MERCURY COMPOUNDS

1. Introduction

Mercury salts exist in two oxidation states: mercurous, Hg^{+}, and mercuric, Hg^{2+}. The former exist as double salts; for example, mercurous chloride[10112-91-1] may be represented as Hg_2Cl_2 in both solution and the solid state, as shown by conductance studies and x-ray analysis. Standard oxidation electrode potentials at 298.15 K (1–3) are as follows:

$$Hg_2^{2+}(aq) + 2\,e^- = 2\,Hg^0 \qquad E^0_{298} = 0.7960\ \text{V}$$

$$Hg^{2+}(aq) + 2\,e^- = Hg^0 \qquad E^0_{298} = 0.8535\ \text{V}$$

$$2\,Hg^{2+}(\ aq) + 2\,e^- = Hg_2^{2+} \qquad E^0_{298} = 0.9110\ \text{V}$$

Many mercury compounds are labile and easily decomposed by light, heat, and reducing agents. In the presence of organic compounds of weak reducing activity, such as amines (qv), aldehydes (qv), and ketones (qv), compounds of lower oxidation state and mercury metal are often formed. Only a few mercury compounds, eg, mercuric bromide[7789-47-1], mercurous chloride, mercuric sulfide[1344-48-5], and mercurous iodide [15385-57-6], are volatile and capable of purification by sublimation. This innate lack of stability in mercury compounds makes the recovery of mercury from various wastes that accumulate with the production of compounds of economic and commercial importance relatively easy.

The toxic nature of mercury and its compounds has caused concern over environmental pollution, and governmental agencies have imposed severe restrictions on release of mercury compounds to waterways and the air (see MERCURY). Methods of precipitation and agglomeration of mercurial wastes from process water have been developed. These methods generally depend on the formation of relatively insoluble compounds such as mercury sulfides, oxides, and thiocarbamates. Metallic mercury is invariably formed as a by-product. The use of coprecipitants, which adsorb mercury on their surfaces facilitating removal, is frequent.

Mercury from these accumulated wastes is generally best recovered by total degradation in stills, where metallic mercury is condensed and collected. The recovery costs are amply compensated by the value of the metal recovered. Moreover, disposal problems are either eliminated or severely diminished.

Concurrent with requirements for low levels of mercurials in discharge water is the problem of their determination. The older methods of wet chemistry are inadequate, and total reliance is placed on instrumental methods. The most popular is atomic absorption spectrophotometry, which relies on the absorption of light by mercury vapor (4). Solutions of mercury compounds not stabilized with an excess of acid tend to hydrolyze to form yellow-to-orange basic hydrates. These frequently absorb onto the walls of containers and may interfere with analytical results when low levels (ppm) of mercury are determined.

The covalent character of mercury compounds and the corresponding ability to complex with various organic compounds explains the unusually wide solubility characteristics. Mercury compounds are soluble in alcohols, ethyl ether, benzene, and other organic solvents. Moreover, small amounts of chemicals such as amines, ammonia (qv), and ammonium acetate can have a profound solubilizing effect (see COORDINATION COMPOUNDS). The solubility of mercury and a wide variety of mercury salts and complexes in water and aqueous electrolyte solutions has been well outlined (5).

Owing to legal restrictions, use of mercury compounds has declined. The most important areas of mercury compound usage as of the mid-1990s are as preservatives and fungicides in coating compositions, as catalysts, as intermediates in the formation of other compounds, and as a component of compositions used as semiconductors (see COATINGS; CATALYSIS; FUNGICIDES, AGRICULTURAL; SEMICONDUCTORS). The use of mercurials as biocides in protective coatings has been prohibited in the United States since 1992. Seed treatment by mercurials is no longer permitted in the United States. As of this writing, however, bis-(2-methoxyethyl mercuric) silicate is used for this purpose in parts of Europe. Some pharmaceutical uses remain, eg, in ophthalmic preparations and antiseptics (see DISINFECTANTS AND ANTISEPTICS).

All mercury compounds should be stored in amber bottles or otherwise protected from light. In manufacture, glass-lined equipment is preferred, although stainless steel may be used. Stainless steel may cause some discoloration at high temperatures if concentrated acetic acid is used.

2. Mercury Salts

2.1. Mercuric Acetate. Mercuric acetate[1600-27-7], $Hg(C_2H_3O_2)_2$, is a white, water-soluble, crystalline powder, soluble in water and many organic solvents. It is prepared by dissolving mercuric oxide in warm 20% acetic acid. A slight excess of acetic acid is helpful in reducing hydrolysis.

Another method of preparing mercuric acetate is the oxidation of mercury metal using peracetic acid dissolved in acetic acid. Careful control of the temperature is extremely important because the reaction is quite exothermic. A preferred procedure is the addition of approximately half to two-thirds of the required total of peracetic acid solution to a dispersion of mercury metal in acetic acid to obtain the mercurous salt, followed by addition of the remainder of the peracetic acid to form the mercuric salt. The exothermic reaction is carried to completion by heating slowly and cautiously to reflux. This also serves to decompose excess peracid. It is possible and perhaps more economical to use 50% hydrogen peroxide instead of peracetic acid, but the reaction does not go quite as smoothly.

