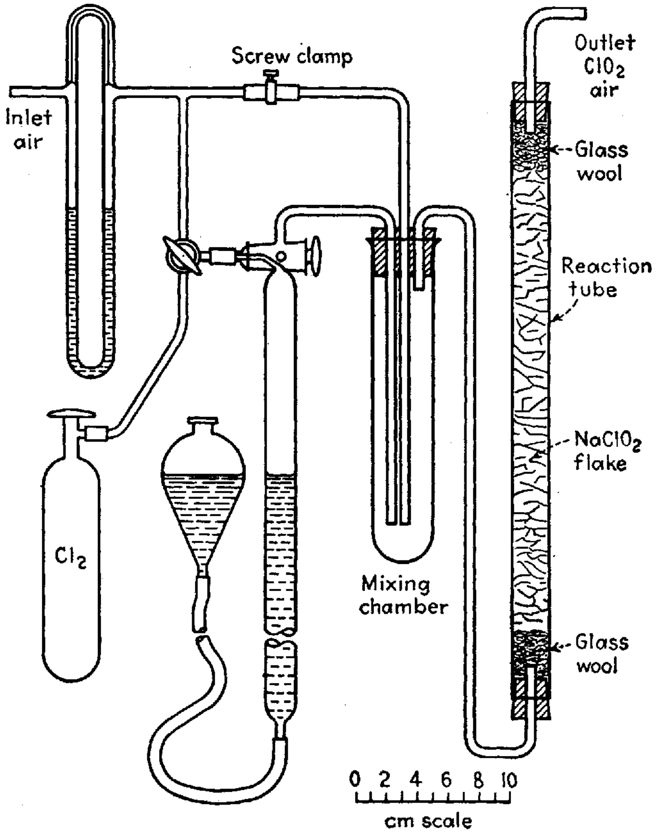

FIG. 17. Apparatus for the preparation of chlorine(IV) oxide free from chlorine.

$$\text{ml. air/min.} = \frac{\text{ml. } ClO_2\text{/min.} \times \text{barometric pressure}}{\text{partial pressure of } ClO_2} - \text{ml. } ClO_2\text{/min.}$$

$$= \frac{10 \text{ ml./min.} \times 740 \text{ mm.}}{30 \text{ mm.}} - 10 \text{ ml./min.}$$

$$= 237 \text{ ml./min.}$$

The sodium chlorite should be flushed with air for several minutes after the chlorine has been used, to ensure complete stripping.

Technical flaked sodium chlorite contains some impurities, including sodium carbonate, which reacts with chlorine and thereby reduces the efficiency of the reaction. The relative humidity and the moisture content of the sodium chlorite also affect the efficiency of the process. Since an aqueous solution is used as a metering fluid, considerable moisture will be present. For these reasons the method described here is considered to be only about 90% efficient, based on the metered chlorine.

The concentration of chlorine(IV) oxide at any instant depends on the rates of flow of the gases and on the condition of the solid sodium chlorite in the tower. In order to estimate the true efficiency of the method, it would be necessary to collect all the effluent gas and perform analyses on aliquot portions. This is impractical because of the large total volume of the gases. Should the conditions under which the chlorine(IV) oxide is to be used require a higher degree of control, the method described in reference 5 is suitable.

Analysis

Sodium Chlorite. An accurately weighed sample of about 2.0 g. of sodium chlorite is dissolved in 1 l. of water; a 25-ml. aliquot serves as the sample for analysis. Two milliliters of 50% potassium iodide and 10 ml. of acetic acid are added to the aliquot, and the ensuing reaction is allowed to proceed in the dark for 5 minutes. The liberated iodine is then titrated with 0.1 *N* standard sodium thiosulfate solution, using starch as an indicator. The equations for the reactions are written below.[1]

$$NaClO_2 + 4CH_3COOH + 4KI \rightarrow NaCl + 2I_2 + 4CH_3COOK + 2H_2O$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

One mol of sodium chlorite is equivalent to 4 mols of sodium thiosulfate. The milliequivalent weight (*MEW*) of the sodium chlorite is 0.0226. The equation for the percentage of sodium chlorite in the original sample is

$$\% \text{ NaClO}_2 = \frac{\text{ml. of Na}_2\text{S}_2\text{O}_3 \times N \text{ of Na}_2\text{S}_2\text{O}_3 \times MEW \text{ of NaClO}_2 \times 100}{\text{weight of sample in aliquot}}$$

Effluent-gas Analysis.[4] This method of analysis gives an estimate both of the chlorine(IV) oxide produced and of the unreacted chlorine present in the effluent-gas mixture. The gas is collected in an opaque 600-ml. Hempel tube; it is then absorbed in a neutral 10% solution of potassium iodide. Starch indicator is added to this solution or to an aliquot, which is then titrated with 0.1 *N* sodium thiosulfate solution (titration A). The amount of sodium thiosulfate used is equivalent to all the chlorine gas in the sample plus one-fifth of the chlorine(IV) oxide. The solution is then acidified with an excess of 30% acetic acid, causing a second release of iodine, which is then titrated with sodium thiosulfate solution (titration B). The amount of sodium thiosulfate used in titration B is equivalent to four-fifths of the chlorine(IV) oxide in the sample. The equations for the reactions involved are shown below.[4]

$$\text{Cl}_2 + 2\text{KI} \rightarrow 2\text{KCl} + \text{I}_2$$
$$2\text{ClO}_2 + 2\text{KI} \rightarrow 2\text{KClO}_2 + \text{I}_2$$
$$\text{KClO}_2 + 4\text{CH}_3\text{COOH} + 4\text{KI} \rightarrow \text{KCl} + 2\text{I}_2 + 4\text{CH}_3\text{COOK} + 2\text{H}_2\text{O}$$

The results are calculated from the following equations:

$$\text{g. of ClO}_2 = (\text{ml. of Na}_2\text{S}_2\text{O}_3\text{, titration B}) \times 5/4 \times MEW \text{ of ClO}_2 \times N \text{ of Na}_2\text{S}_2\text{O}_3$$
$$\text{g. of Cl}_2 = [(\text{ml. of Na}_2\text{S}_2\text{O}_3\text{, titration A} + \text{titration B}) - (\text{ml. of Na}_2\text{S}_2\text{O}_3\text{, titration B}) \times 5/4] \times MEW \text{ of Cl}_2 \times N \text{ of Na}_2\text{S}_2\text{O}_3$$

MEW of ClO_2 in this case is 0.0135; *MEW* of Cl_2, 0.0355.

