TIN COMPOUNDS

1. Introduction

Tin is between germanium and lead in Group 14(IVA) of the Periodic Table. As a bronze component, tin was used as early as 3500 BC. The pure metal was not used until 600 BC (see Tin and tin alloys). The history of tin compounds dates to the Copts of Egypt, who reportedly used basic tin citrate [59178-29-9] in dye preparation. In 1605 stannic chloride was prepared. The alchemists' symbol for tin is 2_+. Tin occurs in the earth's crust to the extent of 40 grams per metric ton and is present in the form of nine different minerals from two types of deposits. The most commercially significant ore is cassiterite [1317-45-9] (tinstone), SnO_2. The more economically valuable deposits of cassiterite are heavily concentrated in bands and layers of varying thickness, in Malaysia, Thailand, Indonesia, and the People's Republic of China. Complex sulfidic ores, combinations of the sulfides of base metals and pyrites, are in lode deposits. These, economically significant only in Bolivia, are stannite [12019-29-3], $SnS_2{\cdot}Cu_2S{\cdot}FeS$; herzenbergite [14752-27-3], SnS; teallite [12294-02-9], $SnS{\cdot}PbS$; franckeite [12294-04-1], $2SnS_2{\cdot}Sb_2S_3{\cdot}5PbS$; cylindrite [12294-05-0, 59858-98-9], $Sn_6Pb_6Sb_2S_{11}$; plumbostannite, $2SnS_2{\cdot}2PbS{\cdot}2(Fe,Zn)S{\cdot}Sb_2S_3$; and canfieldite [12250-27-0], $4Ag_2S{\cdot}SnS_2$. The important tin-producing countries are Malaysia, Bolivia, Indonesia, Nigeria, Thailand, Zaire, and the People's Republic of China. Smaller quantities are produced in the United Kingdom, Burma, Japan, Canada, Portugal, Spain, and Australia. Tin is also normally present in natural waters, in soil, in marine organisms and animals, in the milk of lactating animals, in meteorites, in the tissues of animals, and in minor amounts in human organs.

Tin, having valence of +2 and +4, forms stannous (tin(II)) compounds and stannic (tin(IV)) compounds. Tin compounds include inorganic tin(II) and tin(IV) compounds; complex stannites, $MSnX_3$, and stannates, M_2SnX_6, and coordination complexes, organic tin salts where the tin is not bonded through carbon, and organotin compounds, which contain one-to-four carbon atoms bonded directly to tin.

Of the large volume of tin compounds reported in the literature, possibly only ca 100 are commercially important. The most commercially significant inorganic compounds include stannic chloride, stannic oxide, potassium stannate, sodium stannate, stannous chloride, stannous fluoride, stannous fluoroborate, stannous oxide, stannous pyrophosphate, stannous sulfate, stannous 2-ethylhexanoate, and stannous oxalate. Also important are organotins of the dimethyltin, dibutyltin, tributyltin, dioctyltin, triphenyltin, and tricyclohexyltin families.

2. Inorganic Tin Compounds

Because of its amphoteric nature, tin reacts with strong acids and strong bases but remains relatively resistant to neutral solutions. A thin oxide film forms on tin exposed to oxygen or dry air at ordinary temperatures; heat accelerates this oxide formation. Tin is not attacked by gaseous ammonia even when heated. Chlorine, bromine, and iodine react with tin at normal temperatures, and fluorine reacts at 100°C, forming the appropriate stannic halides. Tin is easily attacked by hydrogen iodide and hydrogen bromide, but less readily by hydrogen chloride; it is weakly attacked by gaseous hydrogen fluoride, and it slowly dissolves in aqueous hydrochloric acid. Hot concentrated sulfuric acid reacts with tin, forming stannous sulfate, whereas dilute sulfuric acid reacts only slowly with tin at room temperature. Reaction of tin with dilute nitric acid yields soluble tin nitrates; in concentrated nitric acid, tin is oxidized to insoluble hydrated stannic oxide. No reaction occurs upon direct union of tin with hydrogen, nitrogen, or carbon dioxide.

If tin and sulfur are heated, a vigorous reaction takes place with the formation of tin sulfides. At 100–400°C, hydrogen sulfide reacts with tin, forming stannous sulfide; however, at ordinary temperatures no reaction occurs. Stannous sulfide also forms from the reaction of tin with an aqueous solution of sulfur dioxide. Molten tin reacts with phosphorus, forming a phosphide. Aqueous solutions of the hydroxides and carbonates of sodium and potassium, especially when warm, attack tin. Stannates are produced by the action of strong sodium hydroxide and potassium hydroxide solutions on tin. Oxidizing agents, eg, sodium or potassium nitrate or nitrite, are used to prevent the formation of stannites and to promote the reactions.

Stannic and stannous chloride are best prepared by the reaction of chlorine with tin metal. Stannous salts are generally prepared by double decomposition reactions of stannous chloride, stannous oxide, or stannous hydroxide with the appropriate reagents. Metallic stannates are prepared either by direct double decomposition or by fusion of stannic oxide with the desired metal hydroxide or carbonate. Approximately 80% of inorganic tin chemicals consumption is accounted for by tin chlorides and tin oxides.

2.1. Halides.

The tin halides of the greatest commercial importance are stannous chloride, stannic chloride, and stannous fluoride. Tin halides of less commercial importance are stannic bromide [7789-67-5], stannic iodide [7790-47-8], stannous bromide [10031-24-0], and stannous iodide [10294-70-9] (1).

Stannous Chloride.

Stannous chloride is available in two forms: anhydrous stannous chloride, $SnCl_2$, and stannous chloride dihydrate [10025-69-1], $SnCl_2 \cdot 2H_2O$, also called tin crystals or tin salts. These forms are sometimes used interchangeably; however, where stability, concentration, and adaptability are important, anhydrous stannous chloride is preferred. Even after long storage, changes in the stannous tin content of anhydrous stannous chloride are extremely low. Physical properties of the tin chlorides are listed in Table 1.

Anhydrous stannous chloride, a water-soluble white solid, is the most economical source of stannous tin and is especially important in redox and plating reactions. Preparation of the anhydrous salt may be by direct reaction of chlorine and molten tin, heating tin in hydrogen chloride gas, or reducing stannic chloride solution with tin metal, followed by dehydration. It is soluble in a number of organic solvents (g/100 g solvent at 23°C): acetone 42.7, ethyl alcohol 54.4, methyl isobutyl carbinol 10.45, isopropyl alcohol 9.61, methyl ethyl ketone 9.43; isoamyl acetate 3.76, diethyl ether 0.49, and mineral spirits 0.03; it is insoluble in petroleum naphtha and xylene (2).

Solutions of anhydrous stannous chloride are strongly reducing and thus are widely used as reducing agents. Dilute aqueous solutions tend to hydrolyze and oxidize in air, but addition of dilute hydrochloric acid prevents this hydrolysis; concentrated solutions resist both hydrolysis and oxidation. Neutralization of tin(II) chloride solutions with caustic causes the precipitation of stannous oxide or its metastable hydrate. Excess addition of caustic causes the formation of stannites. Numerous complex salts of stannous chloride, known as chlorostannites, have been reported (3). They are generally prepared by the evaporation of a solution containing the complexing salts.

Anhydrous stannous chloride is used extensively in the plating industry, eg, in the high speed electrotinning of continuous strip steel by the halogen process involving an aqueous solution of stannous chloride and alkali–metal fluorides, in a variety of formulations in immersion tinning processes, and in tin alloy plating (4,5) (see ELECTROPLATING). The strongly reducing nature of this chloride has contributed to its commercial development and success. Established applications of this property include its use as an analytical reducing reagent, a reducing agent in inorganic and organic chemicals manufacture and in the photoleaching of dyes, and as a sensitizing agent for nonconductive surfaces before silver coating or other metallization processes. Originally, surface sensitization with stannous chloride solutions was used only on glass prior to silvering (6). It has come to be used to sensitize plastics prior to their electroless coating with metals, eg, nickel or copper (7–9) (see ELECTROLESS PLATING).

Stannous chloride is also used as a food additive, for which use it has FDA GRAS approval (10). Other approvals include its use as a preservative for canned soda water, a color-retention agent in canned asparagus, and a component in food-packaging materials (10–14). It catalyzes a variety of organic reactions, eg, condensation, curing of resins and rubbers, esterification, halogenation, hydrogenation, oxidation, polymerization, hydrocarbon conversion, etc. Minor applications include the use of stannous chloride as an additive to drilling muds, an antisludge agent for oils, in tin coating of sensitized paper, and to improve the dyeing fastness of synthetic fibers, eg, polyamides (see PETROLEUM, DRILLING FLUIDS; POLYAMIDES, FIBERS).

Stannous Chloride Dihydrate. A white crystalline solid, stannous chloride dihydrate is prepared either by treatment of granulated tin with hydrochloric acid followed by evaporation and crystallization or by reduction of a stannic chloride solution with a cathode or tin metal followed by crystallization. It is soluble in methanol, ethyl acetate, glacial acetic acid, sodium hydroxide solution, and dilute or concentrated hydrochloric acid. It is soluble in less than its own weight of water, but with much water it forms an insoluble basic salt.

Stannic Chloride. Stannic chloride is available commercially as anhydrous stannic chloride, $SnCl_4$ (tin(IV) chloride); stannic chloride pentahydrate, $SnCl_4{\cdot}5H_2O$; and in proprietary solutions for special applications. Anhydrous stannic chloride, a colorless fuming liquid, fumes only in moist air, with the subsequent hydrolysis producing finely divided hydrated tin oxide or basic chloride. It is soluble in water, carbon tetrachloride, benzene, toluene, kerosene, gasoline, methanol, and many other organic solvents. With water, it forms a number of hydrates, of which the most important is the pentahydrate. Although stannic chloride is an almost perfect electrical insulator, traces of water make it a weak conductor.

Stannic chloride is made by the direct chlorination of tin at 110–115°C. Any stannous chloride formed in the process is separated from the stannic chloride by volatilization and subsequently chlorinated to stannic chloride. The latter is inert to steel in the absence of moisture and is shipped in plain steel drums of special design. Because prolonged contact with the skin causes burns, goggles and protective clothing should be used in the handling of stannic chloride. Stannic chloride, like stannous chloride, also forms many complexes (3).

The main uses of stannic chloride are as a raw material for the manufacture of other tin compounds, especially organotins, and in the surface treatment of glass (qv) and other nonconductive materials, whereby deposition of stannic oxide from stannic chloride solutions onto the nonconductive substrate gives it strength, abrasion-resistance, and conductivity. Very thin stannic oxide films (less than 100 nm thick) are thus used to strengthen glassware for returnable and nonreturnable foodstuff bottles and jars and for restaurant and catering glasses, which are subject to rigorous use (16). Glass treated in this way can also be made considerably lighter, which is advantageous to packing, shipping, and handling. The process involves passing freshly formed glassware through an oven maintained in an atmosphere containing stannic chloride vapor. The chloride breaks down, leaving at the glass temperature a stannic oxide deposit on the glass surface (17,18).

Where electrical conductivity and optical transparency are required, thicker (greater than 1 μm) films of stannic oxide are necessary. Such treated glasses are used in low intensity lighting panels and display signs, fluorescent lights, electron-beam control in cathode-ray tubes, and deicing windshields in aircraft. The deposition of stannic oxide films on glass surfaces is accomplished by the decomposition of stannic chloride vapor at 500–600°C and depositing it onto the glass surface or by spraying it from aqueous or mixed-organic solutions.

Stannic chloride is also used widely as a catalyst in Friedel-Crafts acylation, alkylation and cyclization reactions, esterifications, halogenations, and curing and other polymerization reactions. Minor uses are as a stabilizer for colors in soap (19), as a mordant in the dyeing of silks, in the manufacture of blueprint and other sensitized paper, and as an antistatic agent for synthetic fibers (see DYES, APPLICATION AND EVALUATION; ANTISTATIC AGENTS).