The primary use of mercuric acetate is as a starting material for the manufacture of organic mercury compounds.

2.2. Mercuric Carbonate. Basic mercuric carbonate[76963-38-7], $HgCO_3 \cdot 3\,HgO$, may be prepared by the addition of sodium carbonate to a solution of mercuric chloride. The brown precipitate, which lacks usefulness, is generally not isolated; rather, the slurry is refluxed, whereupon the carbonate decomposes to red mercuric oxide.

2.3. Mercuric Cyanides. Mercuric cyanide[592-04-1], $Hg(CN)_2$, is a white tetragonal crystalline compound, little used except to a small degree as an antiseptic. It is prepared by reaction of an aqueous slurry of yellow mercuric oxide (the red is less reactive) with excess hydrogen cyanide. The mixture is heated to 95°C, filtered, crystallized, isolated, and dried. Its solubility in water is 10% at 25°C.

Mercuric oxycyanide[1335-31-5], or basic mercuric cyanide, $Hg(CN)_2 \cdot HgO$, is prepared in the same manner as the normal cyanide, except that the mercuric oxide is present in excess. The oxycyanide is white and crystalline but only one-tenth as soluble in water as the normal cyanide. Because this compound is explosive, it normally is supplied as a 1:2 mixture of oxycyanide to cyanide.

2.4. Mercuric Fulminate. Mercuric fulminate[20820-45-5], $Hg(ONC)_2$, is used as a catalyst in the oxynitration of benzene to nitrophenol (see NITRATION). Its most common use is as a detonator for explosives (see EXPLOSIVES AND PROPELLANTS).

2.5. Mercury Fluorides. See FLUORINE COMPOUNDS, INORGANIC–MERCURY.

2.6. Mercurous Chloride. Mercurous chloride[10112-91-1], Hg_2Cl_2, also known as calomel, is a white powder, insoluble in water. It sublimes when heated in an open container, but this probably occurs at least in part as a result of dissociation to mercury metal and mercuric chloride:

$$Hg_2Cl_2 \longrightarrow Hg^0 + HgCl_2$$

Its relatively low toxicity is probably the result of very low aqueous solubility (0.002 g/L) and lack of reactivity with acidic (HCl) digestive fluids.

The compound is generally prepared in one of two ways. The purer grade is made by the direct oxidation of mercury by a quantity of chlorine gas insufficient to produce mercuric chloride, which is always a side product. The chlorine gas is run into a heated silica retort. The mouth of the retort leads to a large chamber made of chlorine-resistant material. Lead is frequently used, but great care must be exercised to exclude moisture; otherwise lead chloride could be formed as well. The chamber should be large, approximately 5.1 m^3 (180 ft^3), because cooling occurs by convection and dissipation of heat by conduction throughout the walls. The mercury burns with a green flame and the product settles to the floor of the chamber from which it is subsequently removed. The correct balance of mercury to chlorine yields about 70–80% mercurous chloride. The remainder is mercuric chloride. No unreacted mercury should remain, as mercury metal gives a grayish tinge to the product and cannot be washed out. The material from the chamber is slurried with water and washed several times by decantation. It is filtered and washed on the filter until it is free of soluble chloride.

The second method of preparation involves precipitation from a cold acidic solution of mercurous nitrate. Mercurous chloride is isolated after washing in a manner similar to the chamber method described. This product, which generally contains small amounts of occluded sodium nitrate, is satisfactory as a technical-grade material. Difficulty may be encountered in having it pass NF or reagent-grade specifications (see FINE CHEMICALS).

For the preparation of mixtures of mercurous and mercuric chlorides used to control turf-fungus diseases, the precipitated product of the second method may be mixed with the required amount of mercuric chloride. Alternatively, the chamber material, if the ratios of mercurous and mercuric chloride are correct, may be used directly.

The mercury contained in the mother liquid and washings of either method is recovered by treatment with sodium hydroxide solution. Yellow mercuric oxide is precipitated and filtered. The filtrate is treated further to remove the last traces of mercury before it is discarded.

2.7. Mercuric Chloride. Mercuric chloride[7487-94-7], $HgCl_2$, is also known as corrosive sublimate of mercury or mercury bichloride. It is extremely poisonous, and is particularly dangerous because of high (7 g/L at 25°C) water solubility and high vapor pressure. It sublimes without decomposition at 300°C, and has a vapor pressure of 13 Pa (0.1 mm Hg) at 100°C, and 400 Pa (3 mm Hg) at 150°C. The vapor density is high (9.8 g/cm^3), and therefore mercuric chloride vapor dissipates slowly (5).

In addition to high aqueous solubility (7% at 30°C and 38% at 100°C), $HgCl_2$ is very soluble in methyl alcohol (53% at 36°C), ethyl alcohol (34% at 31°C), and amyl alcohol (ca 10% at 30°C). It also is soluble in acetone, formic acid, the lower acetate esters, and other polar organic solvents.