Properties

Chlorine(IV) oxide is a strongly oxidizing, orange-red gas at room temperature. It condenses at 9.9° (731 mm.) or at 11° (760 mm.)[6] and solidifies to yellowish-red crystals at −59°.[6] The gas is unstable in light and decomposes explosively when brought in contact with organic materials or when heated rapidly. Pure chlorine(IV) oxide is stable indefinitely in the dark; chlorides catalyze its decomposition even in the dark. It has an odor similar to that associated with chlorine and also reminiscent of that of nitric acid; when the gas is very dilute, its odor is like that of ozone. It is comparable to chlorine in its toxicity.

Chlorine(IV) oxide is soluble in water[7] and in alkaline and sulfuric acid solutions. It forms a hydrate which conforms approximately to the formula $ClO_2 \cdot 8H_2O$.[8]

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CHAPTER VIII

52. IRON(II) FORMATE

(Ferrous Formate)

$$\mathrm{Fe + 2HCOOH + 2H_2O \rightarrow Fe(HCOO)_2{\cdot}2H_2O + H_2}$$

Submitted by Richard N. Rhoda* and Anthony V. Fraioli*
Checked by William Lloyd Taylor† and Jacob Kleinberg†

Iron(II) formate can be prepared by the action of formic acid on pure iron or by a number of double-displacement reactions.[1] The method based on the reaction of iron with acid was adopted because of the ease of isolating the final product and of preventing the oxidation of the iron(II) compound. Care must be taken along two lines: contact of the solutions or wet salt with air must be minimized, and an excess of acid must be present in the aqueous solutions.

Procedure

Thirty grams of pure iron powder (0.54 mol) is placed in the bottom of a three-necked 2-l. flask equipped with (1) a reflux condenser with a stopper and small glass tube or Bunsen valve at the terminal end to allow venting of the hydrogen and to minimize entrance of air into the system; (2) a siphon line‡ with a glass-wool plug as a strainer, filled with water and closed with a stopcock or pinch clamp until needed; and (3) a separatory funnel. Twelve hundred milliliters of distilled water and 100 ml. of 45% formic acid are introduced into the flask. The contents are boiled until

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* Lehigh University, Bethlehem, Pa. This work was carried out with the approval of the Office of Naval Research under a research project devoted to the preparation of ultrafine ferromagnetic powders.

† University of Kansas, Lawrence, Kan.

‡ The checkers performed the operation without the siphon, using a two-necked flask, and filtering directly into a Büchner funnel.

hydrogen evolution ceases (2 to 3 hours). Fifty milliliters of 45% formic acid is added, and another 50 ml. of the acid is placed in a 2-l. filter flask. The iron(II) formate solution is then siphoned into the filter flask. The filter flask is closed with a cork stopper, heated on a hot plate, and simultaneously evacuated with a water aspirator, until crystals form (2 to 4 hours). The filter flask should be held firmly in place to avoid movement of the flask when crystals precipitate. The flask is then removed from the hot plate and cooled in an ice bath.

The crystals are filtered on a Büchner funnel, some solution being constantly maintained over the crystals. A second batch of crystals is obtained by adding ethanol to the filtrate until crystallization begins. This second crop is added to the original batch of crystals. The product is washed with 95% ethanol and dried in a vacuum desiccator. Recrystallization does not improve the purity of the product. Yield, 90%. *Anal.* Calcd. for $Fe(HCOO)_2 \cdot 2H_2O$: Fe, 30.70; C, 13.19; H, 3.32. Found: Fe, 30.61; C, 13.17; H, 3.50. Qualitative test for ferric ion: negative.

Properties

Iron(II) formate 2-hydrate crystallizes from water as pale green, hexagonal platelets. Crystallization by addition of ethanol to the saturated aqueous solution gives interesting results depending upon the ratio of water to alcohol. As the concentration of ethanol is increased and the ratio approaches 1:1, a change in the mode of precipitation occurs and needlelike crystals are formed. The first crystals formed are somewhat thick and short and are macro in nature. After 5 or 10 minutes, a second nucleation occurs, and the resulting microcrystals are elongated and thinner than those in the preceding batch. Iron(II) formate loses its water of hydration in the range 140 to 150°. Gradual decomposition occurs above 200°. It is slightly soluble in water and insoluble in ethanol. The dry material

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shows a slight tendency to oxidize in air, the oxidation being more pronounced with finer precipitates.

Reference

1. Scheurer-Kestner: *Bull. soc. chim. France*, **5**, 34 (1863).

53. IRON(II) BROMIDE 6-AMMONIATE

$$Fe + 2HBr \rightarrow FeBr_2 + H_2$$
$$FeBr_2 + 6NH_3 \rightarrow FeBr_2 \cdot 6NH_3$$

Submitted by George W. Watt* and W. A. Jenkins*
Checked by Harry H. Sisler† and F. R. Hurley†

Ammoniates of iron(II) salts have been prepared by the reaction of ammonia with iron(II) salts in solution[1] or in the solid state.[2] In either case, the purity of the final product has been limited by the difficulty of producing and maintaining the iron(II) salts in a high state of purity. The simple procedure outlined below, which is a modification of that described by Weitz and Muller,[1] obviates these difficulties without sacrificing either yield or purity.

Procedure

The reactions are carried out in a 1-l. round-bottomed flask (Fig. 18) sealed to a dropping funnel and a gas inlet tube *A*.‡ The neck of the flask is closed with a rubber stopper bearing a gas inlet *C* and an outlet tube *B* (i.d. at least 5 mm.). The latter is connected to a filter assembly which consists of a 25-mm.-i.d. filter tube with a fritted-glass filter plate *D* (porosity B). The distance from the filter plate to the top of the tube should be at least 35 cm. As shown in Fig. 18, tubes *B* and *C* extend into the flask through glass sleeves and are attached to these sleeves by means of rubber tubing so that *B* and *C* may be raised or lowered.

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† Ohio State University, Columbus, Ohio.

‡ For the sake of simplicity, a three-necked flask may be substituted; gas inlet tube *A* and the dropping funnel may then be connected through rubber stoppers.

Nine and three-tenths grams of pure iron (0.167 mol) in the form of primary-standard iron wire (99.9% Fe) is placed in the flask, and with *C* attached to a source of anhydrous ammonia gas and *B* lowered as shown in Fig. 18, air is completely displaced from the system by means of hydrogen admitted through *A*. Tube *B* is raised, and 236 ml. of 40% hydrobromic acid (sp. gr. 1.38) (1.61 mols) is introduced through the dropping funnel. Tube *B* is lowered to within $2\frac{1}{2}$ cm. of the surface of the liquid, and the flow of hydrogen is maintained at a low rate.