Stannic Chloride Pentahydrate. Stannic chloride pentahydrate [10026-06-9] is a white, crystalline, deliquescent solid that is soluble in water or methanol and stable at 19–56°C. It is used in place of the anhydrous chloride where anhydrous conditions are not mandatory. It is easier to handle than the fuming anhydrous liquid form. The pentahydrate is prepared by dissolving stannic chloride in hot water, thereby forming the pentahydrate at a temperature above the melting point and crystallizing by cooling. The cake is broken into small lumps for packaging.

A stannic chloride pentahydrate–ammonium bifluoride formulation for fireproofing wool is commercially available and used in New Zealand and Australia (20) (see FLAME RETARDANTS FOR TEXTILES).

Stannous Fluoride. Stannous fluoride [7783-47-3] (tin(II) fluoride), mol wt 156.7, mp 219.5°C, occurs as opaque, white, lustrous crystals, which are soluble in potassium hydroxide, fluorides, and water (31 g/100 g H_2O at 0°C, 78.5 g/100 g H_2O at 106°C) and practically insoluble in methanol, ether, and chloroform. Dilute aqueous solutions hydrolyze unless stabilized with excess acid. The specific gravity of a saturated aqueous solution at 25°C is 1.51. Commercially, stannous fluoride is produced by the reaction of stannous oxide and aqueous hydrofluoric acid or by dissolving tin in anhydrous or aqueous hydrofluoric acid.

The principal commercial use of stannous fluoride is in toothpaste formulations and other dental preparations, eg, topical solutions, mouthwash, chewing gum, etc, for preventing demineralization of teeth (21–23) (see DENTIFRICES).

The chemistry involved in cavity prevention is thought to be the reaction of stannous fluoride with hydroxyapatite in the tooth to form insoluble fluoroapatite (22). A formulation that reduces staining in dentifrices has been reported (23).

2.2. Oxides. *Stannous Oxide.* Stannous oxide, SnO ((tin(II) oxide), mol wt 134.70, sp gr 6.5) is a stable, blue-black, crystalline product that decomposes at above 385°C. It is insoluble in water or methanol, but is readily soluble in acids and concentrated alkalies. It is generally prepared from the precipitation of a stannous oxide hydrate from a solution of stannous chloride with alkali. Treatment at controlled pH in water near the boiling point converts the hydrate to the oxide. Stannous oxide reacts readily with organic acids and mineral acids, which accounts and for its primary use as an intermediate in the manufacture of other tin compounds. Minor uses of stannous oxide are in the preparation of gold–tin and copper–tin ruby glass.

Stannous oxide–zirconium oxide complex gel is used in hard coating paint to improve properties (24).

Stannous Oxide Hydrate. Stannous oxide hydrate [12026-24-3], $SnO{\cdot}H_2O$ (sometimes erroneously called stannous hydroxide or stannous acid), mol wt 152.7, is obtained as a white amorphous crystalline product on treatment of stannous chloride solutions with alkali. It dissolves in alkali solutions, forming stannites. The stannite solutions, which decompose readily to alkali-metal stannates and tin, have been used industrially for immersion tinning.

Stannic Oxide. Stannic oxide tin(IV) oxide, white crystals, mol wt 150.69, mp > 1600°C, sp gr 6.9, is insoluble in water, methanol, or acids but slowly dissolves in hot, concentrated alkali solutions. In nature, it occurs as the mineral cassiterite. It is prepared industrially by blowing hot air over molten tin, by atomizing tin with high pressure steam and burning the finely divided metal, or by calcination of the hydrated oxide. Other methods of preparation include treating stannic chloride at high temperature with steam, treatment of granular tin at room temperature with nitric acid, or neutralization of stannic chloride with a base.

In the ceramics (qv) and glass industries, stannic oxide is used for the production of opaque glasses; as an opacifier for glazes and, to a lesser extent, enamels for metals (eg, cast iron) as used in bathtubs, sinks, tile, and other sanitary ware; as a base for certain ceramic colors, eg, chrome–tin pink, vanadium–tin yellow, and antimony–tin blue; and as a component of ceramic capacitor dielectrics. More than 15 large glass-melting furnaces in the world use stannic oxide electrodes in the electromelting of lead glass (24).

Other important uses of stannic oxide are as a putty powder for polishing marble, granite, glass, and plastic lenses and as a catalyst. The most widely used heterogeneous tin catalysts are those based on binary oxide systems with stannic oxide for use in organic oxidation reactions. The tin–antimony oxide system is particularly selective in the oxidation and ammoxidation of propylene to acrolein, acrylic acid, and acrylonitrile. Research has been conducted for many years on the catalytic properties of stannic oxide and its effectiveness in catalyzing the oxidation of carbon monoxide at below 150°C has been described (25).

Transparent electroconductive coatings of stannic oxide are deposited on nonconductive substrates for electrical and strengthening applications. However, the agents used to deposit the oxide film are actually stannic chloride. More recently, some organotin compounds have been employed.

During the past 20 years, one important use of tin oxide is as a component of indium-tin oxide (ITO) used mostly for flat panel displays (26).

Hydrated Stannic Oxide. Hydrated stannic oxide of variable water content is obtained by the hydrolysis of stannates. Acidification of a sodium stannate solution precipitates the hydrate as a flocculent white mass. The colloidal solution, which is obtained by washing the mass free of water-soluble ions and peptization with potassium hydroxide, is stable below 50°C and forms the basis for the patented Tin Sol process for replenishing tin in stannate tin-plating baths. A similar type of solution (Stannasol A and B) is prepared by the direct electrolysis of concentrated potassium stannate solutions (27).

2.3. Metal Stannates. *Soluble Stannates.* Many metal stannates of formula $M_nSn(OH)_6$ are known. The two main commercial products are the soluble sodium and potassium salts, which are usually obtained by recovery from the alkaline detinning process. They are also produced by the fusion of stannic oxide with sodium hydroxide or potassium carbonate, respectively, followed by leaching and by direct electrolysis of tin metal in the respective caustic solutions in cells using cation-exchange membranes (28). Another route is the recovery from plating sludges.

Potassium stannate, $K_2Sn(OH)_6$ (mol wt 298.93), and sodium stannate [12058-66-1], $Na_2Sn(OH)_6$, mol wt 266.71, are colorless crystals and are soluble in water. The solubility of potassium stannate in water is 110.5 g/100 mL water at 15°C and that of sodium stannate is 61.5 g/100 mL water at 15°C. The solubility of sodium stannate decreases with increasing temperature, whereas the solubility of potassium stannate increases with increasing temperature. The solubility of either sodium or potassium stannate decreases as the concentration of the respective free caustic increases. Hydrolysis of stannates yields hydrated stannic oxides and is the basis of the Tin Sol solution, which is used to replenish tin in stannate tin-plating baths (29).

Although sodium stannate formed the basis for the first successful alkaline tin-electroplating bath, both stannates are used in these baths, with potassium stannate being favored in the United States. Potassium stannate is used for an alkaline tin-electroplating bath yielding higher cathode efficiencies and higher conductivities than any other alkaline bath. The stannates are also used in immersion tinning, particularly the immersion plating of aluminum pistons and other parts for the automotive industry, and in the electroplating of alloy coatings, especially tin–zinc and tin–copper alloys from mixed stannate–cyanide baths. Reviews of the use of stannates in tin plating are given in References 4, 30, and 31.

Other. Insoluble alkaline-earth metal and heavy metal stannates are prepared by the metathetic reaction of a soluble salt of the metal with a soluble alkali–metal stannate. They are used as additives to ceramic dielectric bodies (32). The use of bismuth stannate [12777-45-6], $Bi_2(SnO_3)_3{\cdot}5H_2O$, with barium titanate produces a ceramic capacitor body of uniform dielectric constant over a substantial temperature range (33). Ceramic and dielectric properties of individual stannates are given in Reference 34. Other typical commercially available stannates are barium stannate [12009-18-6], $BaSnO_3$; calcium stannate [12013-46-6], $CaSnO_3$; magnesium stannate [12032-29-0], $MgSnO_3$; and strontium stannate [12143-34-9], $SrSnO_3$.

Certain anhydrous stannates are effective as smoke suppressants in glass-reinforced polyester, especially $Na_2Sn(OH)_6$ [12058-66-1] and $ZnSnO_3$ [12036-37-2]. This use has not yet been commercialized (35).

2.4. Salts. *Stannous Sulfate.* Stannous sulfate (tin(II) sulfate), mol wt 214.75, $SnSO_4$, is a white crystalline powder which decomposes above 360°C. Because of internal redox reactions and a residue of acid moisture, the commercial product tends to discolor and degrade at ca 60°C. It is soluble in concentrated sulfuric acid and in water (330 g/L at 25°C). The solubility in sulfuric acid solutions decreases as the concentration of free sulfuric acid increases. Stannous sulfate can be prepared from the reaction of excess sulfuric acid (specific gravity 1.53) and granulated tin for several days at 100°C until the reaction has ceased. Stannous sulfate is extracted with water and the aqueous solution evaporates *in vacuo*. Methanol is used to remove excess acid. It is also prepared by reaction of stannous oxide and sulfuric acid and by the direct electrolysis of high grade tin metal in sulfuric acid solutions of moderate strength in cells with anion-exchange membranes (36).

The main use for stannous sulfate is in tin plating. The sulfate bath is widely used commercially for general plating, especially barrel plating. Significant tin-plating processes involving stannous sulfate baths include flow melting, ie, momentarily melting the coating to attain a bright finish on tin or tin–lead alloy deposits, which is used primarily in the production of printed circuit boards; bright-acid tin plating, which is used in finishing electrical contacts, radio chassis, domestic articles, and kitchen utensils; electrotinning steel strip by the vertical acid process, and liquor finishing, ie, immersion plating of steel wire with tin or copper–tin alloy prior to drawing. All tin-plating and tin-alloy-plating processes are reviewed in Reference 4.

Stannous Fluoroborate. Stannous fluoroborate, $Sn(BF_4)_2$, is available only in solution, as the solid form has not been isolated. It is prepared by dissolving stannous oxide in fluoroboric acid or by direct electrolysis of tin metal in fluoroboric acid in cells with anion-exchange membranes (36). The commercially available 47-wt % solution is widely used in tin and tin–lead alloy plating, especially in the deposition of tin–lead solder alloys for the electronics industry (37,38). Stannous fluoroborate solutions are important in plating because of their good throwing and covering power and high solubility, which promote high rates of deposition. They are used in the tin plating of copper wire, backing of electrotypes, and barrel tin plating of components for subsequent soldering (4).

Stannous Pyrophosphate. Stannous pyrophosphate [15578-26-4], $Sn_2P_2O_7$, mol wt 411.32, sp gr 4.009 at 16°C, is an amorphous white powder, decomposing at above 400°C. It is insoluble in water and soluble in concentrated mineral acids and sodium pyrophosphate. It is prepared from stannous chloride and sodium pyrophosphate, and used as a caries preventative in toothpaste and as a diagnostic aid in radioactive bone scanning and red-blood-cell labeling (23,39–41).

2.5. Toxicology. Inorganic tin and its compounds are generally of a low order of toxicity, largely because of the poor absorption and rapid excretion from the tissues of the metal (42–49). The acidity and alkalinity of their solutions make assessment of their parenteral toxicity difficult. The oral LD_{50} values for selected inorganic tin compounds are listed in Table 2. It is estimated that the average U.S. daily intake of tin, which is mostly from processed foods, is 4 mg (see FOOD PROCESSING).

Tin is normally present in animals, including humans. In the human body, it is present in small amounts in nearly all organs (53). Tin is eliminated almost completely by the alimentary tract and is scantily absorbed by the alimentary tissues. The output and intake of tin balances during adult life (54). In human subjects fed packaged C (canned) rations for 22 successive days, all tin ingested was accounted for in fecal excretion (55). Tin may be an essential trace element for the growth of the mammalian organism (see MINERAL NUTRIENTS). Many inorganic tin compounds have been approved for human contact or use by the FDA (56).

The inorganic tin compound that has received the most study from a toxicological viewpoint is stannic oxide. Autopsies performed on workers in the tin mining and refining industry, who inhaled tin oxide dust for as long as 20 yr, disclosed no pulmonary fibrosis (57). Inhalation for long periods produces a benign, symptomless pneumoconiosis with no toxic systemic effects (58).