The preparation of mercuric chloride is identical to the chamber method for mercurous chloride, except that an excess of chlorine is used to ensure complete reaction to the higher oxidation state. Very pure product results from this method. Excess chlorine is absorbed by sodium hydroxide in a tower.

Mercuric chloride is widely used for the preparation of red and yellow mercuric oxide, ammoniated mercury[10124-48-8] USP, mercuric iodide, and as an intermediate in organic synthesis. It has been used as a component of agricultural fungicides. It is used in conjunction with sodium chloride in photography (qv) and in batteries (qv), and has some medicinal uses as an antiseptic.

Until about 1980, mercuric chloride was used extensively as a catalyst for the preparation of vinyl chloride from acetylene (7). Since the early 1980s, vinyl chloride and vinyl acetate have been prepared from ethylene instead of acetylene, and the use of mercuric chloride as a catalyst has practically disappeared.

2.8. Mercurous Bromide. Mercurous bromide[15385-58-7], Hg_2Br_2, is a white tetragonal crystalline powder, very similar to the chloride, and prepared in much the same way, ie, by the direct oxidation of mercury by bromine or by precipitation from mercurous nitrate by sodium bromide. It is sensitive to light, less stable than the chloride, and is not of appreciable commercial importance.

2.9. Mercuric Bromide. Mercuric bromide[7789-94-7], $HgBr_2$ is a white crystalline powder, considerably less stable than the chloride, and also much less soluble in water (0.6% at 25°C). Therefore, it is prepared easily by precipitation, using mercuric nitrate and sodium bromide solution. Drying of the washed compound is carried out below 75°C. Mercuric bromide has a few medicinal uses.

2.10. Mercurous Iodide. Mercurous iodide [7783-30-4], Hg_2I_2, is a bright yellow amorphous powder, extremely insoluble in water and very sensitive to light. It has no commercial importance but may be prepared by precipitation, using mercurous nirate and potassium iodide. Care must be taken to exclude mercuric nitrate, which may cause the formulation of the water-insoluble mercuric iodide.

2.11. Mercuric Iodide. Mercuric iodide[7774-29-0], HgI_2, is a bright red tetragonal powder, only slightly soluble in water. It dissolves in alkalies to form complex salts. Both sodium iodomercurate[7784-03-4], Na_2HgI_4, and potassium iodomercurate[7783-33-7], K_2HgI_4, are known. Mercuric iodide, made by precipitation from a solution of mercuric chloride and potassium iodide, is used in the treatment of skin diseases and as an analytical reagent.

The range of uses of mercuric iodide has increased because of its ability to detect nuclear particles. Various metals such as Pd, Cu, Al, Tri, Sn, Ag, and Ta affect the photoluminescence of HgI_2, which is of importance in the preparation of high quality photodetectors (qv). HgI_2 has also been mentioned as a catalyst in group transfer polymerization of methacrylates or acrylates (8).

2.12. Complex Halides. Mercuric halides (except the fluoride) form neutral complex salts with metallic halides. Those made with alkali metal salts frequently are more soluble in water than the mercuric halide itself, and take the form of $MHgX_3$ and M_2HgX_4.

Iodomercurates. Potassium iodomercurate dihydrate, $K_2HgI_4 \cdot 2H_2O$, is a yellow, water-and-alcohol-soluble compound prepared by dissolving one mole of mercuric iodide in a solution of two moles of potassium iodide in distilled water. After filtering off any insoluble particles, the filtrate is evaporated to dryness to isolate the compound. The filtrate, known as Mayer's reagent, has uses as an antiseptic and as a precipitant for alkaloids (qv). In strongly alkaline solution, called Nessler's reagent, it is used for the detection and determination of low levels of ammonia.

Cuprous iodomercurate [13876-85-2], Cu_2HgI_4, is a bright red water-insoluble compound prepared by precipitation from a solution of K_2HgI_4 with cuprous chloride. It is used in temperature-indicating paints because it reversibly changes color to brown at 70°C .

Silver iodomercurate [36011-71-9], Ag_2HgI_4, is a bright yellow compound and is prepared similarly to the cuprous salt where silver nitrate is the precipitant. The silver salt, which darkens reversibly at 50°C, is used for the same application as cuprous iodomercurate.

2.13. Mercurous Nitrate. Mercurous nitrate [10415-75-5], $Hg_2N_2O_6$ or $Hg_2(NO_3)_2$, is a white monoclinic crystalline compound that is not very soluble in water but hydrolyzes to form a basic, yellow hydrate. This material is, however, soluble in cold, dilute nitric acid, and a solution is used as starting material for other water-insoluble mercurous salts. Mercurous nitrate is difficult to obtain in the pure state directly because some mercuric nitrate formation is almost unavoidable. When mercury is dissolved in hot dilute nitric acid, technical mercurous nitrate crystallizes on cooling. The use of excess mercury is helpful in reducing mercuric content, but an additional separation step is necessary. More concentrated nitric acid solutions should be avoided because these oxidize the mercurous to mercuric salt. Reagent-grade material is obtained by recrystallization from dilute nitric acid in the presence of excess mercury.