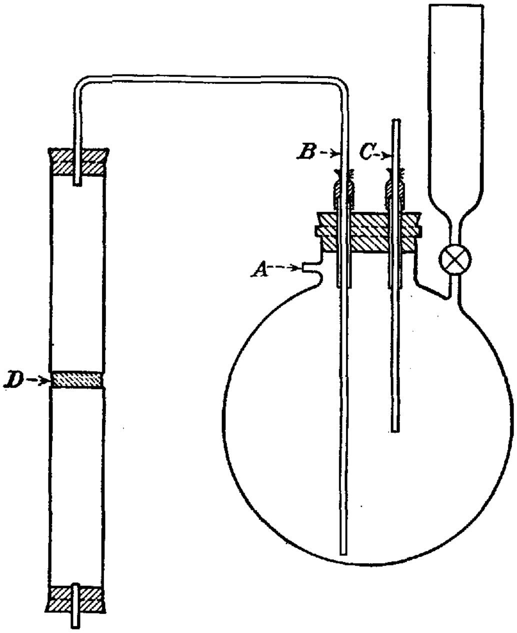

Fig. 18. Apparatus for the preparation of iron(II) bromide 6-ammoniate.

Reaction is accelerated by gentle heating on a steam bath. After the iron has been dissolved, 77 ml. of water is added, and the flask and its contents are cooled with an ice bath while ammonia is admitted through *C*. Tube *C* is then lowered to the bottom of the flask, and ammonia is admitted at a rate such that the green precipitate which forms upon neutralization of the excess hydrobromic acid is not allowed to settle. The green precipitate is progressively replaced by light blue-gray crystals of iron(II) bromide 6-ammoniate. Addition of ammonia is continued until no further color change is observed.

Tube *C* is raised, the flow of ammonia is stopped, tube *B* is lowered, and the crystals and mother liquor are carried over to the filter tube as a slurry by means of the hydrogen gas pressure. The solid product is washed with four or five 100-ml. portions of absolute ethanol which has been saturated with ammonia, followed by four or five 100-ml. portions of absolute ethyl ether. These wash liquids are introduced through the dropping funnel, after first reducing the rate of flow of hydrogen in order to avoid excessive positive pressure within the system. The solid is dried on the filter plate by passing anhydrous ammonia gas through it for 30 min. Thereafter, the filter assembly is transferred to a dry box, and the product is transferred under an atmosphere of ammonia to vials which are subsequently sealed. The yield is essentially quantitative. *Anal.* Calcd. for $FeBr_2 \cdot 6NH_3$: Fe, 17.6; NH_3, 32.1. Found: Fe, 17.9; NH_3, 32.2.

Properties

Iron(II) bromide 6-ammoniate is a pale blue-gray crystalline solid which decomposes to form a brown solid of undetermined composition when exposed to the atmosphere.

References

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2. Jackson and Derby: *Am. Chem. J.* **24**, 15 (1900).

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54. POTASSIUM FERRATE(VI)

$$3ClO^- + 2Fe(OH)_3(H_2O)_3 + 4K^+ + 4OH^- \rightarrow 3Cl^- + 2K_2FeO_4 + 11H_2O$$

Submitted by J. M. Schreyer,[*] G. W. Thompson,[*] and L. T. Ockerman[*]
Checked by Bodie E. Douglas,[†] Milton K. Snyder,[‡] and Therald Moeller[‡]

Potassium ferrate(VI) has been prepared in an impure state and in low yields by the action of chlorine or bromine on hydrous iron(III) oxide suspended in potassium hydroxide solutions. The procedure described here is a modification of the chlorine oxidation method[1] which facilitates the production of 5- to 10-g. samples of potassium ferrate(VI) in a fair state of purity and in good yield.

Procedure[2]

A solution of 30 g. of sodium hydroxide (0.75 mol) in 75 ml. of water is cooled and chlorinated with vigorous stirring while the temperature is kept below 20°. Chlorination is continued until the weight of the solution has increased by 20 g. (about 1 hour). Seventy grams of solid sodium hydroxide (1.75 mols) is added slowly with stirring; the temperature is permitted to rise as high as 25 to 30° to aid in the dissolution of the sodium hydroxide. Finally, the mixture is cooled to 20°. The precipitated sodium chloride is removed by filtration through a fritted-glass filter of large surface area and coarse porosity.[§]

The alkaline hypochlorite solution is maintained at 25 to 30° while 25 g. of pulverized iron(III) nitrate 9-hydrate (0.06 mol) is added in small portions over a period of 45 minutes to 1 hour. Sodium hydroxide is added to the solution until saturation is reached; during this operation the temperature is maintained at 30°. The mixture is then fil-

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[‡] University of Illinois, Urbana, Ill.

[§] Checkers Snyder and Moeller recommend cooling the hypochlorite solution to less than 10° to remove a greater amount of the sodium chloride.

tered with suction through fritted glass. The filter must have a disk of large surface area and of coarse porosity to allow rapid filtration. Glass wool on top of the fritted-glass filter aids in the filtration. Extended periods of filtration greatly reduce the yield of potassium ferrate(VI).*

The filtrate containing the sodium ferrate is transferred to a 250-ml. beaker, which is put in a water bath at 20°, and 100 ml. of saturated potassium hydroxide solution is added with stirring. Stirring is continued for 5 minutes, after which the suspension is filtered through a fritted-glass filter of medium porosity and large surface area (centrifugation may be substituted for filtration here).† The filtrate is discarded.

The precipitate is leached successively on the filter with four or five 10-ml. portions of 3 *M* potassium hydroxide solution. All the washings are drawn through the filter into the same 50-ml. volume of chilled, saturated potassium hydroxide solution. The residue remaining on the filter is discarded. The filtrate is transferred to a 250-ml. beaker, and any solid potassium ferrate(VI) remaining in the filter flask is washed out with a few milliliters of saturated potassium hydroxide solution. An additional 50 ml. of chilled, saturated potassium hydroxide solution is added. The final mixture is approximately 11 *M* in potassium hydroxide. This suspension is stirred for 5 minutes and then filtered through a fritted-glass filter of medium porosity.

The precipitate remaining on the filter is washed with 10 ml. of benzene in order to remove the excess water (the ferrate ion would oxidize ethanol containing as much as 20% water). Three to five 20-ml. portions of 95% ethanol are then drawn through the filter. The precipitate is transferred to a beaker containing 100 ml. of 95% ethanol and

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* The checkers found that best results were obtained by centrifuging for 40 minutes and then filtering rapidly through a coarse filter, instead of filtering the thick suspension directly. In this way, the filtration is rapid and the removal of hydrated iron(III) oxide is complete.