Stannous chloride, an FDA-approved direct food additive with GRAS status, has also been extensively studied (59–62). In three FDA-sponsored studies, it was determined that stannous chloride is nonmutagenic in rats; when administered orally up to 50 mg/kg to pregnant mice for ten consecutive days, stannous chloride has no discernible effect on nidation or on maternal or fetal survival; and, when administered orally at 41.5 mg/kg to pregnant rabbits for 13 consecutive days, it produced no discernible effect on nidation or on maternal or fetal survival (63–65).

Other studies of the toxicity of stannous fluoride, sodium pentafluorostannite, sodium pentachlorostannite, sodium chlorostannate, stannous sulfide [1314-95-0], stannous and stannic oxides, stannous pyrophosphate [15578-26-4], stannous tartrate [815-85-0], and other inorganic tin compounds are reviewed in References (63–72). The OSHA TLV standard for inorganic tin compounds is two milligrams of inorganic tin compounds as tin per cubic meter of air averaged over an eight-hour work shift (47).

3. Organotin Compounds

In an organotin compound, there is at least one tin–carbon bond. The oxidation state of tin in most organotin compounds is +4, although organotin compounds having bulky groups bonded to divalent tin have been reported (73). Five classes of organotin compounds are known: R_4Sn (tetraorganotins), R_3SnX (triorganotins), R_2SnX_2 (diorganotins), $RSnX_3$ (monoorganotins), and R_6Sn_2 (hexaorganoditins). Of commercial importance are those organotins where R is methyl, butyl, octyl, cyclohexyl, phenyl, or b- b-dimethylphenethyl (neophyl). The noncarbon-bonded anionic group is commonly halide, oxide, hydroxide, carboxylate or mercaptide.

It was not until the 1940s that the commercial potential of organotins was realized. Organotins first were used as stabilizers for poly(vinyl chloride), which is normally processed just below its decomposition temperature (see HEAT STABILIZERS). The high biocidal activity of the triorganotins is one of the most applied areas of their usefulness. In addition, organotins are widely used as catalysts and curing agents and in the treatment of glass. A number of organotin subjects, including structural organotin chemistry and industrial applications, are discussed in References (74–78).

3.1. Properties.

As a member of Group 14(IVA) of the Periodic Table, tin has four valence electrons available for bonding. In its usual tetravalent state, tin assumes a typical sp^3 hydrization and the configuration of its covalent bonds is tetrahedral. In the tin atom, *d* orbitals are available and are utilized in the formation of pentacoordinate and hexacoordinate complexes by Lewis bases with organotin halides. These complexes are frequently trigonal bipyramidal or octahedral. Tin forms predominately covalent bonds to other elements, but these bonds exhibit a high degree of ionic character, with tin usually acting as the electropositive member.

Although the mean dissociation energy of tin–carbon bonds is less than that normally associated with carbon–carbon bonds ($\overline{D}_{Sn\text{-}C} = 188 - 230\,kJ/mol$ $(45 - 55\,kcal/mol), \overline{D}_{C\text{-}C} = 335 - 380\,kJ/mol\,(80 - 90\,kcal/mol)$) (75), the difference is not great enough to render the tin–carbon bond very reactive. The bond is stable to water and atmospheric oxygen at normal temperatures. The tin–carbon bond is also quite stable to heat and many organotins can be distilled under reduced pressure with little decomposition. Strong acids, halogens, and other electrophilic reagents readily cleave the tin–carbon bond, although other reactions that are common with other organometallics, eg, Grignard and organolithium reagents, do not occur with organotins. For example, the tin–carbon bond does not add to the carbonyl group, nor does it react with alcohols.

The ionic nature of organotins leads to dissimilar chemical properties. For example, triorganotin hydroxides behave not as alcohols, but more like inorganic bases, although strong bases remove the proton in certain triorganotin hydroxides because tin is amphoteric. The bis(triorganotin) oxides, $(R_3Sn)_2O$, are strong bases and react with inorganic and organic acids forming normal saltlike but nonconducting and water-insoluble compounds. They do not in the least resemble organic ethers, though they can occasionally form peroxides. Tin doubly bonded to oxygen, which is analogous to an organic ketone, does not exist and diorganotin oxides, R_2SnO, are polymers, ie,

$$-\!\!\left(\mathrm{Sn(R_2)O}\right)\!\!-_n,$$

and usually are highly cross-linked via intermolecular tin–oxygen bonds. Unlike the halocarbons, organotin halides are reactive compounds and, because of their ionic character, readily enter into metathetical substitution reactions resembling the inorganic metal halides. Tin–hydrogen bonds are unlike carbon–hydrogen bonds and, although essentially covalent, their partial ionicity makes them true hydrides with hydrogen as the formal electronegative partner. Organotin hydrides are strong reducing agents and are similar to lithium aluminum hydride. Many are organic-soluble and easily distilled and are used increasingly in organic syntheses. Unlike carbon, tin shows much less tendency to catenate, ie, form chains of Sn atoms bonded to each other. Although tin–tin-bonded compounds are known, the tin–tin bond is easily cleaved by oxygen, halogens, and acids.

3.2. Tetraorganotins. *Physical Properties.* Physical properties of typical tetraorganotin compounds are shown in Table 3. All tetraorganotin compounds are insoluble in water but are soluble in many organic solvents.

Chemical Properties. The most important reactions which tetraorganotins undergo are heterolytic, ie, electrophilic and nucleophilic, cleavage and Kocheshkov redistribution (81–84). The tin–carbon bond in tetraorganotins is easily cleaved by halogens, hydrogen halides, and mineral acids:

$$\begin{aligned}
R_4Sn + Br_2 &\longrightarrow R_3SnBr + RBr\\
R_3SnBr + Br_2 &\longrightarrow R_2SnBr_2 + RBr\\
R_4Sn + HCl &\longrightarrow R_3SnCl + RH\\
R_3SnCl + HCl &\longrightarrow R_2SnCl_2 + RH
\end{aligned}$$

With tetraaryltin compounds, the reaction can proceed further to the aryltin trihalides:

$$\underset{[4713-59-1]}{(C_6H_5)_2\,SnBr_2} + Br_2 \longrightarrow \underset{[7727-17-5]}{C_6H_5SnBr_3} + C_6H_5Br$$

$$\underset{[1135-99-5]}{(C_5H_5)_2\,SnCl_2} + HCl \longrightarrow \underset{[1124-19-2]}{C_6H_5SnCl_3} + C_6H_6$$

In practice, these cleavage reactions are difficult to control, and usually mixtures of products form, even with stoichiometric quantities of reagents. Selectivity improves at lower temperatures, higher dilutions, and in the presence of polar solvents, eg, pyridine. This method is not used to prepare the lower alkylated–arylated organotins outside the laboratory.

The most widely utilized reaction of tetraorganotins is the Kocheshkov redistribution reaction, by which the tri-, di-, and in some cases the monoorganotin halides can be readily prepared:

$$\begin{aligned} R_4Sn + SnCl_4 &\longrightarrow 2\,R_2SnCl_2 \\ R_2SnCl_2 + H_4Sn &\longrightarrow 2\,R_3SnCl \\ 3\,R_4Sn + SnCl_4 &\longrightarrow 4\,R_3SnCl \\ R_4Sn + 3\,SnCl_4 &\longrightarrow 4\,RSnCl_3 \end{aligned}$$

These reactions proceed rapidly and in good yield with primary alkyl and phenyl organotin compounds at ca 200°C. The reactions proceed at lower temperatures if anhydrous aluminum chloride is used as a catalyst.

If the reaction temperature is controlled through the use of a low boiling solvent or other means, it is possible to isolate equimolar quantities of monoalkyltin trichloride and trialkyltin chloride using a 1:1 ratio of tetraorganotin and tin tetrachloride:

$$R_4Sn + SnCl_4 \xrightarrow{<100^\circ C} R_3SnCl + RSnCl_3$$

When R is a lower alkyl, the organotin trichloride can be easily separated from the reaction mixture by extraction with dilute aqueous hydrochloric acid, in which it is soluble. This reaction also works well with unsymmetrical tetraorganotins and has been practiced commercially (85).

With tetraaryltins, the redistribution reaction can be made to proceed to the monoorganotin stage with the proper stoichiometry of reactants:

$$Ar_4Sn + 3\,SnCl_4 \longrightarrow 4\,ArSnCl_3$$

Preparation. The tetraorganotins, although of little commercial utility by themselves, are important compounds since they are the starting materials for many of the industrially important mono-, di-, and triorganotins. Among the most widely used preparations of tetraalkyl- and tetraaryltin compounds is the reaction of stannic chloride with tetrahydrofuran-based Grignard reagents or organoaluminum compounds:

$$\begin{aligned} 4\,RMgX + SnCl_4 &\xrightarrow[\text{or } R_2O]{\text{THF}} R_4Sn + 4\,MgXCl \\ 4\,R_3Al + 3\,SnCl_4 &\xrightarrow[\text{or } R_2O]{R_3N} 3\,R_4Sn + 4\,AlCl_3 \end{aligned}$$

Excess alkylating reagent is required if the tetraorganotin is desired as the exclusive product. In commercial practice, the stoichiometry is kept at or below 4:1, since the crude product is usually redistributed to lower organotin chlorides in a subsequent step and an ether is used as the solvent (86). The use of diethyl ether in the Grignard reaction has been generally replaced with tetrahydrofuran.

Organolithium and organosodium reagents can also be used to prepare tetraorganotins:

$$4\,RLi + SnCl_4 \longrightarrow R_4Sn + 4\,LiCl$$

$$4\,RNa + SnCl_4 \longrightarrow R_4Sn + 4\,NaCl$$

The Wurtz reaction, which relies on *in situ* formation of an active organosodium species, is also useful for preparing tetraorganotin compounds and is practiced commercially. Yields are usually only fair and a variety of by-products, including ditins, also form:

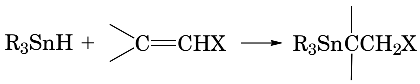
$$SnCl_4 + 8Na + 4\,RCl \longrightarrow R_4Sn + 8\,NaCl$$

A variant of the Wurtz reaction is the preparation of tetrabutyltin from activated magnesium chips, butyl chloride, and stannic chloride in a hydrocarbon mixture. Only a small amount of tetrahydrofuran is required for the reaction to proceed in high yield (86).

The use limitations of an active metal organometallic, eg, Grignard or organolithium reagents, allow preparation of only tetraorganotins, which have no functional groups reactive to the organometallic reagent on the molecule. The preparation of tetraorganotins with functional groups, eg, hydroxyl, amino, nitrile, etc, bonded to the organic group requires special measures, eg, blocking the functional group with an inert function then deblocking, usually mildly, after the formation of the tin–carbon bonds. The nitrile derivative, tetrakis(cyanoethyl)tin [15961-16-7], is prepared in good yield via a unique electrochemical reaction of tin metal with acrylonitrile (87). Unsymmetrical tetraorganotins can be prepared from the mono-, di-, or triorganotin halides and the appropriate organometallic reagent of magnesium, lithium, sodium, or aluminum:

$$\begin{gathered}
RSnCl_3 + 3\,R'MgX \longrightarrow RR'_3Sn + 3\,MgXCl \\
R_2SnCl_2 + 2\,R'MgX \longrightarrow R_2R'_2Sn + 2\,MgXCl \\
R_3SnCl + R'MgX \longrightarrow R_3R'Sn + MgXCl \\
R_2SnCl_2 + 2\,R'Li \longrightarrow R_2R'_2Sn + 2\,LiCl
\end{gathered}$$

Unsymmetrical functional tetraorganotins are generally prepared by tin hydride addition (hydrostannation) to functional unsaturated organic compounds (88) (see Hydroboration). The realization that organotin hydrides readily add to aliphatic carbon–carbon double and triple bonds forming tin–carbon bonds led to a synthetic method which does not rely on reactive organometallic reagents for tin–carbon bond formation and, thus, allows the synthesis of organofunctional tetraorganotins containing a wide variety of functional groups. Typical compounds which undergo such a reaction include tributyltin hydride and triphenyltin hydride, which can be prepared by the reaction of the chlorides with lithium aluminum hydride or sodium borohydride (89,90). Representative organic substrates include acrylonitrile, acrylate and methacrylate esters, allyl alcohol, vinyl ethers, styrene, and other olefins:



$$R_3SnH + {>}C{=}CHX \longrightarrow R_3Sn\overset{|}{\underset{|}{C}}CH_2X$$

Compounds with active halogens, eg, allyl chloride, also undergo reduction. Diorganotin dihydrides, monoorganotin trihydrides, and even stannane [2406-52-2], SnH_4, undergo analogous reactions, but the stability of the organotin hydrides decreases with increasing number of hydride groups, so these hydrostannation reactions generally proceed in poorer yield with more by-products.