2.14. Mercuric Nitrate. Mercuric nitrate [10045-94-0], $Hg(NO_3)_2$, is a colorless deliquescent crystalline compound prepared by the exothermic dissolution of mercury in hot, concentrated nitric acid. The reaction is complete when a cloud of mercurous chloride is not formed when the solution is treated with sodium chloride solution. The product crystallizes upon cooling. Mercuric nitrate is used in organic synthesis as the starting material and for the formulation of a great many other mercuric products.

2.15. Mercuric Oxide.

Mercuric oxide[21908-53-2], HgO, is a red or yellow water-insoluble powder, rhombic in shape when viewed microscopically. The color and shade depend on particle size. The finer particles (< 5 μm) appear yellow; the coarser particles (> 8 μm) appear redder. The product is soluble in most acids, organic and inorganic, but the yellow form, which has greater surface area, is more reactive and dissolves more readily. Mercuric oxide decomposes at 332°C and has a high (11.1) specific gravity.

Yellow mercuric oxide may be obtained by precipitation from solutions of practically any water-soluble mercuric salt through the addition of alkali. The most economical are mercuric chloride or nitrate. Although yellow HgO has some medicinal value in ointments and other such preparations, the primary use is as a raw material for other mercury compounds, eg, Millon's base [12529-66-7], Hg_2NOH, which is formed by the reaction of aqueous ammonia and yellow mercuric oxide.

Red mercuric oxide generally is prepared in one of two ways: by the heat-induced decomposition of mercuric nitrate or by hot precipitation. Both methods require careful control of reaction conditions. In the calcination method, mercury and an equivalent of hot, concentrated nitric acid react to form mercurous nitrate:

$$6\,Hg^0 + 8\,HNO_3 \longrightarrow 3\,Hg_2(NO_3)_2 + 2\,NO + 4\,H_2O$$

After the water and nitrogen oxide are driven off, continued heating drives off vapors of nitric acid, additional water, NO_2, and some mercury–metal vapor:

$$Hg(NO_3)_2 \longrightarrow 2\,HgO + 2\,NO_2$$

This secondary reaction starts at about 180°C, but the mass must be heated to 350–400°C to bring the reaction to completion and produce a nitrate-free product. The off-gases are extremely corrosive and poisonous, and considerable attention and expense is required for equipment maintenance and caustic-wash absorption towers. Treatment of the alkaline wash liquor for removal of mercury is required both for economic reasons and to comply with governmental regulations pertaining to mercury in plant effluents.

In the hot precipitation method, sodium carbonate solution is added slowly to a refluxing solution of mercuric chloride, followed by an additional reflux period of 1 to 2 h. The washed precipitate is then dried. A variation allows the substitution of mercuric nitrate for the chloride if substantial quantities of sodium chloride are used. Sodium hydroxide, in the presence of sodium carbonate, is the precipitant.

Red mercuric oxide, identical chemically to the yellow form, is somewhat less reactive and more expensive to produce. An important use is in the Ruben-Mallory dry cell, where it is mixed with graphite to act as a depolarizer (see BATTERIES). The overall cell reaction is as follows:

$$Zn^0 + HgO \longrightarrow ZnO + Hg^0$$

Yellow mercuric oxide is considered less suitable because it is less dense and would not permit adequate packing in the cell casing.

2.16. Mercurous Sulfate. Mercurous sulfate[7783-36-0], Hg_2SO_4, is a colorless-to-slightly-yellowish compound, sensitive to light and slightly soluble in water (0.05 g/100 g H_2O). It is more soluble in dilute acids. The compound is prepared by precipitation from acidified mercurous nitrate solution and dilute sulfuric acid. The precipitate is washed with dilute sulfuric acid until nitrate-free. Its most important use is as a component of Clark and Weston types of standard cells.

2.17. Mercuric Sulfate. Mercuric sulfate[7783-35-9], $HgSO_4$, is a colorless compound soluble in acidic solutions, but decomposed by water to form the yellow water-insoluble basic sulfate, $HgSO_4^{\cdot}2HgO$. Mercuric sulfate is prepared by reaction of a freshly prepared and washed wet filter cake of yellow mercuric oxide with sulfuric acid in glass or glass-lined vessels. The product is used as a catalyst and with sodium chloride as an extractant of gold and silver from roasted pyrites.

2.18. Mercuric Sulfide. Mercuric sulfide[1344-48-5], HgS, exists in two stable forms. The black cubic tetrahedral form is obtained when soluble mercuric salts and sulfides are mixed; the red hexagonal form is found in nature as cinnabar (vermilion pigment). Both forms are very insoluble in water (see PIGMENTS, INORGANIC). Red mercuric sulfide is made by heating the black sulfide in a concentrated solution of alkali polysulfide. The exact shade of the pigment varies with concentration, temperature, and time of reaction.