† The checkers recommend filtration through a coarse porosity filter at this point.

stirred for 20 minutes. This washing is repeated three times. The precipitate is isolated by filtration and dried with 50 ml. of ethyl ether. During this drying operation, a calcium chloride tube is used to protect the potassium ferrate(VI) from the moisture of the atmosphere. Suction is continued for 20 minutes, and final drying is accomplished by the use of a vacuum desiccator. The potassium ferrate sample should be stored in a desiccator.

By this procedure, samples ranging in purity from 90 to 97% potassium ferrate(VI) are obtained in yields as high as 50%. If centrifugation is used instead of filtration, yields up to 75% can be obtained.*

If it is desirable to obtain a sample of greater purity than those prepared by the recommended procedure, the sample may be subjected to an additional reprecipitation from 6 *M* potassium hydroxide solution, using the same procedure as described above. Such additional purifications of samples give products ranging in purity from 98.5 to 99% potassium ferrate(VI); however, a large amount of the potassium ferrate(VI) is lost in the process.

Analysis[3]

Solutions Required

Chromium(III) chloride stock solution: 25 g. of chromium(III) chloride 6-hydrate (0.0938 mol) is dissolved in 150 ml. of distilled water.

Saturated sodium hydroxide, reducing-agent-free: 0.05 g. of potassium ferrate(VI) is added to 500 ml. of cooled, saturated sodium hydroxide solution, and the solution is decolorized by boiling.

Sulfuric acid–phosphoric acid mixture: 60 ml. of concen-

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* Since solutions of the ferrate(VI) ion are extremely unstable, good yields are not easily obtained. Checkers Snyder and Moeller obtained a maximum yield of 42%. Checker Douglas obtained only 30% of the theoretical amount in 93% purity, but was able to obtain a higher yield (68%) in a poorer state of purity.

trated sulfuric acid (sp. gr. 1.84) and 150 ml. of 85% phosphoric acid are added to 240 ml. of distilled water.

Procedure. Twenty milliliters of saturated sodium hydroxide, free from reducing agents, is added to 5 ml. of chromium(III) chloride stock solution and 5 ml. of distilled water in a 500-ml. flask. The solution is cooled to room temperature. (A fresh solution should be prepared immediately prior to each analysis.) A weighed sample, containing approximately 0.10 to 0.20 g. of potassium ferrate(VI), is introduced into the flask containing the alkaline chromite solution. The potassium ferrate(VI) sample is added very carefully so that the sample does not strike the sides of the flask. The liquid is swirled rapidly until dissolution of the potassium ferrate(VI) is complete (addition of acid before dissolving is complete will result in low values). The flask is placed in an ice bath, and 100 ml. of 6 *N* sulfuric acid, 100 ml. of water, and 15 ml. of the sulfuric acid–phosphoric acid mixture are added. The solution is titrated immediately with standard ferrous solution, using 5 to 6 drops of sodium diphenylaminesulfonate as the indicator. The percentage of potassium ferrate(VI) is calculated using the equivalent weight, 198.04/3.

Properties

Pure potassium ferrate(VI) is a dark, reddish-black powder exhibiting numerous silvery iridescent flashes due to the reflection of light by the small crystals. Dry potassium ferrate(VI) is stable at temperatures below 198°. Potassium ferrate(VI) is very soluble in water, giving a blood-red solution with a color intensity comparable to that of potassium permanganate solutions. Water solutions of potassium ferrate(VI) decompose upon standing, evolving oxygen and precipitating hydrous iron(III) oxide. The alkalinity of the solutions increases as decomposition proceeds. Potassium ferrate(VI) dissolved in strongly alkaline solution is relatively stable; however, the ferrate(VI) ion is a powerful oxidizing agent, even in alkaline solution.

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2. Thompson, Ockerman, and Schreyer: *J. Am. Chem. Soc.*, **73**, 1379 (1951).
3. Schreyer, Thompson, and Ockerman: *Anal. Chem.*, **22**, 1426 (1950).

55. NITROSYLPENTAMMINECOBALT(II) CHLORIDE, BLACK, AND NITROSYLPENTAMMINECOBALT(III) CHLORIDE, PINK

$$CoCl_2 \cdot 6H_2O + 5NH_3 + NO \rightarrow [Co(NH_3)_5NO]Cl_2 + 6H_2O$$

Submitted by Therald Moeller* and Glendall L. King*
Checked by Fred Basolo†

Compounds containing the cation $[Co(NH_3)_5NO]^{++}$ are obtained when aqueous cobalt(II) salt solutions containing ammonia are saturated with nitrogen(II) oxide.[1] These compounds are either black or pink, depending upon the conditions used in their preparation. The black chloride and iodate are formed in the absence of air,[2-4] whereas many members of the pink series are obtained in the presence of air.[2-4] The method of preparation for the black chloride described here is a composite of those recommended by various authors[1-5] and gives a product of considerable stability. The same reaction, using cobalt(II) nitrate, when run in the presence of air and at room temperature, may be used for the preparation of the pink nitrate. This may be converted into the pink chloride by treatment with concentrated hydrochloric acid.[3]

Procedure

An apparatus is set up as indicated in Fig. 19. The reaction vessel *A* is a sintered-glass filter funnel, about 4 in. in diameter. This is surrounded by a bath *B*, constructed from a bottle with the bottom removed and containing an

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† Northwestern University, Evanston, Ill.

ice-salt mixture.* Stopcocks *C* and *D* are opened, and the apparatus is flushed with nitrogen for 30 minutes. Stopcock *C* is closed, and the apparatus is flushed for at least 15 minutes with nitrogen(II) oxide generated by adding acidified iron(II) sulfate solution to solid sodium nitrite.[6] Toward the end of this period, stopcock *D* is closed.

Twenty-five grams of cobalt(II) chloride 6-hydrate (0.105 mol) is dissolved in 50 to 60 ml. of distilled water. The solution is cooled with an ice-salt bath, and 150 ml. of concentrated aqueous ammonia (sp. gr. 0.90) (2.25 mols) is added slowly with stirring. Any pink precipitate which forms is removed by filtration and discarded. The cold filtrate is transferred through the dropping funnel *E* to the reaction vessel *A*, care being exercised to close stopcock *C* just before the last of the solution flows through. Nitrogen(II) oxide is passed through the solution in the reaction vessel by means of a large-bore inlet tube for 3 to 4 hours. The mother liquor is then removed from the precipitated product by opening stopcock *D* and applying suction to the filter flask *F*. The nitrogen(II) oxide atmosphere is replaced with nitrogen, and the shiny black crystals on the filter are washed successively with 150 ml. of absolute alcohol (in several portions) and 50 to 60 ml. of ether which has been dried over sodium metal. Both wash solutions are introduced through the funnel *E*, care being taken that no air enters the apparatus when stopcock *C* is manipulated.

