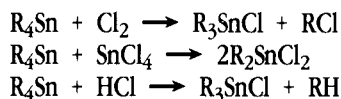# INTRODUCTION TO ORGANOTIN CHEMISTRY AND APPLICATIONS

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In common with the other Group 4 elements, C, Si, Ge, and Pb, tin has four electrons in the outer electronic shell and thus forms compounds in which tin has oxidation states of +II and +IV. In organotin compounds at least one group is bound to tin through a carbon to tin bond forming a compound of the formula R_nSnY_{4-n}, where n is one to four. Y may be hydrogen, a metal, or a group attached to tin through oxygen, sulfur, nitrogen, halogen, etc. The number and nature of carbon-tin bonds and Y affect the electronegativity at tin and thus the chemical and physical properties of its compounds. Thus tetrabutyltin is soluble in non-polar solvents and insoluble and unreactive in water, while monobutyltin trichloride is soluble in polar organic solvents and water.

Although the carbon to tin bond is weaker than the carbon-carbon or carbon-silicon bond it is relatively non-polar and is therefore stable in the presence of air and moisture as well as many nucleophilic species. Cleavage of carbon-tin bonds occurs with a variety of agents, including halogens, metal halides, mineral acids, alkali, etc.

$$R_4Sn + Cl_2 \longrightarrow R_3SnCl + RCl$$
$$R_4Sn + SnCl_4 \longrightarrow 2R_2SnCl_2$$
$$R_4Sn + HCl \longrightarrow R_3SnCl + RH$$

Cleavage of aryl, allyl, or vinyl groups occurs more readily than alkyl groups and lower alkyl groups are cleaved more readily than higher alkyl groups.

The ligand Y is labile and often participates in exchange reactions such as replacement of a halide with hydroxyl in aqueous solution.

Because of the large size of the tin atom and availability of low-lying empty 5d atomic orbitals, coordination numbers greater than four are frequently encountered in organotin structures.

Thus the reactivity and applications of organotin compounds depend upon the stability of the C-Sn bond, the lability of the anion Y, and the possibility of expansion to coordination numbers greater than four. These characteristics largely account for its applications in a variety of chemical transformations including transmetallation reactions, addition to unsaturated compounds, catalysts, and PVC stabilizers.
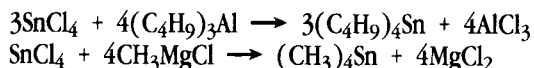
Although organotin compounds have been known since the 1850's, commercial application of organotins for use as PVC stabilizers in the 1940's promoted extensive studies in the area. Since that time the number of organotin compounds which have been prepared is in the hundreds; the most common organic groups bound to tin and those manufactured industrially include methyl, butyl, octyl, phenyl, and cyclohexyl. Four excellent books reviewing organotin chemistry have been published. [1,2,3,4]

Toxicity

The toxicity of tin compounds varies widely, depending first on the number of organic groups attached to tin and second on the nature of the organic groups. Inorganic tin compounds generally have very low toxicity. The highest toxicity is observed in triorganotin compounds, while diorganotin and monoorganotin compounds show successively lower toxicity. The toxicity of tetraorganotin compounds is low; however under environmental conditions they will decompose to toxic triorganotins. The organic group attached to tin also plays a significant role in the toxicity; triethyltins are the most toxic, followed by methyl, propyl, butyl. Trioctyltin compounds have very low toxicity, while triphenyl and tricyclohexyltins show considerable toxicity. Toxicology data for organotin compounds are reported in reference [5].

R_4Sn

The most common method of preparation of organotins is through reaction of a Grignard or trialkyl aluminum reagent with $SnCl_4$.

$$3SnCl_4 + 4(C_4H_9)_3Al \longrightarrow 3(C_4H_9)_4Sn + 4AlCl_3$$
$$SnCl_4 + 4CH_3MgCl \longrightarrow (CH_3)_4Sn + 4MgCl_2$$
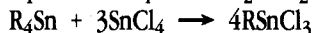
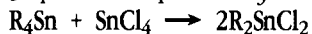Organolithium or sodium reagents may also be used.