Other methods for preparing tetraorganotin compounds include the use of diorganozinc compounds, halomethylzinc halides, electrolysis of organoaluminum reagents with a tin anode, and the electrolysis of diethyl sulfate with a zinc cathode and a tin anode (91–94). The latter method probably involves the *in situ* generation of an organozinc intermediate.

The reaction of an organotin–lithium, organotin–sodium, or organotin–magnesium reagent is occasionally useful for the preparation of tetraorganotins in the laboratory (78). These reagents or organostannylanionoids are air- and moisture-sensitive and can be prepared from most triorganotin halides and some tetraorganotins:

$$(CH_3CH_2CH_2)_3SnCl \xrightarrow[\text{or Li in THF}]{\text{Na in liquid NH}_3} \underset{[84474-09-9]}{(CH_3CH_2CH_2)_3SnNa} \quad \text{or} \quad \underset{[84474-08-8]}{(Li)}$$

$$(CH_3CH_2CH_2)_3SnNa(Li) + RX \rightarrow (CH_3CH_2CH_2)_3SnR + Na(Li)X$$

$$(CH_3)_4Sn \xrightarrow{\text{Na in liquid NH}_3} \underset{[16643-09-7]}{(CH_3)_3SnNa} + NaNH_2 + CH_4$$

Primary and secondary alkyl halides react well, but *tert*-alkyl halides are preferentially dehydrohalogenated by the tin reagents.

Uses. The main use for tetraorganotin compounds is as (usually captive) intermediates for the tri-, di-, and monoorganotins. Although there have been reports in the patent literature of the use of tetraorganotins as components of Ziegler-Natta-type catalysts for the polymerization of olefins, there is no evidence that such catalysts are used commercially.

3.3. Triorganotins.

Triorganotins and diorganotins constitute by far the most important classes of organotins.

Physical Properties. Physical properties of some typical triorganotin halides are listed in Table 4 and those of commercially important triorganotin compounds are listed in Table 5. The triorganotin halides are insoluble in water, except for $(CH_3)_3SnCl$ which is completely water soluble, but are soluble in most organic solvents. The fluorides are insoluble in most organic solvents because of their highly associated structure resulting from strong SnF–Sn interactions.

Reactions. The utility of triorganotin chlorides and their application as starting materials for most other triorganotin compounds results from the ease of nucleophile displacement, as indicated in Figure 1. The commercially important triorganotin compounds are most frequently the oxides or hydroxides, the fluorides, and the carboxylates.

The basic hydrolysis of trialkyltin halides and other salts forms bis(oxide)s since, except for trimethyltin, hydroxides are unstable towards dehydration at room temperature. With tin aryl, aralkyl, and cycloalkyltin compounds, the hydroxides can be isolated. Although quite stable, they exist in mobile equilibrium with the bisoxide and water and are easily dehydrated. Trimethyltin hydroxide is exceptionally stable towards dehydration.

Triorganotin oxides and hydroxides are moderately strong bases and react readily with a wide variety of acidic compounds:

$$\mathrm{R_3SnOH + HX \longrightarrow R_3SnX + H_2O}$$
$$\mathrm{(R_3Sn)_2O + 2\,HX \longrightarrow 2\,R_3SnX + H_2O}$$

This reaction is useful in the preparation of anionic derivatives from the chlorides when the nucleophilic displacement route is unsatisfactory. Even weak acids, eg, phenols, mercaptans, and cyclic nitrogen compounds, can be made to undergo reaction with triorganotin hydroxides or bisoxides if the water of reaction is removed azeotropically as it forms.

Triorganotin compounds of strong acids are generally quite stable to hydrolysis under neutral conditions. Under basic conditions, the hydroxide or bisoxide forms. Strong acids, halogens, and other electrophiles can cause cleavage of tin–carbon bonds with the formation of diorganotins. The triorganotin oxides of lower alkyl groups (C_1–C_4) are sufficiently basic to react with carbon dioxide in air, resulting in the precipitation of triorganotin carbonates.

Preparation. Triorganotin chlorides of the general formula R_3SnX are the basic starting materials for other triorganotins. They are generally prepared by Kocheshkov redistribution from the crude tetraorganotin:

$$\mathrm{4\,R_4Sn + SnCl_4 \longrightarrow 4\,R_3SnCl}$$

The stoichiometric reaction of Grignard or alkylaluminum reagents with stannic chloride to give the trialkyltin chloride usually gives a mixture of products. Only in a very few cases is it possible to alkylate tin tetrachloride directly to the triorganotin chloride in good yield with few by-products using a Grignard reagent. In such cases, the formation of the triorganotin is favored because of steric hindrance (96):

$$\mathrm{3\,C_6H_{11}MgCl + SnCl_4 \longrightarrow (C_6H_{11})_3SnCl + 3\,MgCl_2}$$

Acid, hydrogen halide, or halogen cleavage of tetraorganotins is not used except on a laboratory scale because they are wasteful of tin–carbon bonds and uneconomical on a commercial scale.

Tribenzyltin chloride [3151-41-5] is a unique example of a triorganotin chloride that can be prepared directly from the organic halide and tin metal:

$$3\,C_6H_5CH_2Cl + 2\,Sn \xrightarrow[\text{reflux}]{H_2O} (C_6H_5CH_2)_3SnCl + SnCl_2$$

This reaction only proceeds in water. In a solventless system, only organic condensation products of benzyl chloride form, including dibenzyl. In toluene, dibenzyltin dichloride [3002-01-5] is the principal reaction product (97).

The production of triphenyltin hydroxide [76-87-9] and triphenyltin acetate [900-95-8] start with triphenyltin chloride, which is prepared by the Kocheshkov redistribution reaction from tetraphenyltin and tin tetrachloride. The hydroxide is prepared from the chloride by hydrolysis with aqueous sodium hydroxide. The acetate can be made directly from the chloride using sodium acetate or from the hydroxide by neutralization with a stoichiometric quantity of acetic acid.

For the preparation of tricyclohexyltin chloride, the Kocheshkov redistribution reaction is not suitable, since tetracyclohexyltin decomposes in the presence of stannic chloride at the normal redistribution temperatures. Two alternative routes are practiced for the manufacture of tricyclohexyltin chloride. The closely controlled reaction of cyclohexylmagnesium chloride and stannic chloride in a three-to-one molar ratio can be made to give the desired product in a good yield (96). Another method involves two steps for the preparation of tricyclohexyltin chloride (98). In the first step, butyltin trichloride [1118-46-3] reacts with three moles of cyclohexylmagnesium chloride forming butyltricyclohexyltin [7067-44-9]. This tetraorganotin then reacts with stannic chloride under mild conditions in an inert solvent, cleaving a butyl group and yielding tricyclohexyltin chloride and butyltin trichloride. The latter is recovered and recycled. The reactions are shown below:

$$C_4H_9SnCl_3 + 3\,C_6H_{11}MgCl \rightarrow (C_6H_{11})_3SnC_4H_9$$

$$(C_6H_{11})_3SnC_4H_9 + SnCl_4 \rightarrow (C_6H_{11})_3SnCl + C_4H_9SnCl_3$$

Tricyclohexyltin chloride is converted to the hydroxide with sodium hydroxide. The triazole can be prepared from the chloride with sodium or potassium hydroxide and 1,2,4-triazole.

Bis(trineophyltin) oxide [60268-17-4] is prepared from the chloride in the normal manner. The chloride can either be prepared directly from the reaction of three moles of neophylmagnesium chloride and stannic chloride or by the butyl transfer reaction between butyltrineophyltin and stannic chloride. The hydroxide derivative initially formed on hydrolysis of the chloride is readily dehydrated to the bis(oxide) at ca 100°C.

Uses. Triorganotin compounds are widely used as industrial biocides, agricultural chemicals, wood preservatives, and marine antifoulants. Although the *in vitro* fungicidal biological activity of the triorganotins was recognized in the mid-1950s, commercial development was not seriously undertaken until the early 1960s (99,100). The triorganotins that are most useful as biological control agents, in general, are the tributyltins, triphenyltins, and tricyclohexyltins.

The lower trialkyltins from trimethyl to tri-*n*-pentyl show high biological activity. The trimethyltins are highly insecticidal and the tripropyl-, tributyl-, and tripentyltin compounds have a high degree of fungicide and bactericide activity. Dialkyltin compounds are less active than the analogous trialkyltins. The maximum activity towards bacteria and fungi is exhibited by the tripropyl and tributyltin compounds, with the tributyltins providing the optimum balance between fungicidal and bactericidal activity and mammalian toxicity. Tributyltin compounds, especially the oxide and benzoate, are used as antimicrobials and slimicides for cooling-water treatment and as hard-surface disinfectants. These and similar compounds have been used as laundry sanitizers and mildewcides to prevent mildew formation in the dried film of water-based emulsion paints. In most microbiocide applications, the tributyltin compound is used in conjunction with another biocide, usually a quaternary ammonium compound, to complement the activity of the organotin which is most effective against gram-positive bacteria.

Although the lower trialkyltins show high fungicide activity, they are unlikely candidates for agricultural fungicide use because of their high phytotoxicity to the host plant. Various attempts have been made to moderate the phytotoxicity of the lower trialkyltins by changing the anion portion of the molecule. These have not been successful because the nature of the anionic group has little influence on the spectrum of biological activity, provided that the anion is not biologically active and it confers a sufficient minimal solubility on the compound.

In the early 1960s, the first organotin-based agricultural fungicide, triphenyltin acetate, was introduced in Europe commercially by Farbwerke Hoechst AG as Brestan. Brestan, which is a protectant foliar fungicide, was recommended for the control of *phytophthora* (late blight) on potatoes and *cercospora* on sugar beets at application rates of a few ounces per acre (101). Shortly thereafter, triphenyltin hydroxide was introduced as Du-Ter by Philips-Duphar, NV, with about the same activity and spectrum of disease control as Brestan. Du-Ter is registered with the EPA in the United States as a fungicide for potatoes, sugar beets, pecans, and peanuts. Both compounds also exhibit a strong antifeedant effect on some insects and are fly sterilants at sublethal concentrations.

Tricyclohexyltin hydroxide was introduced into the U.S. market by the Dow Chemical Company as Plictran. Plictran was originally recommended for the control of phytophagous (plant-feeding) mites on apples and pears. It is also registered in the United States and in many European and Asian countries for this use as well as for mite control on citrus, stone fruits, and hops. This product has since been joined in the market by similar-acting, competitive products.

Bis(tributyltin) oxide [56-35-9] is widely used in Europe for the preservation of timber, millwork, and wood joinery, eg, window sashes and door frames. It is applied from organic solution by dipping or vacuum impregnation. It imparts resistance to attack by fungi and insects but is not suitable for underground use. An advantage of bis(tributyltin) oxide is that it does not interfere with subsequent painting or decorative staining and does not change the natural color of the wood. Tributyltin phosphate, $((C_4H_9)_3Sn)_3PO_4$, has also been suggested as a wood preservative.

Most surfaces in prolonged contact with seawater and freshwater are susceptible to the attachment of marine growths, eg, algae and barnacles.