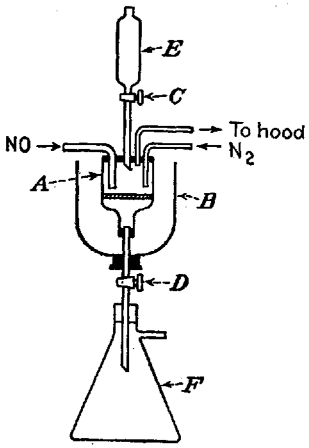

FIG. 19. Apparatus for the preparation of nitrosylpentamminecobalt(II) chloride.

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* Although bath *B* as indicated in Fig. 19 is desirable, good results may also be obtained by omitting this bath, stoppering the bottom of *A*, placing *A* in a beaker containing ice and salt until the reaction is complete, and then attaching *A* to filter flask *F* for the remainder of the procedure.

After the ether wash, the apparatus is dismantled, and the crystals are removed and stored in a desiccator over anhydrous calcium chloride. The yield is about 20 g. (78%, based on cobalt(II) chloride). *Anal.* Calcd. for $[Co(NH_3)_5NO]Cl_2$: Co, 24.1; Cl, 28.9. Found: Co, 23.9; Cl, 28.3.

Properties

Black nitrosylpentamminecobalt(II) chloride is a lustrous, crystalline solid. It is stable when perfectly dry, but in the presence of moisture it changes rapidly to the pink isomer. Samples prepared by the above procedure appear to be particularly stable, some having been kept for at least 5 years without decomposition.

The relations between the black and the pink series are interesting but incompletely elucidated. The black compounds not only are unstable with respect to the pink but also evolve nitrogen(II) oxide and give cobalt(II) salts on treatment with acids. The pink compounds are reasonably stable in contact with acids, although direct replacement of the NO groups by species such as chloride can occur. Compounds of the black series are paramagnetic, whereas those of the pink series are diamagnetic.[3–5,7,8] Chemical and magnetic evidences indicate strongly that the black compounds contain dipositive cobalt.[4,7] Both dimeric structures based upon $—N_2O_2—$ groups[2,7] and monomeric structures based upon 3-electron bonds in neutral NO groups[4,5] seem to be consistent with available data. The pink compounds contain tripositive cobalt and NO^- groups[7] and are, therefore, members of the acidopentammine series, $[Co(NH_3)_5X]^{++}$. Conversion of a black compound to its pink isomer thus involves removal of an electron from the cobalt(II) ion and conversion of a neutral NO group to an NO^- ion.

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56. ACIDOPENTAMMINECOBALT(III) SALTS

Submitted by Fred Basolo* and R. Kent Murmann*
Checked by James E. Whitney† and Carl L. Rollinson†

Many methods have been used for the preparation of various acidopentamminecobalt(III) salts.[1] In some instances these procedures are specific for the synthesis of a particular salt. The procedure suggested here involves the reaction of carbonatopentamminecobalt(III) nitrate with an acid or acid salt. The resulting reaction mixture may then be digested for a short time to yield the desired product, or the aquo complex is isolated and converted to the acido compound at an elevated temperature. This method appears to be completely general and has been used to synthesize complexes containing coordinated bromide, chloride, thiocyanate, sulfate, formate, and various substituted acetates, benzoates, and benzenesulfonates in addition to those described here.

Procedure

A. CARBONATOPENTAMMINECOBALT(III) NITRATE[2]

$$4Co(NO_3)_2 + 4(NH_4)_2CO_3 + 16NH_3 + O_2 \rightarrow 4[Co(NH_3)_5CO_3]NO_3 + 4NH_4NO_3 + 2H_2O$$

A solution of 300 g. of cobalt(II) nitrate 6-hydrate (1.03 mols) in 150 ml. of water is thoroughly mixed with a solution of 450 g. of ammonium carbonate (4.68 mols) in 450 ml. of water and 750 ml. of concentrated aqueous ammonia (sp. gr. 0.90, 28% NH_3). A stream of air is bubbled slowly through the mixture for 24 hours. After the mixture has been cooled in an ice-salt bath overnight, the product is collected on a filter, washed with not more than 50 ml. of ice-

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† University of Maryland, College Park, Md.

cold water, followed by alcohol and ether, and dried at 50°. Yield, 180 g. (64%). This crude material is purified by recrystallization from water. The 180 g. of solid is dissolved, with stirring, in 550 ml. of water at 90°. The solution is filtered, and the filtrate is cooled in an ice-salt bath. The crystals are collected on a filter, washed with 50 ml. of ice-cold water, followed by alcohol and ether, and dried at 50°. Yield, 120 g. (42%). *Anal.** Calcd. for $[Co(NH_3)_5CO_3]NO_3 \cdot \frac{1}{2}H_2O$: NH_3, 30.9. Found: NH_3, 30.4.

B. FLUOROPENTAMMINECOBALT(III) NITRATE

$$[Co(NH_3)_5CO_3]NO_3 + 2NH_4HF_2 \rightarrow [Co(NH_3)_5F]FNO_3 + 2NH_4F + CO_2 + H_2O$$

$$[Co(NH_3)_5F]FNO_3 + NH_4NO_3 \rightarrow [Co(NH_3)_5F](NO_3)_2 + NH_4F$$

Ten grams of carbonatopentamminecobalt(III) nitrate (0.036 mol) is suspended in 25 ml. of water, and 4.5 g. of ammonium hydrogen fluoride (0.079 mol) and 15 g. of ammonium fluoride (0.405 mol) are added. The reaction mixture is kept at approximately 90° in a water bath for 1 hour, with occasional stirring. During this digestion some decomposition takes place, and noticeable quantities of ammonia are evolved. The mixture is then cooled to room temperature, 75 ml. of water being added to keep the products in solution. This solution is filtered, and 20 g. of solid ammonium nitrate (0.25 mol) is added to the filtrate. Pink crystals separate immediately after the mixture is cooled in an ice-salt bath. The product is collected on a filter, washed with 10 ml. of ice-cold water, followed by alcohol and ether, and then dried at 90°. Yield, 6 g. (58%).

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* The submitters of the synthesis analyzed these compounds for ammonia by the method of Horan and Eppig [*J. Am. Chem. Soc.*, **71**, 581 (1949)]. This involves heating the sample in excess alkali and determining the amount of ammonia liberated. Arsenic(III) oxide is added to prevent oxidation of the ammonia by the cobalt(III). In the hands of the checkers, however, this method gave low results. Analysis for carbon, hydrogen, and cobalt by the microcombustion procedures is difficult but gives satisfactory results.