2.19. Mercury Telluride. Compounds of mercury with tellurium have gained importance as semiconductors with applications in infrared detection (9) and solar cells (10). The ratio of the components is varied, and other elements such as cadmium, zinc, and indium are added to modify the electronic characteristics.

3. Organomercury Compounds

3.1. Phenylmercurics. Phenylmercuric acetate [62-38-4] (PMA), $HgC_8H_8O_2$, melts at 149°C and is slightly soluble in water, but much more soluble in solutions of ammonium acetate in aqueous ammonia. Such solutions are articles of commerce, and may contain 30% phenylmercuric acetate (PMA-30) or the equivalent of 18% mercury as metal. Phenylmercuric acetate is also soluble in various organic solvents. The compound is prepared by refluxing a mixture of mercuric acetate and acetic acid in a large excess of benzene. This is generally referred to as a mercuration reaction. A large excess of benzene is necessary because more than one hydrogen on the benzene ring can be replaced:

$$C_6H_6 + n\ \left[Hg(OOCCH_3)_2\right] \longrightarrow C_6H_{6-n}(HgOOCCH_3)_n + n\ HOOCCH_3$$

where n may be anywhere from 1–4. It is generally desirable to limit the amount of polymercurated benzene formed. The technical grade of phenylmercuric acetate contains about 85% pure compound. The remaining 15% is di- and trimercurated product. Polymercurated products are less soluble than monomercurated material and are removed by recrystallization. Solvents such as water, acetone, benzene, and benzene ethylene glycol monoethyl ether may be used.

The reaction is complete in about 15 hours, as indicated by the formation of a white precipitate of phenylmercuric sulfide[20333-30-6] when sulfide is added to an ammoniacal solution of the reaction mixture. The product is isolated after distillation of excess benzene and acetic acid.

The ammoniacal solution of phenylmercuric acetate contains polymercurates. The low solubility of polymercurates is an advantage in exterior coatings, where bactericidal and fungicidal activity is unimpaired and these materials are leached out more slowly.

Prior to the 1990s phenylmercuric acetate was the primary bactericide and fungicide in latex and waterborne paints. Because of the increasing concerns of mercury toxicity and the potential for high consumer and occupational exposures to mercury when present in paints, the U.S. Environmental Protection Agency (EPA) induced U.S. manufacturers of PMA and other mercury compounds to withdraw their registrations for use of these substances as biocides in paints (see MERCURY). Mercury compounds are used only for very limited, specific purposes, such as the use of phenylmercuric nitrate[55-68-5] as a bactericide in cosmetic eye preparations (see COSMETICS).

Phenylmercuric acetate is used as the starting material in the preparation of many other phenylmercury compounds, which are generally prepared by double-decomposition reactions using the sodium salts of the desired acid groups in aqueous solution. The lower alkylate esters, such as the propionate and butyrate, are prepared directly in the same manner as the acetate. Another double-decomposition method uses phenylmercuric hydroxide[100-57-2], prepared by reaction of phenylmercuric acetate and hot dilute sodium hydroxide. Other phenylmercury compounds in use are the oleate[104-60-9], dodecenyl succinate, propionate[103-27-5], nitrate, and dimethyldithiocarbamate[32407-99-1]. All of these are toxic. The *N*,*N*′-dimethyldithiocarbamate is the least soluble and exhibits the highest tolerated levels in humans. The phenylmercury compounds are less toxic than soluble inorganic mercury, perhaps because the phenylmercury forms the highly insoluble phenylmercuric chloride in the stomach. Phenylmercury compounds serve as catalysts for the manufacture of certain polyurethanes (see URETHANE POLYMERS).

3.2. 3-Chloro-2-Methoxypropylmercuric Acetate. 3-Chloro-2-methoxypropylmercuric acetate, $ClCH_2C(OCH_3)HCH_2HgOOCCH_3$, is difficult to isolate and generally is sold as an ammoniacal solution containing 10% mercury as metal, in much the same way as phenylmercuric acetate solution is sold. It is prepared by the reaction of allyl chloride, methanol, and mercuric acetate in acetic acid, followed by the addition of ammonia and water. It has many of the same applications as phenylmercuric acetate and was used as a preservative or bactericide for aqueous systems. Because of its superior solubility and compatibility, the compound is not precipitated by anionic dispersants, as is phenylmercuric acetate, and therefore lower levels of this compound often may be used to achieve the same protective biocidal effect.

3.3. Alkyl Mercuric Compounds. Alkyl mercuric compounds, RHgX, are no longer manufactured in most of the world because of the long-lasting toxic hazards and destructive effect on the brain and central nervous system of animals, where these tend to accumulate. Until 1970, they were, however, widely used as seed disinfectants. They have some utility in organic synthesis and in the preparation of other organometallics (qv). In general, they are white stable solids of appreciable volatility and are often prepared by a Grignard reaction in ethyl ether:

$$\mathrm{RMgX} + \mathrm{HgX}_2' \longrightarrow \mathrm{RHgX}' + \mathrm{MgXX}'$$

4. Miscellaneous Compounds of Pharmaceutical Interest

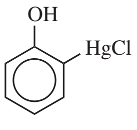
4.1. Antiseptics.