The most common method for preventing marine fouling has been to paint the underwater structure of the vessel with an antifouling paint containing a toxicant. For many years, the antifouling agent of choice was cuprous oxide, but there has been a strong trend towards the use of triorganotin compounds, both alone and in combination with cuprous oxide (102). Preferred compounds for use in this application are tributyltin fluoride, triphenyltin hydroxide, and triphenyltin fluoride because they are highly active against a wide range of fouling species. Bis(tributyltin) oxide, tributyltin acetate, and other tributyltin carboxylates have also been successfully used as antifoulants. Triorganotin compounds offer many advantages over cuprous oxide. Because they are colorless, they can be used in the preparation of paints of a variety of colors. Unlike cuprous oxide, they do not contribute to galvanic corrosion on steel or aluminum hulls. The triorganotins are rapidly degraded into lower alkylated species and then to nontoxic inorganic tin once released from the coating. Inorganic copper, on the other hand, is toxic in all its forms (see COATINGS, MARINE).

There has been much interest in eroding antifouling paints that are based on tributyltin acrylate [13331-52-7] or methacrylate [2155-70-6] copolymers with various organic acrylate esters as the combined toxicant and paint binder resin (102). Such paints erode in moving seawater because the triorganotin portion slowly hydrolyzes from the acrylic backbone in normally basic seawater, releasing the active species tributyltin chloride and bis(tributyltin) oxide. The depleted surface layer of the paint film, containing hydrophilic-free carboxylic acid groups, becomes water-swollen and is easily eroded by moving seawater. A fresh surface of triorganotin acrylate polymer is thereby exposed and the process repeats. Coatings based on organotin polymers can be formulated to release the toxicant at a rate which is linear with time. Such coatings are claimed to reduce fuel costs over and above the savings resulting from a clean hull by providing a surface which becomes smoother with time.

The advantages claimed for organotin polymer-based antifouling paints include constant toxicant delivery vs time, erosion rate and toxicant delivery are controllable, no depleted paint residue to remove and dispose, 100% utilization of toxicant, polishing at high erosion rates, surface is self-cleaning, and function is continuously reactivated.

Triorganotin compounds have also been used experimentally in controlled-release formulations to control the infective snail vector in the debilitating tropical disease schistosomiasis (bilharzia) and to control mosquitoes in stagnant ponds (103). As yet, the large-scale use of such methods has little support in the host third world countries where these problems are most severe. Tributyltin chloride has been used to confer rodent-repellent properties on wire and cable coatings (104).

3.4. Diorganotins.

Physical Properties. Physical properties of some typical diorganotin compounds are shown in Table 6. The diorganotin chlorides, bromides, and iodides are soluble in many organic solvents and, except for dimethyltin dichloride, are insoluble in water.

Commercial grades of diorganotin carboxylates frequently have wider melting ranges because of the use of less pure grades of carboxylic acids in their manufacture which, for many applications, permits more facile handling of the liquids.

Reactions. Although there are few industrial applications for the diorganotin halides, these compounds are the basic intermediates for the preparation of all the commercially important diorganotin derivatives. They are prepared by nucleophilic displacement similar to that used for triorganotin derivatives (see Fig. 1). Basic hydrolysis of the diorganotin halides gives the diorganotin oxides in high yield. Except in rare cases, dihydroxide derivatives are unknown. As with the triorganotins, diorganotin oxides are sometimes used as intermediates from which other derivatives can be obtained by neutralization with strong or weak acids:

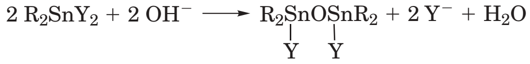
$$R_2SnCl_2 \xrightarrow{OH^-} R_2SnO$$

$$R_2SnO + 2\,HY \longrightarrow R_2SnY_2 + H_2O$$

Diorganotin dihalides are moderately strong Lewis acids and form stable complexes with ammonia and amines. The commercially important diorganotin compounds are most frequently the oxides, carboxylates, and mercaptocarboxylic acid esters. The oxides are amorphous or polycrystalline, highly polymeric, infusible, and insoluble solids. They are moderately strong bases and react readily with a wide variety of strongly and weakly acidic compounds. Their insolubility in all nonreactive solvents makes the choice of proper reaction conditions for such a neutralization reaction an important consideration for optimum yields.

Diorganotin esters of strong acids are relatively stable to hydrolysis under neutral conditions, but generally, diorganotin compounds are more reactive chemically than the triorganotins. Diorganotin esters of weak acids are somewhat susceptible to hydrolysis, even under neutral conditions, but this reactivity is moderated somewhat by their hydrophobicity.

On partial hydrolysis, diorganotin halides and carboxylates may form basic salts having a rather complicated structure:



$$2\,R_2SnY_2 + 2\,OH^- \longrightarrow R_2\underset{\displaystyle Y}{\underset{|}{Sn}}O\underset{\displaystyle Y}{\underset{|}{Sn}}R_2 + 2\,Y^- + H_2O$$

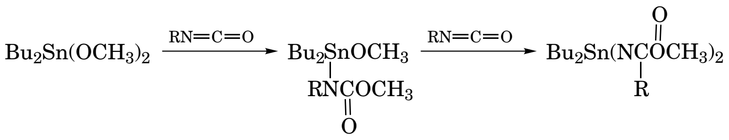
Diorganotin sulfides can be prepared from the chlorides or oxides by the exchange of a reactive substituent for sulfur:

$$R_2SnCl_2 + S^{2-} \longrightarrow R_2SnS + 2\,Cl^-$$

$$R_2SnO + CS_2 \longrightarrow R_2SnS + COS$$

The sulfides are associated like the oxides, but to a lesser degree. They are crystalline, sharp-melting, soluble in many organic solvents, and resistant to hydrolysis. Most are cyclic trimers (106).

Some diorganotin compounds, eg, the alkoxides, add to heterounsaturated systems, eg, isocyanates. This reaction is believed to occur in stages (107).



$$\mathrm{Bu_2Sn(OCH_3)_2} \xrightarrow{\mathrm{RN{=}C{=}O}} \mathrm{Bu_2\underset{\substack{|\\ RN\underset{\substack{\|\\ O}}{C}OCH_3}}{Sn}OCH_3} \xrightarrow{\mathrm{RN{=}C{=}O}} \mathrm{Bu_2Sn(\underset{\substack{|\\ R}}{N}\overset{\substack{O\\ \|}}{C}OCH_3)_2}$$

Preparation. Diorganotin dichlorides are the usual precursors for all other diorganotin compounds; three primary methods of manufacture are practiced. Dibutyltin dichloride is manufactured by Kocheshkov redistribution from crude tetrabutyltin and stannic chloride and usually is catalyzed with a few tenths of a percent aluminum trichloride:

$$(C_4H_9)_4Sn + SnCl_4 \rightarrow 2\,(C_4H_9)_2SnCl_2$$

Yields are almost quantitative and product purity is good with formation of only minute amounts of mono- and tributyltin by-products.

Many organic halides, especially alkyl bromides and iodides, react directly with tin metal at elevated temperatures (>150°C). Methyl chloride reacts with molten tin metal, giving good yields of dimethyltin dichloride, which is an important intermediate in the manufacture of dimethyltin-based PVC stabilizers. The presence of catalytic metallic impurities, eg, copper and zinc, is necessary to achieve optimum yields (108):

$$2\,CH_3Cl + Sn \xrightarrow[Cu]{235^\circ C} (CH_3)_2SnCl_2$$

The reaction of higher alkyl chlorides with tin metal at 235°C is not practical because of the thermal decomposition which occurs before the products can be removed from the reaction zone. The reaction temperature necessary for the formation of dimethyltin dichloride can be lowered considerably by the use of certain catalysts. Quaternary ammonium and phosphonium iodides allow the reaction to proceed in good yield at 150–160°C (109). An improvement in the process involves the use of amine–stannic chloride complexes or mixtures of stannic chloride and a quaternary ammonium or phosphonium compound (110). Use of these catalysts is claimed to yield dimethyltin dichloride containing less than 0.1 wt % trimethyltin chloride. Catalyzed direct reactions under pressure are used commercially to manufacture dimethyltin dichloride.

The direct reaction of tin metal with higher haloalkanes is less satisfactory even when catalysts are used, except with alkyl iodides. The reaction of butyl iodide with tin metal is used commercially in Japan to prepare dibutyltin diiodide, from which dibutyltin oxide is obtained on hydrolysis with base:

$$2\,C_4H_9I + Sn \rightarrow (C_4H_9)_2SnI_2 \overset{OH^-}{\rightarrow} (C_4H_9)_2SnO + 2\,I^-$$

The economics of this process depend on near-quantitative recovery and recycle of the iodine to prepare butyl iodide.

Tin metal also reacts directly with a number of activated organic halides, including allyl bromide, benzyl chloride, chloromethyl methyl ether, and β-halocarboxylic esters and nitriles giving fair-to-good yields of diorganotin dihalides (97,111–114).

The facile reaction of metallic tin in the presence of hydrogen chloride with acrylic esters to give high yields of bis(b-alkoxycarbonylethyl)tin dichlorides is reported in References 115 and 116. This reaction proceeds at atmospheric pressure and room temperature and has been practiced commercially. Halogenostannanes have been postulated as intermediates (105).

Uses. Poly(Vinyl Chloride) Stabilizers. The largest single industrial application for organotin compounds is in the stabilization of PVC. Organotins are added to PVC to prevent its degradation by heat (180–200°C) during processing and by long-term exposure to sunlight (117–139).

Dialkyltin compounds are the best general-purpose stabilizers for PVC, especially if colorlessness and transparency are required. Commercial organotin stabilizers include the carboxylates, especially the maleates, laurates, and substituted maleates; the mercaptide, the mercaptoacid, and mercaptoalcohol ester derivatives; and the estertins, 2-carboalkoxyethyltin derivatives. The common industrial organotin stabilizers are listed in Table 7.

Sulfur-containing organotins impart excellent heat stability to PVC, but nonsulfur-containing organotins are used when resistance to light and weathering are required. The two main markets for organotin stabilizers are in the packaging and building industries. In the packaging industry, certain organotin stabilizers are used in PVC food packaging and drink containers. In the United States and Germany, dioctyltin maleate [16091-18-2], dioctyltin bis(isooctylmercaptoacetate), and butylthiostannoic acid [26410-42-4] are approved for use in PVC food packaging; in Germany, dimethyltin bis(isooctylmercaptoacetate), 2-carbobutoxyethyltin tris(isooctylmercaptoacetate) [63438-80-2], and bis(2-carbobutoxyethyltin) bis(isooctylmercaptoacetate) are also approved. These uses reflect the low toxicity of these organotin stabilizers.

In the building industry, rigid PVC is stabilized with diorganotin carboxylates, especially dibutyltin maleate, for use in floorings and light fixture glazing and with diorganotin mercaptides and mercaptoacid esters for use in sidings, profiles, roofing, fencing, window frames, and piping. The dibutyltin, dimethyltin, and estertin sulfur-containing derivatives are used for these nonfood applications as well as in PVC potable-water piping.

Polyurethane Foam Catalysts. Early production of polyurethane foams involved a two-step reaction in which a polyether glycol reacted with toluene diisocyanate forming a urethane prepolymer having reactive isocyanate end groups. Water was then added to condense the neighboring isocyanate groups to urethane linkages. In the process, carbon dioxide formed, which acted on the gelling polymer to produce a rigid or elastomeric foam. Inorganic tin compounds and diorganotin compounds, eg, dibutyltin diacetate [1067-33-0], dilaurate [77-58-7], and di(2-ethylhexanoate) [2781-10-4], catalyze the glycol–isocyanate reaction as well as the urethane condensation step and enable the preparation of foams in one step in a semicontinuous process (140,141). In the United States, dibutyltin compounds are used mostly in the catalysis of rigid foams and the laurate has been the catalyst of choice (142) (see URETHANE POLYMERS).

Diorganotin compounds have been used increasingly as catalysts for high resiliency foam in automotive seating. In high resiliency foam, diorganotin mercaptocarboxylates and mercaptides as catalysts improve some key physical properties (143). Some diorganotins, eg, the mercaptocarboxylates and mercaptides, are stable enough to be used in the preparation of masterbatches containing premixed polyol, water surfactant, amine, and organotin catalyst which are stored for up to six months (144).