Anal. Calcd. for $[Co(NH_3)_5F](NO_3)_2$: NH_3, 29.6. Found: NH_3, 29.5.

C. IODOPENTAMMINECOBALT(III) NITRATE[3]

$$[Co(NH_3)_5CO_3]NO_3 + KI \rightarrow [Co(NH_3)_5CO_3]I + KNO_3$$
$$[Co(NH_3)_5CO_3]I + 2HI \rightarrow [Co(NH_3)_5H_2O]I_3 + CO_2$$
$$[Co(NH_3)_5H_2O]I_3 \rightarrow [Co(NH_3)_5I]I_2 + H_2O$$
$$[Co(NH_3)_5I]I_2 + 2NH_4NO_3 \rightarrow [Co(NH_3)_5I](NO_3)_2 + 2NH_4I$$

Ten grams of carbonatopentamminecobalt(III) nitrate (0.036 mol) is dissolved in 40 ml. of water at 80 to 90°, and 12.5 g. of finely powdered potassium iodide (0.075 mol) is added. The solution is cooled in an ice-salt bath, and the crystals which separate are collected on a filter. After it is washed with 10 ml. of ice-cold water, followed by alcohol and ether, the salt is dried at 50°. Yield, 9 g. (76%). *Anal.* Calcd. for $[Co(NH_3)_5CO_3]I$: NH_3, 25.6. Found: NH_3, 25.5.

The 9 g. of salt obtained above is suspended in 25 ml. of water, and 20 ml. of hydriodic acid (1:1 concentrated acid and water) is added with stirring. When the reaction is complete, as indicated by cessation of evolution of carbon dioxide, 100 ml. of methanol is added to the slurry. The precipitate is collected on a filter, washed with methanol and ether, and dried at room temperature. Yield, 13 g. (88%). *Anal.* Calcd. for $[Co(NH_3)_5H_2O]I_3$: NH_3, 15.7. Found: NH_3, 16.0. The salt is next placed in a drying oven at 60°. In approximately 8 hours the calculated loss in weight corresponding to the escape of 1 mol of water is obtained. *Anal.* Calcd. for $[Co(NH_3)_5I]I_2$: NH_3, 16.2. Found: NH_3, 16.3.

Twelve and one-half grams of iodopentamminecobalt(III) iodide (0.023 mol) is ground in a mortar with 200 g. of ammonium nitrate (2.50 mols) and 100 ml. of water. The residue is collected on a filter and returned to the mortar. Ammonium nitrate and water are added as before, and the grinding procedure is repeated. The residue is again collected on a filter and washed with cold water until the filtrate is no longer orange, but instead is faintly greenish. The salt is finally washed with methanol and ether and dried at 50°. Yield, 7.8 g. (86%). *Anal.* Calcd. for $[Co(NH_3)_5I](NO_3)_2$: NH_3, 21.8. Found: NH_3, 21.8.

D. NITROPENTAMMINECOBALT(III) NITRATE[4]

$$[Co(NH_3)_5CO_3]NO_3 + 2HNO_3 + NaNO_2 \rightarrow [Co(NH_3)_5NO_2](NO_3)_2 + NaNO_3 + CO_2 + H_2O$$

Ten grams of carbonatopentamminecobalt(III) nitrate (0.036 mol) is suspended in 25 ml. of water, and 10 g. of sodium nitrite (0.14 mol) and 10 ml. of colorless nitric acid (1:1 concentrated acid and water) are added. The mixture is stirred for 15 minutes at room temperature, and then 200 ml. of methanol is added to the slurry. The precipitate is collected on a filter, washed with methanol and ether, and dried at 50°. Yield, 10 g. (88%). *Anal.* Calcd. for $[Co(NH_3)_5NO_2](NO_3)_2$: NH_3, 27.1. Found: NH_3, 27.1.

E. NITRATOPENTAMMINECOBALT(III) NITRATE[5]

$$[Co(NH_3)_5CO_3]NO_3 + 2HNO_3 \rightarrow [Co(NH_3)_5H_2O](NO_3)_3 + CO_2 + H_2O$$

$$[Co(NH_3)_5H_2O](NO_3)_3 \rightarrow [Co(NH_3)_5NO_3](NO_3)_2 + H_2O$$

Ten grams of carbonatopentamminecobalt(III) nitrate (0.036 mol) is suspended in 25 ml. of water, and 20 ml. of colorless nitric acid (1:1 concentrated acid and water) is added with stirring. When the evolution of carbon dioxide has stopped (10 minutes), 100 ml. of methanol is added, the aquopentammine cobalt(III) nitrate is collected on a filter, and washed with alcohol and ether. This salt is heated at 100° for 18 hours (until 1 mol of water is lost), yielding 10 g. (83%) of the desired material. *Anal.* Calcd. for $[Co(NH_3)_5NO_3](NO_3)_2$: NH_3, 25.8. Found: NH_3, 25.6.

F. ACETATOPENTAMMINECOBALT(III) NITRATE

$$2[Co(NH_3)_5CO_3]NO_3 + 4HC_2H_3O_2 \rightarrow [Co(NH_3)_5C_2H_3O_2](NO_3)_2 + [Co(NH_3)_5C_2H_3O_2](C_2H_3O_2)_2 + 2CO_2 + 2H_2O$$

$$[Co(NH_3)_5C_2H_3O_2](C_2H_3O_2)_2 + 2NH_4NO_3 \rightarrow [Co(NH_3)_5C_2H_3O_2](NO_3)_2 + 2NH_4C_2H_3O_2$$

Five grams of carbonatopentamminecobalt(III) nitrate (0.018 mol) is suspended in 15 ml. of water, and 12 g. of glacial acetic acid (0.20 mol) is added. The reaction mixture is concentrated on a steam bath for 1.5 hours, during which time a red crystalline salt separates. After cooling to room temperature, 50 ml. of water is added, and the product is collected on a filter. After removing the mother liquor from the filter flask, the salt is washed with 50 ml. of cold water, followed by alcohol and ether, and dried at 50°. Yield, 3 g. (53%). *Anal.** Calcd. for $[Co(NH_3)_5C_2H_3O_2](NO_3)_2$: NH_3, 26.0. Found NH_3, 26.2. An additional 2 g. (over-all yield, 88%) of the salt may be obtained by adding 15 g. of ammonium nitrate (0.19 mol) to the mother liquor. The precipitated salt is collected, washed, and dried as described above.