Ammoniated mercury [10124-48-8], $\mathrm{Hg(NH_2)Cl}$, is a white odorless powder that is insoluble in water and has a specific gravity of 5.38. It is formed by the reaction of aqueous ammonia (qv) and mercuric chloride.

o-(Chloromercuri)phenol[90-03-9] (mercarbolide) (1) is prepared in the same way as PMA, but from phenol instead of benzene. The phenol group is highly activating and thus the reaction proceeds quickly. The product is precipitated by aqueous sodium chloride and purified from hot water as a white, leafy crystalline compound.

Merbromin[129-16-8], disodium 2,7-dibromo-4-hydroxymercurifluorescein, (2), commonly called mercurochrome, is prepared by refluxing dibromofluorescein with mercuric acetate in acetic acid. The precipitate is dissolved in water containing the stoichiometric amount of sodium hydroxide and evaporated.

Merthiolate[54-64-8] (3), sodium ethylmercurithiosalicylate, known also as thimersol, is prepared from a 1:1 ratio of ethylmercuric chloride[107-27-7] and disodium thiosalicylate in ethanol. After removal of the sodium chloride by filtration, the free acid is precipitated by acidification with dilute sulfuric acid. Purification is achieved by recrystallization from 95% ethanol, and the product, merthiolate, is obtained by neutralization with a stoichiometric amount of sodium hydroxide.



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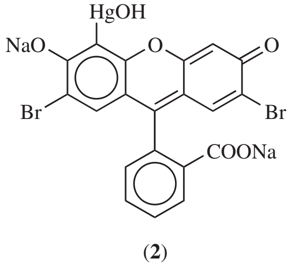

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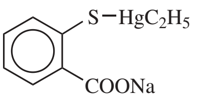

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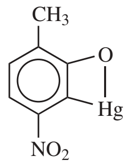

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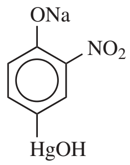

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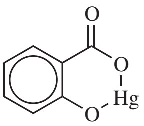
Nitromersol[133-58-4] (4) and mercurophen [52486-78-9] (5) are prepared by the same mercuration reaction as phenylmercuric acetate, only 4-nitro-*o*-cresol and *o*-nitrophenol are used, respectively, instead of benzene. The second step is reaction with sodium hydroxide to form the anhydride or sodium salt, respectively.

Other organic mercurials used as antiseptics include mercocresol [8063-33-0], acetomeroctol [584-18-9], acetoxymercuri-2-ethylhexylphenosulfonate [1301-13-9], and sodium 2,4-dihydroxy-3,5-dihydroxymercuribenzophenone-2-sulfonate[6060-47-5] (see Disinfectants and antiseptics).

4.2. Antisyphilitics. Mercuric salicylate[5970-32-1] (6) and mercuric succinimide [584-43-0] (7) are simple salts prepared by the reaction in water of mercuric oxide and salicylic acid or succinimide, respectively. Use as antisyphilitics has been substantially eliminated by virtue of the discovery of more potent and effective nonmetallic biocides.



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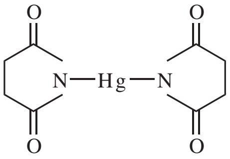

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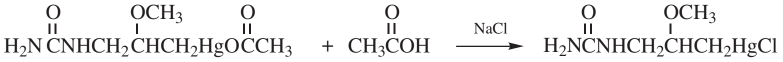
4.3. Diuretics. Chlormeodrin [62-37-3] (methoxy(urea)propylmercuric chloride) (8), is prepared in the same sort of reaction used for chloromethoxypropylmercuric acetate. Allyl urea is used instead of allyl chloride, together with methanol and mercuric acetate. The product, after dilution with water and neutralization, is precipitated with sodium chloride:



$$H_2N\overset{O}{\overset{\|}{C}}NHCH_2\overset{OCH_3}{\overset{|}{C}}HCH_2HgO\overset{O}{\overset{\|}{C}}CH_3 + CH_3\overset{O}{\overset{\|}{C}}OH \xrightarrow{NaCl} H_2N\overset{O}{\overset{\|}{C}}NHCH_2\overset{OCH_3}{\overset{|}{C}}HCH_2HgCl$$

(**8**)

Other organic mercurials similar in chemical structure to chlormerodrin are meralluride[104-20-5], mercaptomerin[20223-84-1], and mersalyl [486-67-9]. Mercury-based diuretics (qv) are no longer in use.

5. Health and Safety Factors

Upon discovery of the biomethylation of mercury in 1968 (11,12), the mercurials industry, involving both manufacture and application of mercury and mercury compounds, underwent an extensive change. This change resulted in part from the rapid development of powerful analytical tools capable of detection, identification, and analysis of compounds and elements in the ranges of fractional parts per billion (ppb). Coincidentally, certain chemical moieties were shown to be not only toxic sources, but also potential carcinogens and mutagens (see Analytical methods; Trace and residue analysis; Toxicology). Realization that mercury compounds were being accumulated in the environment by biodegradation to methylmercury[16056-34-1], CH_3Hg, led to the development and enforcement of rules and regulations concerning the safe preparation, use, and disposal of mercury compounds.