Esterification Catalysts. Dibutyltin compounds as well as monobutyltins are used increasingly as esterification (qv) catalysts for the manufacture of organic esters used in plasticizers (qv), lubricants, and heat-transfer fluids (see LUBRICATION AND LUBRICANTS; HEAT-EXCHANGE TECHNOLOGY). Although esterification reactions catalyzed by organotins require higher temperatures (200–230°C) than those involving strong acid catalysts, eg, *p*-toluenesulfonic acid, side reactions are minimized and the products need no extensive refining to remove acidic ionic catalyst residues. Additionally, equipment corrosion is eliminated and the products have better color and odor properties because fewer by-products form (145). Usual catalyst levels are 0.05–0.3 wt % based on the total reactants charged. Dibutyltin compounds are also useful in catalyzing the transesterification and polycondensation of dimethyl terephthalate to poly(ethylene terephthalate) for packaging applications and in the manufacture of polyester-based alkyd resins (146).

Other. Dibutyltin dilaurate [77-58-7] has been successfully used for many years as a coccidiostat in the treatment of intestinal worm infections in chickens and turkeys (see ANTIPARASITIC AGENTS).

In Japan and Europe, dimethyltin dichloride that has been purified to remove all traces of trimethyltin chloride is used to provide a thin coating of stannic oxide on glass upon thermal decomposition at 500–600°C. Thin deposits of stannic oxide improve the abrasion resistance and bursting strength of glass bottles. Dimethyltin dichloride is manufactured and marketed as Glahard by Chugoku Toryo Company, Ltd., Shiga, Japan. Electroconductive films can be formed with thick coatings of tin oxide that are deposited in this manner.

Dibutyltin and dioctyltin diacetate, dilaurate, and di-(2-ethylhexanoate) are used as catalysts for the curing of room-temperature-vulcanized (RTV) silicone elastomers to produce flexible silicone rubbers used as sealing compounds, insulators, and in a wide variety of other applications. Diorganotin carboxylates also catalyze the curing of thermosetting silicone resins, which are widely used in paper-release coatings.

In addition, diorganotin compounds are used as transesterification catalysts for the curing of cathodic, electrocoated paints (147). The biological activity and toxicity of diorganotins are much less than of analogous triorganotins with the same carbon-bonded organic groups.

3.5. Monoorganotins. *Physical Properties.* Properties of some monoorganotin trihalides are listed in Table 8. The monoorganotin trihalides are hygroscopic, low melting solids or liquids which are to varying extents hydrolyzed in water or moist air, liberating the hydrogen halides. They are soluble in most organic solvents and in water that contains enough acid to retard hydrolysis.

Chemical Properties. The monoorganotin trihalides are strong Lewis acids and form complexes with ammonia, amines, and many other oxygenated organic compounds, eg, ethers. In many ways, they resemble acid chlorides. As with the diorganotin dichlorides, the halogens on the molecule are easily replaced by a wide variety of nucleophilic reagents, making these trihalides useful intermediates for other monoorganotins. Typical compounds, which are easily formed by displacement reactions, include tris(alkoxides), tris(carboxylates), tris(mercaptides), and tris(mercaptocarboxylate esters). These compounds are generally more easily hydrolyzed than the analogous diorganotins.

The oxide monobutyltin oxide [51590-67-1], is a sesquioxide, $C_4H_9SnO_{1.5}$, from which it is difficult to remove the last traces of water. It is an infusible, insoluble, amorphous white powder that forms when butyltin trichloride is hydrolyzed with base. The partially dehydrated material, butylstannoic acid [2273-43-0], is slightly acidic and forms alkali metal salts. These salts, ie, alkali metal alkylstannonates, form when excess alkali is used to hydrolyze the organotin trichloride:

$$\mathrm{RSnCl_3 + 4\,NaOH \rightarrow RSnO_2Na + 3\,NaCl + 2\,H_2O}$$

Partially hydrolyzed products of the form $RSn(OH)_2Cl$ are believed to be mixtures in most cases.

When organotin trihalides are treated with alkali metal sulfide, the sesquisulfides form (148):

$$\mathrm{2\,RSnCl_3 + 3\,Na_2S \rightarrow 2\,RSnS_{1.5} + 6\,NaCl}$$

At least one, the monobutyl compound, is a tetramer in benzene (148).

Preparation and Manufacture. Monoorganotin halides are the basic raw materials for all other triorganotin compounds and are generally prepared by Kocheshkov redistribution from the tetraorganotin, eg, tetrabutyltin or the higher organotin halides:

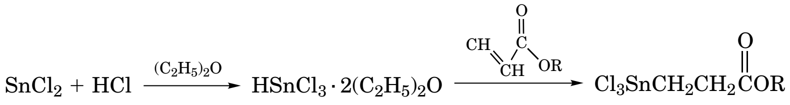
$$\mathrm{R_4Sn + 3\,SnCl_4 \rightarrow 4\,RSnCl_3}$$
$$\mathrm{R_2SnCl_2 + SnCl_4 \rightarrow 2\,RSnCl_3}$$

The oxidative addition of aliphatic organic halides to stannous chloride has long been of interest for the preparation of monoorganotin trihalides:

$$\mathrm{SnCl_2 + RCl \rightarrow RSnCl_3}$$

This reaction gives fair-to-good yields of monoorganotin tribromides and trichlorides when quaternary ammonium or phosphonium catalysts are used (149). Better yields are obtained with organic bromides and stannous bromide than with the chlorides. This reaction is also catalyzed by trialkylantimony compounds at 100–160°C, bromides are more reactive than chlorides in this preparation (150,151). a, w-Dihaloalkanes also react in good yield giving w-haloalkyltin trihalides when catalyzed by organoantimony compounds (152).

A significant advance in the synthesis of monoorganotin trihalides was the preparation of b-substituted ethyltin trihalides in good yield from the reaction of stannous chloride, hydrogen halides, and a, b-unsaturated carbonyl compounds, eg, acrylic esters, in common solvents at room temperature and atmospheric pressure (153,154). The reaction is believed to proceed through a solvated trichlorostannane intermediate (155):



$$SnCl_2 + HCl \xrightarrow{(C_2H_5)_2O} HSnCl_3\cdot 2(C_2H_5)_2O \xrightarrow{CH{=}CH\overset{O}{\overset{\|}{C}}OR} Cl_3SnCH_2CH_2\overset{O}{\overset{\|}{C}}OR$$

This reaction can be extended to unsaturated nitriles, eg, acrylonitrile, which can give trihalostannyl-functional carboxylic acids, esters, and amides by the proper choice of solvents and reaction conditions (156).

Uses. Poly(Vinyl Chloride) Stabilizers. Although generally less effective as PVC stabilizers than dialkyltin derivatives, monoalkyltin compounds added to the dialkyltin compounds in amounts of 5–20 wt % exert a synergistic effect on stabilizer effectiveness, preventing early yellowing. They supposedly function by reacting more quickly and at lower processing temperatures than the dialkyltin species, thus preventing the early onset of yellowing; conversely, diorganotins are more effective in retarding the long-term degradation of the polymer. Butylthiostannoic acid anhydride is used as a sole stabilizer for certain grades of PVC in Germany, but elsewhere is rarely used alone (157). It is approved in Germany and in the United States for food packaging (158). In Germany, the following monoorganotins alone or in mixtures are also approved for this use: butylthiostannoic acid anhydride with either dioctyltin compounds or 2-carbobutoxyethyltin compounds, 2-carbobutoxyethyltin tris(isooctylmercaptoacetate) alone or mixed with its dicounterpart, monomethyltin tris(isooctylmercaptoacetate) [56225-49-1] plus its dicounterpart in a 24:76 wt % ratio, and monooctyltin tris[alkyl (C_{10}–C_{16}, isooctyl) mercaptoacid esters] with their dicounterparts.

Treatment of Glass. The use of monobutyltin trichloride in the hot-end coating of glass to improve the abrasion resistance and bursting strength of glass bottles has been patented, and the deposition process variables and product advantages have been described (159–161). Highly efficient utilization of tin is one of the main benefits.

3.6. Compounds with Tin–Tin Bonds. The most important class of catenated tin compounds is the hexaorganoditins. The ditin compounds are usually prepared by reductive coupling of a triorganotin halide with sodium in liquid ammonia:

$$2\,R_3SnCl + 2\,Na \xrightarrow{NH_3(1)} R_3SnSnR_3 + 2\,NaCl$$

This reaction proceeds in stages via an organostannylsodium compound:

$$R_3SnCl + 2\,Na \longrightarrow R_3SnNa + NaCl$$

$$R_3SnNa + R_3SnCl \longrightarrow R_3SnSnR_3 + NaCl$$

Lithium metal in tetrahydrofuran can also be used as the coupling reagent, and unsymmetrical ditins can be prepared when the reaction is conducted in stages (162,163).

Hexaorganoditins with short-chain aliphatic groups are colorless liquids, distillable under vacuum, soluble in organic solvents other than the lower alcohols, and insoluble in water. They are generally unstable in air, undergoing ready oxidation to a mixture of organotin compounds. Hexaarylditins are usually crystalline solids and are much more stable towards oxidation.

The ditins as of yet are insignificant commercially, although there has been interest in hexamethylditin [661-69-8] (Pennwalt TD-5032) as an insecticide (164,165).

3.7. Salts. Organic tin salts are tin compounds containing an organic radical in which the tin is bonded with an element other than carbon. The most common of these are the tin carboxylates, especially the stannous carboxylates. The latter are manufactured by reaction of stannous oxide or chloride with the appropriate acid. The most commercially significant of the stannous carboxylates is stannous 2-ethylhexanoate [301-10-0]. The second most important industrial organic tin salt is stannous oxalate [814-94-8]. Other commercially available organic tin salts that are of minor commercial importance are listed in Table 9.

Stannous 2-Ethylhexanoate. Stannous 2-ethylhexanoate, $Sn(C_8H_{15}O_2)_2$ (sometimes referred to as stannous octanoate, mol wt 405.1, sp gr 1.26), is a clear, very light yellow, and somewhat viscous liquid that is soluble in most organic solvents and in silicone oils (166). It is prepared by the reaction of stannous chloride or oxide with 2-ethylhexanoic acid.

The primary use for stannous 2-ethylhexanoate is as a catalyst with certain amines for the manufacture of one-shot polyether urethane foams (167). Resulting foams exhibit good dry-heat stability over a wide range of catalyst concentrations. Food-grade stannous 2-ethylhexanoate is approved by the FDA for use in polymers and resins used in food packaging (168). Other industrial applications include its use as a catalyst in silicones, including room-temperature-vulcanizing (RTV) silicone rubbers and silicone–oil emulsions; in epoxy formulations; and in various urethane coatings and sealants (qv) (169,170). Proprietary catalyst formulations based on stannous 2-ethylhexanoate are also available.

Stannous Oxalate. Stannous oxalate, $Sn(C_2O_4)$ (mol wt 206.71, dec 280°C, sp gr 3.56 at 18°C), is a white crystalline powder, is soluble in hot concentrated hydrochloric acid and mixtures of oxalic acid and ammonium oxalate, and is insoluble in water, toluene, ethyl acetate, dioctyl phthalate, THF, isomeric heptanes, and acetone (171). It is prepared by precipitation from a solution of stannous chloride and oxalic acid and is stable indefinitely.

Stannous oxalate is used as an esterification and transesterification catalyst for the preparation of alkyds, esters, and polyesters (172,173). In esterification reactions, it limits the undesirable side reactions responsible for the degradation of esters at preparation temperatures. The U.S. Bureau of Mines conducted research on the use of stannous oxalate as a catalyst in the hydrogenation of coal (174) (see COAL).

3.8. Toxicology. The toxicological properties of organotin compounds are reviewed in References 43, (74–77), and 175. The toxicity of organotin compounds is a reflection of their biological activity. Thus, the most toxic to mammals, including man, are the lower trialkyltin compounds, ie, trimethyltin and triethyltin. As with the fungicidal activity, the toxicity seems little affected by the nature of the anionic group bonded to the trialkyltin moiety. There is some evidence that triorganotin compounds that are five-coordinate and intramolecularly chelated are less toxic than similar unchelated four-coordinate compounds (176,177). As a general rule, the toxicity of the trialkyltins decreases with increasing chain length of the alkyl group.