Properties

The acidopentamminecobalt(III) salts have characteristic colors dependent upon the atom coordinated, *i.e.*, salts in which there is a cobalt-oxygen bond vary in color from pink to red; the fluoro complex is pink; the chloro, red; the bromo, purple; the iodo, olive green; and the nitro, orange. The nitrate salts of most of these complexes are only slightly soluble in water. None of these compounds is soluble in nonpolar solvents. Solutions of the compounds may decompose after long standing, liberating ammonia and cobalt hydroxide. Rates of aquation and of hydrolysis

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* Since the calculated percentage of ammonia in $[Co(NH_3)_5C_2H_3O_2](C_2H_3O_2)_2$ is 26.5, the above analysis does not distinguish between the acetate and nitrate salt. The presence of nitrate ion is readily demonstrated by means of a qualitative test. Acetate ion may also be present.

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have been determined for some of these salts.[6] A detailed discussion of the properties and formation of several such compounds appears in the treatise edited by Friend.[1]

References

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4. JÖRGENSEN: *Z. anorg. Chem.*, **5,** 147, (1894).
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6. LAMB and MARDEN: *J. Am. Chem. Soc.*, **33,** 1873 (1911); GARRICK: *Trans. Faraday Soc.*, **33,** 486 (1937); PUENTE: *Anales asoc. quim. argentina,* **31,** 5 (1943); *ibid.*, **33,** 43 (1945).

57. *cis*- AND *trans*-DINITROBIS(ETHYLENEDIAMINE) COBALT(III) NITRATE

SUBMITTED BY HENRY F. HOLTZCLAW, JR.,* DAVID P. SHEETZ,* AND BILL D. MCCARTY*
CHECKED BY DARYLE H. BUSCH† AND MILTON TAMRES†

Classical methods for the synthesis of *trans*-dinitrobis(ethylenediamine)cobalt(III) nitrate involve conversion of the cis isomer by heat[1] or action of sodium nitrite on *trans*-chloronitrobis(ethylenediamine)cobalt(III) nitrate.[2] These methods involve isolation of intermediate coordination compounds and consequently are subject to low yields, based upon original cobalt(II) salt. The following procedure for the preparation of the trans compound gives an 84% yield; it depends upon oxidation of cobalt(II) to cobalt(III) in the presence of sodium nitrite, ethylenediamine, and nitric acid.

Werner[1,3] prepared *cis*-dinitrobis(ethylenediamine)cobalt(III) nitrate by heating ethylenediamine with potassium hexanitrocobaltate(III) to give the dinitrobis(ethylenediamine)cobalt(III) nitrite, followed by conversion to the nitrate with nitric acid. The procedure given here for the cis compound utilizes this method.

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Procedure

A. *trans*-DINITROBIS(ETHYLENEDIAMINE)COBALT(III) NITRATE

$$4\{Co(NO_3)_2 \cdot 6H_2O\} + 8NaNO_2 + 4C_2H_4(NH_2)_2 + 4C_2H_4(NH_2)_2 \cdot HNO_3 + O_2 \rightarrow 4\ \textit{trans}\text{-}[Coen_2(NO_2)_2]NO_3 + 8NaNO_3 + 26H_2O$$

A mixture of 6.85 g. of 70% ethylenediamine (0.080 mol) and 10 ml. of water is partially neutralized by the addition of 3 ml. of concentrated nitric acid (0.048 mol). The resulting solution is added to a solution of 11.5 g. of cobalt(II) nitrate 6-hydrate (0.040 mol) and 6.0 g. of sodium nitrite (0.087 mol) in 20 ml. of water.

A vigorous stream of air is drawn or passed through the solution. The yellow *trans*-dinitrobis(ethylenediamine)-cobalt(III) nitrate begins to precipitate after a few minutes, and the reaction is complete in about 20 minutes. The mixture is cooled in an ice-salt bath and filtered. The yellow crystalline solid is recrystallized from boiling water, washed with alcohol and ether, and air-dried. The yield of *trans*-dinitrobis(ethylenediamine)cobalt(III) nitrate is 11.2 g. (84%, based on cobalt(II) nitrate 6-hydrate). *Anal.* Calcd. for $[Coen_2(NO_2)_2]NO_3$: Co, 17.7; N, 29.44. Found: Co, 17.5; N, 29.52.

B. *cis*-DINITROBIS(ETHYLENEDIAMINE)COBALT(III) NITRATE

$$K_3[Co(NO_2)_6] + 2C_2H_4(NH_2)_2 \rightarrow \textit{cis}\text{-}[Coen_2(NO_2)_2]NO_2 + 3KNO_2$$

$$2\ \textit{cis}\text{-}[Coen_2(NO_2)_2]NO_2 + 2HNO_3 \rightarrow 2\ \textit{cis}\text{-}[Coen_2(NO_2)_2]NO_3 + NO_2 + NO + H_2O$$

Forty-eight grams of a 10% ethylenediamine solution (0.080 mol of en) is added to 20 g. of potassium hexanitrocobaltate(III) (0.044 mol). The mixture is stirred constantly while it is heated slowly on a steam bath to about

70°,* whereupon the reaction occurs, as evidenced by the dissolving of the yellow hexanitrocobaltate to form a dark brown solution. While it is still hot, the reaction mixture is filtered to remove any traces of unreacted hexanitrocobaltate, and the filtrate is cooled in an ice-salt bath to precipitate the brown *cis*-dinitrobis(ethylenediamine)cobalt(III) nitrite.† The crystals are removed by filtration. A second crop of crystals can be obtained by concentrating the solution to about two-thirds of its volume at room temperature, and then cooling in an ice-salt bath. This second fraction may, however, be contaminated with the trans isomer.

The *cis*-dinitrobis(ethylenediamine)cobalt(III) nitrite is dissolved in a minimum volume of lukewarm water (no warmer than 60°). Concentrated nitric acid is added dropwise until gas evolution ceases. During the addition of the acid, *cis*-dinitrobis(ethylenediamine)cobalt(III) nitrate precipitates. The mixture is cooled in an ice-salt bath, and the brown-yellow crystals are removed by filtration. The salt is recrystallized twice from water, care being taken to keep the temperature of the solution below 60°. The yield of *cis*-dinitrobis(ethylenediamine)cobalt(III) nitrate is 2.0 g. (15% based on ethylenediamine). *Anal.* Calcd. for $[Coen_2(NO_2)_2]NO_3$: Co, 17.7. Found: Co, 17.8.