The toxic effects of mercury and mercury compounds as well as their medicinal properties have been known for many centuries. In the first century AD, Pliny indicated the use of mercuric sulfide (cinnabar or vermilion) in medicine and in cosmetics. This compound was probably known to the Greeks in the time of Aristotle (13).

Galen, a physician whose views outlived him by about a thousand years, died about 200 AD. He believed that mercurials were toxic, and did not use any mercury compound therapeutically. However, as a result of Arabian influence, the therapeutic uses of mercury were slowly recognized by Western Europe. In the thirteenth century mercury ointments were prescribed for treating chronic diseases of the skin. Mercury and its compounds, such as mercurous chloride, mercuric oxide, mercuric chloride, and mercuric sulfide, were used widely from the fifteenth to the nineteenth centuries, and to some extent in the twentieth century. During the first half of the twentieth century, the primary therapeutic uses of mercury included bactericidal preparations, such as mercuric chloride, mercuric oxycyanide, and mercuric oxide; and diuretics, such as aryl HgX (Novasural) and mercurated allyl derivatives (14).

Alkyl mercury compounds were used widely in the United States as seed disinfectants until prohibited in 1970. Subsequently, in 1972, the EPA prohibited the use of all mercury compounds in agriculture (15).

5.1. Toxicity. Inorganic mercury compounds, aryl mercury compounds, and alkoxy mercurials are generally considered to be quite similar in their toxicity. Alkyl mercury compounds are considered to be substantially more toxic and hazardous. Mercury and its compounds can be absorbed by ingestion, absorption through the skin, or by inhalation of the vapor. The metal itself, however, rarely produces any harmful effects when ingested (16).

After inorganic mercuric salts are absorbed and dissociated into the body fluids and in the blood, they are distributed between the plasma and erythrocytes. Aryl mercuric compounds and alkoxy mercuric compounds are decomposed to mercuric ions, which behave similarly.

Alkyl mercury compounds in the blood stream are found mainly in the blood cells, and only to a small extent in the plasma. This is probably the result of the greater stability of the alkyl mercuric compounds, as well as their peculiar solubility characteristics. Alkyl mercury compounds affect the central nervous system and accumulate in the brain (17,18). Elimination of alkyl mercury compounds from the body is somewhat slower than that of inorganic mercury compounds and the aryl and alkoxy mercurials. Methylmercury is eliminated from humans at a rate indicating a half-life of 50–60 d (19); inorganic mercurials leave the body according to a half-life pattern of 30–60 d (20). Elimination rates are dependent not only on the nature of the compound but also on the dosage, method of intake, and the rate of intake (21,22).

5.2. Environmental Factors. The control, recovery, and disposal of mercury-bearing waste products are as important to the mercurials industry as the manufacturing process. The difficulties involved in removing mercury from waste-product streams and the problems of recovery or disposal have resulted in a substantial reduction in the number of manufacturers of mercury compounds as well as in the variety of mercury compounds being manufactured. Moreover, the manufacturing process used for a mercury compound may not necessarily be the most efficient or economical. Rather, the choice may depend on the nature of the by-products, the toxic hazard of the process, and the ease of recovery of the mercury from the waste-product stream.

5.3. Safety. The maximum acceptable concentration (MAC) for mercury in all forms except alkyl compounds is 0.05 mg Hg/m^3 air (23). For alkyl mercury compounds the TLV is set at 0.01 mg Hg/m^3 air.

Suitable ventilating equipment, consisting mainly of carbon absorbers which effectively absorb mercury vapor from recirculated air, must be employed to maintain standards below the value permitted in the occupational environment. When the possibility of higher exposures exists, small disposable masks utilizing a mercury vapor absorbent may be employed.

Most inorganic mercury compounds have very low vapor pressures, and generally do not contribute to high mercury vapor readings. Metallic mercury is the most potent and troublesome in this respect. Organic mercurials also contribute to mercury vapor readings, possibly by virtue of the presence of extremely small amounts of metallic mercury present as an impurity.

To safeguard the health of persons working in plants producing mercurials, the following precautions should be observed: maintaining adequate ventilation; use of disposable uniforms so that a contaminated uniform is not a source of absorption through the skin; use of disposable mercury vapor-absorbing masks; careful attention to good housekeeping, eg, avoidance of spills, and prompt and proper cleaning if a spill occurs; ensuring that all containers of mercury and its compounds are kept tightly closed; ensuring that floors are washed on a regular basis with dilute calcium sulfide solution or other suitable reactant; use of floors that are nonporous; requiring that all workers directly involved in the plant operation shower thoroughly each day before leaving; and conducting periodic medical examinations, including analysis of blood and urine for mercury content, of all workers directly involved in production of mercurials, or otherwise exposed to contact with mercury compounds or mercury vapor.