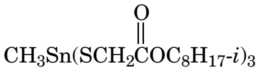
The acute oral mammalian toxicities of typical triorganotin compounds, including some which are not used commercially, are listed in Table 10. In some cases, two or more substantially different values are reported in the literature for the same test animal. In these cases, both high and low values are tabulated. The toxicity of triorganotins is strongly dependent on the nature of the organic groups bonded to tin. The toxicity varies from the highly toxic lower alkyl trimethyl and triethyltins, which are not used in any commercial applications, to the substantially less toxic trineophyl and trioctyl derivatives. The widely used tributyl-, triphenyl-, and tricyclohexyltin derivatives are intermediate in mammalian oral toxicity. The highest trialkyl and triaryltins are less toxic when given orally than when given parentally because of their poor absorption from the gastrointestinal tract (180). Uncoupling of oxidative phosphorylation in cellular mitochondria has been suggested as one of the mechanisms of lower trialkyltin toxicity (181).

Most triorganotins that have been studied and all commercial ones are eye and skin irritants. Animal studies have shown that, particularly with tributyl and triphenyltin compounds, untreated eye contact can result in permanent corneal damage. If allowed to remain in contact with the skin for prolonged periods, these compounds can produce severe irritation and, in some cases, severe chemical burns (49). Thus, eye and skin protection must be worn when handling triorganotin compounds. Sometimes the irritant effect is delayed and may not be apparent for several hours. In the event of acute local dermal contact episodes with tributyltin compounds, pruritis, minor edema, and follicular pustules in hirsute areas occur. Systemic effects are observed in percutaneous tests of tributyltin iodide, bromide, chloride and bis-oxide in tests with rabbits, so it could be assumed that these compounds are absorbed through the skin. Bis(tributyltin) oxide produces a typical lower trialkyltin response dermally, characterized by redness, swelling, and skin discoloration in test animals. Its effects on the eyes are serious with damage to the cornea (49).

Among the most widely studied triorganotin compounds are triphenyltin hydroxide, triphenyltin acetate, and tricyclohexyltin hydroxide because of their use as agricultural chemicals. Triphenyltin hydroxide is a severe eye irritant in rabbits but is nonirritating to dry rabbit skin (49). In contrast, triphenyltin chloride on rabbits produces erythema and edema with tissue damage. The injuries are worsened by washing with organic solvent (49). In feeding tests on rats and mice, triphenyltin hydroxide shows no evidence of carcinogenicity (182).

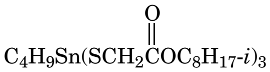
Diorganotin compounds as a class are substantially less toxic than the analogous triorganotins. Some compounds of this class are used as additives in plastics intended to be in contact with food or potable water or used as PVC stabilizers. The acute oral toxicities of common commercial diorganotin compounds are given in Table 11. The dialkyltin chlorides and oxides generally show decreasing oral toxicity with increasing length of the alkyl chain. The toxicity of the lower dialkyltins is believed to be related to their ability to combine with enzymes containing two thiol groups in a suitable stereochemical conformation and thereby inhibiting the oxidation of a-ketoacids in the cell (185). 2,3-Dimercapto-1-propanol, $HSCH_2CH(SH)CH_2OH$, has been reported as an effective antidote for lower dialkyltin poisoning (68). The lower dialkyltin halides are somewhat less irritating to the skin than the analogous triorganotins, but skin contact should be avoided. Other studies of the toxicities of specific diorganotin compounds are reported in References 49, 178, and 186.

Monoorganotin compounds present no special toxicological problems. In general, they show the familiar trend of decreasing toxicity with increasing alkyl chain length, but of a lower order of toxicity than the diorganotins. As with most organotin compound classes, there are conflicting toxicity data and exceptions to general rules. Monobutyltin sulfide [15666-29-2] (butylthiostannoic anhydride, BTSA, poly[(1,3-dibutyldistannthiondiylidene)-1,3-dithiol] is allowed as a stabilizer in semirigid or rigid PVC used in food packaging. Typical LD_{50} values for monoorganotin compounds are



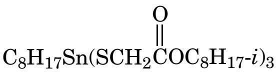
$$CH_3Sn(SCH_2\overset{\overset{O}{\|}}{C}OC_8H_{17}\text{-}i)_3$$

920 mg/kg (rats) (184);



$$C_4H_9Sn(SCH_2\overset{\overset{O}{\|}}{C}OC_8H_{17}\text{-}i)_3$$

1063 mg/kg (rats) (184). $(C_4H_9SnS_{1.5})_n$, >20,000 mg/kg (rats) (186);



$$C_8H_{17}Sn(SCH_2\overset{\overset{O}{\|}}{C}OC_8H_{17}\text{-}i)_3$$

3400 mg/kg (rats) (184). The lower monoorganotin trihalides can present special problems, however, because of their facile reaction with moisture, resulting in the liberation of hydrochloric acid.

The toxicity of the tetraorganotins has been little studied. Available literature indicates that tetrabutyltin and the higher tetraalkyltins are substantially less toxic than triorganotins to mammals if taken orally (175). The high toxicity reported for tetraethyltin ($LD_{50} = 9-16$ mg/kg) appears to be caused by its rapid conversion in the liver to a triethyltin species.

The inhalation toxicities (50% fatality in rats) of dimethyltin dichloride, monomethyltin trichloride, and dibutyltin dichloride are 1070, 600, and 73 mg/(L·h) (187).

The current OSHA TLV standard for exposure to all organotin compounds is 0.1 mg of organotin compounds (as tin)/m^3 air averaged over an 8-h work shift (188). NIOSH has recommended a permissible exposure limit of 0.1 mg/m^3 of tin averaged over a work shift of up to 10 h/d, 40 h/wk; Reference 189 should be consulted for more detailed information. Additional information on the health effects of organotin compounds is given in Reference 48.

4. Economic Aspects

Tin has not been mined in the United States since 1993, consequently the country is most reliant on imports and recycling for its needs. The major uses for tin metal are electrical solders, 24%; metal containers, 21%; transportation, 14%; construction, 11%; and other, 30%.

Table 12 gives data on U.S. consumption of tin, by finished product and shows where chemicals fit in the total (190).

Tin compounds are used in a wide variety of industries as catalysts and stabilizers for many materials, including polymers (see HEAT STABILIZERS); and as biocidal agents, eg, bactericides, insecticides, wood preservatives, acaricides, and antifouling paints; ceramic opacifiers; textile additives; in metal finishing operations; as food additives; and in electroconductive coatings (see CATALYSIS; COATINGS, MARINE; DENTIFRICES; INDUSTRIAL ANTIMICROBIAL AGENTS; INSECT CONTROL TECHNOLOGY).

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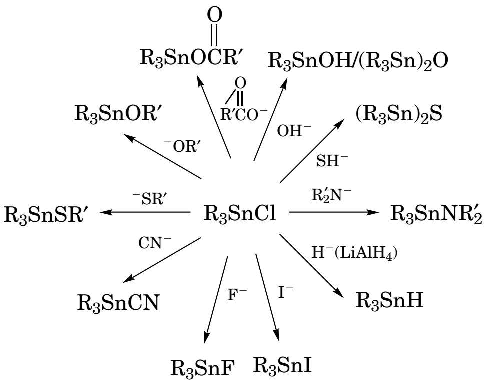


Fig. 1. Reactions of triorganotin chlorides (95).

Table 1. **Physical Properties of Tin Chlorides**

Property	$SnCl_2$	$SnCl_2·2H_2O$	$SnCl_4$	$SnCl_4·5H_2O$
mol wt	189.60	225.63	260.50	350.58
mp, °C	246.8	37.7	−33	ca 56 dec
bp, °C	623		114	
density, at 25°C, g/cm^3	3.95	2.63	2.23[a]	2.04

[a] At 20°C.

Table 2. **Acute Oral Toxicity of Selected Inorganic Tin Compounds**[a]

Compound	CAS Registry Number	LD_{50}, mg/kg	Test animal
stannous chloride	[7772-99-8]	700	rat
		1,200	mouse
stannous ethylene glycoxide	[68921-71-1]	>10,000	rat
stannous 2-ethylhexanoate	[301-10-0]	5,870	rat
stannous fluoride	[7783-47-3]	128.4	mouse
		188.2	rat
stannous oxalate	[814-94-8]	3,400	rat
stannous oxide	[21651-19-4]	>10,000	rat
sodium pentafluorostannite	[22578-17-2]	595	male mouse
		221	male rat
		227	female rat

[a] Refs. 51 and 52.

Table 3. **Physical Properties of Typical Tetraorganotin Compounds**[a]

Compound	CAS Registry Number	Mp, °C	Bp, °C	n_D^{20}	d^{20}, g/cm^3
$(CH_3)_4Sn$	[594-27-4]	−54	78	1.4415	1.2905[b]
$(C_4H_9)_4Sn$	[1461-25-2]	−97	$127_{1.3\,kPa}$[c,d]	1.4727	1.0541
$(C_8H_{17})_4Sn$	[3590-84-9]			1.4677[d]	0.9609[d]
$(C_6H_5)_4Sn$	[595-90-4]	228			1.521
$(C_6H_{11})_4Sn$	[1449-55-4]	261	160−163		
$(CH_2{=}CH)_4Sn$	[1112-56-7]		$70_{0.59\,kPa}$[c]	1.4914[b]	1.257
$(CH_3)_2(C_4H_9)_2Sn$	[1528-00-3]		$73{-}75_{0.5\,kPa}$[c]	1.4640[b]	1.124[b]
$(C_2H_5)_3(C_4H_9)Sn$	[17582-53-5]			1.4736	1.1457

[a] Ref. 79, except where noted.

[b] At 25°C.

[c] To convert kPa to mm Hg, multiply by 7.5.

[d] Ref. 80.

Table 4. **Physical Properties of Typical Triorganotin Halides**[a]

Compound	CAS Registry Number	Mp, °C	Bp, °C	n_D^{20}	d^{20}, g/cm^3
$(CH_3)_3SnCl$	[1066-45-1]	37.5	154–156		
$(CH_3)_3SnBr$	[1066-44-0]	26–27	163–165		
$(C_4H_9)_3SnCl$	[1461-22-9]		$152–156_{1.9\,kPa}$[b]	1.4930	1.2105
$(C_4H_9)_3SnF$	[1983-10-4]	218–219 (dec)			1.27[c]
$(C_6H_5)_3SnCl$	[639-58-7]	106			
$(C_6H_5)_3SnF$	[379-52-2]	357 (dec)			
$(C_6H_{11})_3SnCl$	[3091-32-5]	129–130			

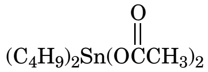
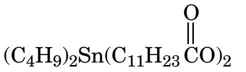
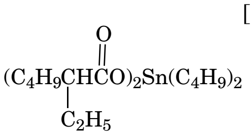
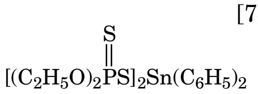
[a] Ref. 110.
[b] To convert kPa to mm Hg, multiply by 7.5.
[c] At 25°C.

Table 5. **Physical Properties of Commercially Important Triorganotin Compounds**

Compound	CAS Registry Number	Mp, °C	Bp, °C	n_D^{20}	d^{20}, g/cm^3
$[(C_4H_9)_3Sn]_2O$	[56-35-9]	< -45	$210–214_{1.3\,kPa}$[a]	1.488	1.17
$(C_4H_9)_3SnF$	[1983-10-4]	218–219 dec			1.27[b]
$(C_4H_9)_3SnOCOC_6H_5$	[4342-36-3]		$166–168_{0.13\,kPa}$[a]	1.5157	1.1926
$(C_4H_9)_3SnOCOCH_3$	[56-36-0]	80–85			1.27
$(C_6H_5)_3SnOH$	[76-87-9]	118–120 dec			1.552[b]
$(C_6H_5)_3SnF$	[379-52-2]	357 dec			1.53
$(C_6H_5)_3SnOCOCH_3$	[900-95-8]	119–120			
$(C_6H_{11})_3SnOH$	[13121-70-5]	[c]			
$(C_6H_{11})_3SnN_3C_2H_2$[d]	[41083-11-8]	218.8			
$(Neoph_3Sn)_2O$[e]	[13356-08-6]	138–139[f]			

[a] To convert kPa to mm Hg, multiply by 7.5.
[b] At 25°C.
[c] No true melting point; converts to bis-oxide at >120°C.
[d] $N_3C_2H_2$=1, 2, 4-triazole.
[e] Neoph = neophyl = β,β - dimethylphenethyl.
[f] Technical material.