Properties

The isomeric dinitrobis(ethylenediamine)cobalt(III) nitrates are relatively insoluble, 1.20 g. of the cis compound

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* The reaction occurs at temperatures ranging from 55 to 80°. If reaction has not occurred by the time the temperature reaches 75°, the reaction mixture should be removed from the steam bath and stirred for a few minutes without further heating. If no indication of reaction is evident, the mixture may be heated 2 to 3° higher with stirring. A temperature of 75° or less is usually sufficient. Experience enables one to recognize the first signs of reaction, after which further heating is not necessary. The cis isomer is readily converted to the trans upon heating, so care must be taken to keep the temperature as low as possible.

† If supersaturation occurs, precipitation can be induced by use of the common techniques or by allowing the solution to stand overnight.

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and 2.202 g. of the trans compound dissolving in 100 ml. of water at 22°.[4]

When crystallized rapidly, the cis isomer appears as a mass of golden-yellow needles, whereas the trans isomer precipitates as small yellow plates.

The configurations of the cis and trans forms of dinitrobis(ethylenediamine)cobalt(III) ion were established by Werner,[4] who resolved the cis form into its optical antipodes. The cis and trans isomers may also be distinguished chemically by utilization of the fact that a warm aqueous 3% solution of the cis form yields precipitates when treated with concentrated solutions of potassium chromate, ammonium oxalate, or sodium thiosulfate; a warm 10% solution of the trans form gives no precipitate with any of these reagents.[3]

References

1. Werner: *Ann.*, **386**, 248 (1912).
2. Werner: *ibid.*, 252.
3. Werner and Humphrey: *Ber.*, **34**, 1720 (1901).
4. Werner: *ibid.*, **44**, 2445 (1911).

58. *trans*-DINITRODIAMMINEPALLADIUM(II)

$$PdCl_2 + 4NH_3 \rightarrow [Pd(NH_3)_4]^{++} + 2Cl^-$$

$$[Pd(NH_3)_4]^{++} + 2NO_2^- + 2H^+ \rightarrow \textit{trans}\text{-}[Pd(NH_3)_2(NO_2)_2] + 2NH_4^+$$

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Checked by H. F. Holtzclaw† and K. W. R. Johnson†

trans-Dinitrodiamminepalladium(II) has been prepared by the action of silver nitrite upon the *trans*-dichlorodiamminepalladium(II) complex[1] and by the prolonged treatment of an aqueous suspension of the dichlorodiamminepalladium(II) complex with a sodium nitrite solution.[2] Both methods require the preparation of the dichloro complex as a starting material. The method given here utilizes palladium(II) chloride as a starting material and is not so

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tedious as those mentioned above, although the yields obtained are slightly lower.

Procedure

Two and one-half grams of palladium(II) chloride (0.014 mol) is treated with 75 ml. of a solution containing equal amounts of water and concentrated ammonia (sp. gr. 0.8980^{24}_{4}). The solution is evaporated on a steam bath until only a faint odor of ammonia is noticeable. The resulting light yellow solution is filtered, and the volume is adjusted to about 50 ml. The solution is then cooled in an ice bath to 10 to 15°.

A solution of 3.5 g. of sodium nitrite (0.051 mol) in 10 ml. of water is cooled to 10 to 15° in an ice bath. One milliliter of 90% formic acid is added, and the resulting solution is poured slowly with stirring into the cooled tetramminepalladium(II) solution. Within approximately 5 minutes a light yellow powder settles out. The solution is filtered on a Hirsch funnel, and the precipitate is washed successively with water, alcohol, and ether. The product is dried at 100 to 110° for 1 hour. The product so obtained is a yellow microcrystalline powder which melts at 227 to 228°. Yield, 1.7 g. (52%). Recrystallization from hot water results in a product which melts at 230 to 231°. Melting is accompanied by gas evolution.[2]

Analysis

Nitrogen is determined by the micro Dumas method. Palladium is determined by ignition. The mixture of metallic palladium and its oxides is reduced with formic acid and dried at 200°. *Anal.* Calcd. for $[Pd(NH_3)_2(NO_2)_2]$: Pd, 45.83; N, 24.07. Found: Pd, 45.75; N, 23.70.

Properties

trans-Dinitrodiamminepalladium(II) is a light yellow powder which is slightly soluble in water (0.2 g./100 g. of water) and insoluble in the common organic solvents. An aqueous solution of the compound, when treated with a concentrated solution of potassium iodide, immediately deposits a yellow precipitate of diiododiamminepalladium(II); the solution then becomes red in color within an hour. The trans isomer melts at 230 to 231° with evolution of a gas. These two last-mentioned properties are used to differentiate between the *cis-* and *trans*-dinitrodiammine isomers, since the cis compound melts at 234 to 235°, with no evolution of gas, and its solution, upon treatment with potassium iodide, remains colorless for several hours.

References

1. LANG, *J. prakt. Chem.*, **83**, 415 (1861).
2. MANN, CROWFOOT, GATTIKER, and WOOSTER: *J. Chem. Soc.*, **1935**, 1642.

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SUBJECT INDEX

Names employed in the cumulative subject index for Volumes I to IV 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 organosilicon compounds, see Vol. III, page 55.

Headings are alphabeted straight through, letter by letter, as in *Chemical Abstracts* indexes, not word by word. Roman numerals in Stock names are ignored unless two or more names are otherwise the same.

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): $PtCl_4K_2$; $[Al(C_2O_4)_3]K_3\cdot 3H_2O$; $(IO_6)_2Ba_3H_4$. 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; NH_2SO_3H and SO_3HNH_2.

Formulas for organic compounds are structural or semistructural so far as possible: $CH_3COCH_2COCH_3$. 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: $Zr(C_5H_7O_2)_4\cdot 10H_2O$; $NaC{\equiv}CH$ and $CH{\equiv}CNa$.

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:

$NH_2SO_3NH_4$
$(NH_2)_2C_2H_4$ (instead of $N_2H_4C_2H_4$, $N_2H_8C_2$, or $C_2H_8N_2$)
NH_3

$Si(CH_3)Cl_3$
$Si(CH_3)_3Cl$
$Si(CH{=}CH_2)Cl_3$
$Si(C_2H_4Cl)Cl_6$

$Cr(CN)_6K_3$ (instead of $CrC_6N_6K_3$)
$Cr(C_2H_3O_2)_2$ (instead of $CrC_4H_6O_4$)
$[Cr(C_2O_4)_3]K_3\cdot 3H_2O$ (instead of $CrC_6O_{12}K_3\cdot H_6O_3$ or $CrC_6O_{15}K_3H_6$)
$[Cr(en)_2Cl_2]Cl\cdot H_2O$ ("en" is retained for simplicity and is alphabeted as such rather than as $C_2H_4(NH_2)_2$ or $(NH_2)_2C_2H_4$)