Mercury spills should be cleaned up immediately by use of a special vacuum cleaner. The area should then be washed with a dilute calcium sulfide solution. Small quantities of mercury can be picked up by mixing with copper metal granules or powder, or with zinc granules or powder. To avoid or minimize spills, some plants use steel trays as pallets so that a spill, whether of mercury or a mercury compound, is contained on the steel tray.

Mercury vapor discharge from vents of reactors or storage tanks at normal atmospheric pressure is controlled readily by means of activated carbon. Standard units (208-L (55-gal) drums) of activated carbon equipped with proper inlet and outlet nozzles can be attached to each vent. To minimize the load on the carbon-absorbing device, a small water-cooled condenser is placed between the vent and the absorber.

The control of mercury in the effluent derived from the manufacturing processes used in the preparation of inorganic and organic mercurials is mandated by law in the United States. The concentrations and the total amounts vary with the industry and the location, but generally it is required that the effluent contain not more than 0.01 mg Hg/L. However, individual states and individual publicly owned sewage-treatment plants have set up their own standards.

5.4. Mercury Removal From Gases. Removal of mercury from ambient air in the workplace and prevention of discharge of mercury vapor are of the greatest importance in the protection of the health of the worker. Mercury vapor, as metallic mercury or in the form of its various compounds, can be absorbed readily by a number of different media (see AIR POLLUTION CONTROL METHODS). Whereas activated charcoal adsorbs mercury, it is not particularly efficient. Specially treated charcoal containing sulfur compounds is fairly effective but cannot be regenerated after it is saturated (see ADSORPTION, GAS SEPARATION). Because of the problems involved in disposing of mercury-containing wastes such as unregenerated adsorbents, it is preferable to use other systems.

Mercury amalgamates readily with gold and silver, and systems have been developed using these metals distributed on various carriers to remove mercury vapor from an airstream. When the system is saturated, the mercury can be removed easily and recovered by heating the unit and condensing the mercury. Other metals, such as copper and zinc, can also be used.

When the mercury present in the atmosphere is primarily in the form of an organic mercury compound, it may be preferable to utilize an aqueous scrubber. This method is particularly useful for control of emissions from reactors and from dryers. For efficient and economical operation, an aqueous solution of caustic soda, sodium hypochlorite, or sodium sulfide is recirculated through the scrubber until the solution is saturated with the mercury compound.

From Liquids. The chlor-alkali producers employing mercury cathode electrolytic cells for the production of chlorine and caustic soda face the greatest problem in removal of mercury from aqueous effluent streams, and most of the patent literature is concerned with the processes for treatment of mercury-containing brine so produced (see ALKALI AND CHLORINE PRODUCTS). One procedure involves the use of a bed of activatedcarbon impregnated with silver (24). The alkali-brine solution is passed through a bed of this material which is combined with supporting material, such as nickel turnings or polyethylene shreds. Another process allows the brine solution to contact a strong anion-exchange organic resin of the quaternary ammonium cross-linked type (25) (see ION EXCHANGE).

Soluble sulfides such as sodium sulfide, potassium sulfide, and calcium polysulfides have been used to precipitate mercury salts from alkaline solutions. When this procedure is used, exercise of caution is required to maintain the pH within a given alkaline range so as to prevent evolution of H_2S. Because the solubility of mercuric sulfide in water is 12.5 μg/L at 18°C or 10.7 ppb of mercury, use of this method for removal of mercury is adequate for most purposes. However, the presence of excess alkali, such as sodium hydroxide or sodium sulfide, increases the solubility of mercuric sulfide as shown:

Na_2S, g/100 g soln	HgS solubility, g/100 g soln
0.95	0.21
1.50	0.57
2.31	1.45
3.58	2.91
4.37	4.12
6.07	7.27
9.64	15.59

Thus, at a concentration of 0.95 g Na_2S/100 g solution, the solubility of mercuric sulfide has increased to 2100 ppm. It is customary to use no greater than a 20% excess of the alkali sulfide. Because the particle size of the precipitated mercuric sulfide is so small, it is helpful to add a ferric compound such as ferric chloride or ferric sulfate to effect flocculation. Sometimes other flocculating agents (qv) may also be added, eg, starch or gum arabic.

Another method of removing mercury compounds from aqueous solution is to treat them with water-soluble reducing agents, thus liberating metallic mercury (26). The use of formaldehyde (qv) at a pH of 10–12 also is recommended.

Problems of removal of mercury from aqueous effluents are more complicated in plants that manufacture a variety of inorganic and organic mercury compounds; it is generally best to separate the effluent streams of inorganic and organic mercurials. When phenylmercuric acetate is precipitated from its solution in acetic acid by addition of water, the filtrate is collected and reused for the next precipitation. This type of recycling is necessary not only for economic reasons but also to minimize recovery operations.

When an aqueous effluent stream containing organomercurials cannot be recycled, it may be treated with chlorine to convert the organomercury to inorganic mercury. The inorganic compounds thus formed are reduced to metallic mercury with sodium borohydride. The mercury metal is drained from the reactor, and the aqueous solution discarded. The process utilizing sodium borohydride is known as the Ventron process (27).

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