Table 6. **Physical Properties of Diorganotin Compounds**[a]

Compound	CAS Registry Number	Mp, °C	Bp, °C	n_D^{20}	d^{20}, g/cm^3
$(CH_3)_2SnCl_2$	[753-73-1]	107–108	185–190		
$(C_4H_9)_2SnCl_2$	[683-18-1]	41–42	140–143$_{1.3\,kPa}$[b]		
$(C_4H_9)_2SnBr_2$	[996-08-7]	21–22	90–92$_{0.04\,kPa}$[b]	1.5400	1.3913[c]
$(C_4H_9)_2SnI_2$	[2865-19-2]		145$_{0.8\,kPa}$[b]	1.6042	1.996[c]
$(C_6H_5)_2SnCl_2$	[1135-99-5]	42–44	180–185$_{0.7\,kPa}$[b]		
$(CH_3O\text{-}C(O)CH_2CH_2)_2SnCl_2$	[10175-01-6]	132			
$(CH_3)_2Sn(SC_4H_9)_2$	[1000-40-4]		81$_{0.013\,kPa}$[b]	1.5400	1.280
$(C_4H_9)_2Sn(OCH_3)_2$	[1067-55-6]		126–128$_{7\,Pa}$[b]	1.4880	
$[(C_4H_9)_2SnS]_3$	[15220-82-3]	63–69			
 $(C_4H_9)_2Sn(O\overset{O}{\overset{\|}{C}}CH_3)_2$	[1067-33-0]	8.5–10	142–145$_{1.3\,kPa}$[b]	1.4706	
 $(C_4H_9)_2Sn(C_{11}H_{23}\overset{O}{\overset{\|}{C}}O)_2$	[77-58-7]	22–24		1.4683	1.05
 $(C_4H_9\underset{C_2H_5}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}O)_2Sn(C_4H_9)_2$	[2781-10-4]	54–60	215–220$_{0.3\,kPa}$[b]	1.4653	1.070[c]
 $[(C_2H_5O)_2\overset{S}{\overset{\|}{P}}S]_2Sn(C_6H_5)_2$	[74097-03-3]	149.5			

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[a] Refs. 95 and 105.

[b] To convert kPa to mm Hg, multiply by 7.5.

[c] At 25°C.

Table 7. **Typical Commercially Significant Organotin PVC Stabilizers**

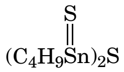
Compound	CAS Registry Number	Structure
dibutyltin bis(isooctyl mercaptoacetate)	[25168-24-5]	$(C_4H_9)_2Sn(SCH_2CO_2C_5H_{17}\text{-}i)_2$
dioctyltin bis(isooctyl mercaptoacetate)	[26401-97-8]	$(C_8H_{17})_2Sn(SCH_2CO_2C_8H_{17}\text{-}i)_2$
dimethyltin bis(isooctyl mercaptoacetate)	[26636-01-1]	$(CH_3)_2Sn(SCH_2CO_2C_8H_{17}\text{-}i)_2$
bis(2-carbobutoxyethyltin) bis(isooctyl mercaptoacetate)	[63397-60-4]	$(C_4H_9OCOCH_2CH_2)_2Sn(SCH_2CO_2\text{-}C_8H_{17}\text{-}i)_2$
dibutyltin sulfide	[4253-22-9]	$(C_4H_9)_2SnS$
dibutyltin bis(lauryl mercaptide)	[1185-81-5]	$(C_4H_9)_2Sn(SC_{12}H_{25})_2$
dibutyltin β-mercaptopropionate	[27380-35-4]	$-\!\!\left[(C_4H_9)_2SnSCH_2CH_2COO\right]_n\!\!-$ $(n = 1–3)$
dibutyltin bis(mercaptoethyldecanoate) (also other esters)	[28570-24-3]	$(C_4H_9)_2Sn(SCH_2CH_2OC(O)C_{11}H_{25})_2$
butylthiostannoic acid anhydride	[15666-29-2]	 $(C_4H_9\overset{\overset{S}{\|}}{Sn})_2S$
butyltin tris(isooctyl-mercaptoacetate)	[25852-70-4]	$C_4H_9Sn(SCH_2CO_2C_8H_{17}\text{-}i)_3$
dibutyltin dilaurate	[77-58-7]	$(C_4H_9)_2Sn(OOCC_{11}H_{23})_2$
dibutyltin maleate	[32076-99-6]	$-\!\!\left[(C_4H_9)_2SnOOCCH{=}CHCOO\right]_n\!\!-$ $(n = 1–3)$
(dioctyltin derivative)	[16091-18-2]	
dibutyltin bis(monoisooctylmaleate) (also other alkyl maleate esters)	[25168-21-2]	$(C_4H_9)_2Sn(OOCCH{=}CHCOO\text{-}C_8H_{17}\text{-}i)_2$

Table 8. **Physical Properties of Typical Organotin Trihalides**

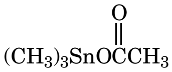
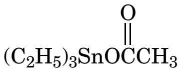
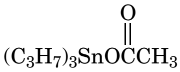
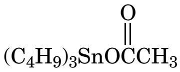
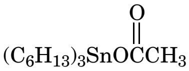
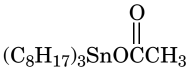
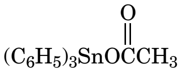
Compound	CAS Registry Number	Mp, °C	Bp, °C	n_D^{20}
CH_3SnCl_3	[993-16-8]	45–46		
CH_3SnBr_3	[993-15-7]	53	211	
$C_4H_9SnCl_3$	[1118-46-3]		$102-103_{1.6\,\mathrm{kPa}}$[a]	1.5233
$C_6H_5SnCl_3$	[1124-19-2]		$142-143_{3.3\,\mathrm{kPa}}$[a]	1.5871

[a] To convert kPa to mm Hg, multiply by 7.5.

Table 9. **Physical Properties of Organic Tin Salts of Minor Commercial Importance**

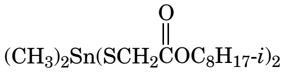
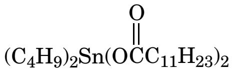
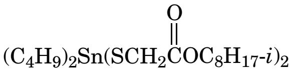
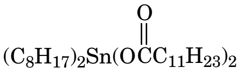
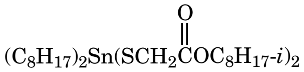
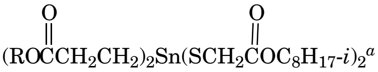
Salt	CAS Registry Number	Mp, °C	Density, g/cm^3	Use
stannous acetate	[638-39-1]	182.5–183	2.31	promotes dye uptake by fabrics
stannous ethylene glycoxide	[68921-71-1]	dec >300	2.87	esterification catalyst
stannous formate	[2879-85-8]	dec >100		catalyst for hydrogenation of liquid fuels
stannous gluconate	[35984-19-1]		1.35	silicone catalyst
stannousoleate	[1912-84-1]		1.06	silicone catalyst
stannous stearate	[6994-59-8]	90; dec 340	1.05	catalyst
stannous tartrate	[815-85-0]	dec 280	2.6	dyeing and printing of textiles

Table 10. **Acute Oral Toxicities of Triorganotin Compounds**

Compound	CAS Registry Number	LD_{50}, mg/kg	Test animal	Reference
 $(CH_3)_3SnO\overset{\overset{O}{\|}}{C}CH_3$	[1118-14-5]	9	rat	178
 $(C_2H_5)_3SnO\overset{\overset{O}{\|}}{C}CH_3$	[1907-13-7]	4	rat	178
 $(C_3H_7)_3SnO\overset{\overset{O}{\|}}{C}CH_3$	[3267-78-5]	118	rat	178
 $(C_4H_9)_3SnO\overset{\overset{O}{\|}}{C}CH_3$		133	rat	175
		380	rat	
$[(C_4H_9)_3Sn]_2O$	[56-35-9]	ca 200	rat	175
$(C_4H_9)_3SnF$		200	rat	175
 $(C_6H_{13})_3SnO\overset{\overset{O}{\|}}{C}CH_3$	[2897-46-3]	1,000	rat	178
 $(C_8H_{17})_3SnO\overset{\overset{O}{\|}}{C}CH_3$	[919-28-8]	>1,000	rat	178
 $(C_6H_5)_3SnO\overset{\overset{O}{\|}}{C}CH_3$		136	rat	175
		491	rat	175
$(C_6H_5)_3SnOH$		108	rat	179
		209	mouse	179
$(C_6H_{11})_3SnOH$		540	rat	179
		780	guinea pig	179
$(Neoph_3Sn)_2O$[a]		1,450	mouse	179
		>1,500	dog	179
		2,630	rat	179

[a] Neoph = neophyl = β,b-dimethylphenethyl.

Table 11. **Acute Oral Toxicities of Diorganotin Compounds**

Compound	CAS Registry Number	LD_{50} (rat), mg/kg	Reference
$(CH_3)_2SnCl_2$		74	175
 $(CH_3)_2Sn(SCH_2\overset{\overset{O}{\Vert}}{C}OC_8H_{17}\text{-}i)_2$	[26636-01-1]	1380	175
$(C_4H_9)_2SnCl_2$		126	175
$(C_4H_9)_2SnO$	[818-08-6]	600–800	183
 $(C_4H_9)_2Sn(O\overset{\overset{O}{\Vert}}{C}C_{11}H_{23})_2$		175	175
 $(C_4H_9)_2Sn(SCH_2\overset{\overset{O}{\Vert}}{C}OC_8H_{17}\text{-}i)_2$	[25168-24-5]	500	175
$(C_8H_{17})_2SnCl_2$	[3542-36-7]	5500	175
$(C_8H_{17})_2SnO$	[870-08-6]	2500	175
 $(C_8H_{17})_2Sn(O\overset{\overset{O}{\Vert}}{C}C_{11}H_{23})_2$	[3648-18-8]	6450	175
 $(C_8H_{17})_2Sn(SCH_2\overset{\overset{O}{\Vert}}{C}OC_8H_{17}\text{-}i)_2$	[26401-97-8]	2000	175
 $(RO\overset{\overset{O}{\Vert}}{C}CH_2CH_2)_2\,SnCl_2$[a]		2350	184
 $(RO\overset{\overset{O}{\Vert}}{C}CH_2CH_2)_2Sn(SCH_2\overset{\overset{O}{\Vert}}{C}OC_8H_{17}\text{-}i)_2$[a]		1430	184

[a] R is undefined; probably C_2H_5.

Table 12. **U.S. Consumption of Tin, by Finished Product, t of Contained Tin**[a,b]

	2002			2003		
Product	Primary	Secondary	Total	Primary	Secondary	Total
alloys, miscellaneous[c]	W	W	W	W	W	W
Babbitt	1,310	W	1,310	2,570	W	2,570
bar tin	617	W	617	849	W	849
bronze and brass	1,330	1,720	3,040	1,260	1,340	2,600
chemicals	8,400	W	8,400	8,720	W	8,720
collapsible tubes and foil	W	W	W	W	W	W
solder	10,000	3,790	13,800	7,660	2,950	10,600
tinning	679	W	679	833		833
tinplate[d]	7,750		7,750	7,790		7,790
tin powder	W	W	W	W	W	W
type metal	W	W	W	W	W	W
white metal[e]	1,320	W	1,320	1,220	W	1,220
other	2,590	327	2,920	1,980	202	2,180
Total	*34,000*	*5,830*	*39,800*	*32,900*	*4,490*	*37,400*

[a] Ref. 194.

[b] W Withheld to avoid disclosing company proprietary data; include with "Other."

[c] Includes terne metal.

[d] Includes secondary pig tin and tin acquired in chemicals.

[e] Includes pewter, britannia metal, and jewelers' metal.