Hundreds of compounds having four organic groups attached to tin are known, including fully symmetrical compounds and mixed species with alkyl, aryl, and unsaturated groups. The lower tetraalkyl compounds are liquids which can be distilled without decomposition; tetraaryl compounds tend to be crystalline solids.

The main application of tetraorganotins is for use as intermediates in preparation of tri-, di-, and monoorganotins. In addition to carbon-tin bond cleavage, tetraorganotin compounds readily undergo redistribution reactions.

$$2R_2R'_2Sn \rightleftharpoons R_4Sn + R'_4Sn$$
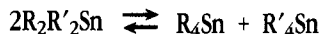
Organotin Halides

Organotin halides are prepared by cleavage reactions of a tetraorganotin with halogen, hydrogen halide, or $SnCl_4$. Of greatest importance are the redistribution reactions leading to mono-, di-, and triorganotin compounds, which are controlled by the stoichiometry of the reactants.

$$3R_4Sn + SnCl_4 \longrightarrow 4R_3SnCl$$
$$R_4Sn + SnCl_4 \longrightarrow 2R_2SnCl_2$$
$$R_4Sn + 3SnCl_4 \longrightarrow 4RSnCl_3$$

Redistribution reactions occur readily with heat and sometimes a Lewis acid catalyst. Small amounts of the other redistribution products are present in the products.

Direct reaction of Sn metal or $SnCl_2$ with activated olefins such as acrylic esters leads to mono- and diorganotin compounds, the "ester tins".[6]

$$SnCl_2 + HCl + CH_2 = CHCOOR \longrightarrow ROCOCH_2CH_2SnCl_3$$
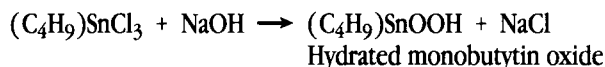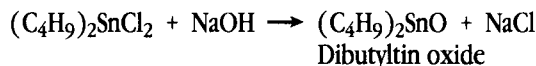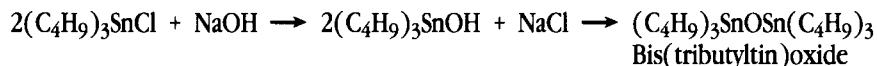$$Sn + 2HCl + 2CH_2 = CHCOOR \longrightarrow [ROCOCH_2CH_2]_2SnCl_2$$

The major use of the organotin halides is in the preparation of other organotin derivatives through replacement of halide with a nucleophile such as OH^-, $R'COO^-$, $R'S^-$, OR''^-, H^-, NCO^-. Because of the electronegativity of halide, organotin halides are Lewis acids which readily form complexes with electron donors such as amines, pyridine alcohols, and halides. In these complexes the coordination number around tin is 5, 6, or 7. The Lewis acidity increases in the sequence $R_3SnX < R_2SnX_2 < RSnX_3$.

Organotin Compounds with Tin-Oxygen Bonds

This category includes oxides, carboxylates, alkoxides, phenoxides, mineral acid derivatives (sulfates, phosphates, etc.), and metallostannoxanes, SnOM. Hydroxides are rarely encountered due to the tendency for elimination of water to form a stannoxane,-SnOSn-.
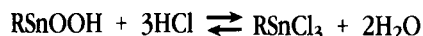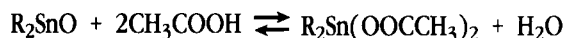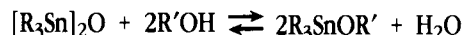
Organotin oxides are usually prepared by alkaline hydrolysis of the halides.

$$2(C_4H_9)_3SnCl + NaOH \longrightarrow 2(C_4H_9)_3SnOH + NaCl \longrightarrow (C_4H_9)_3SnOSn(C_4H_9)_3$$
Bis(tributyltin)oxide

$$(C_4H_9)_2SnCl_2 + NaOH \longrightarrow (C_4H_9)_2SnO + NaCl$$
Dibutyltin oxide

$$(C_4H_9)SnCl_3 + NaOH \longrightarrow (C_4H_9)SnOOH + NaCl$$
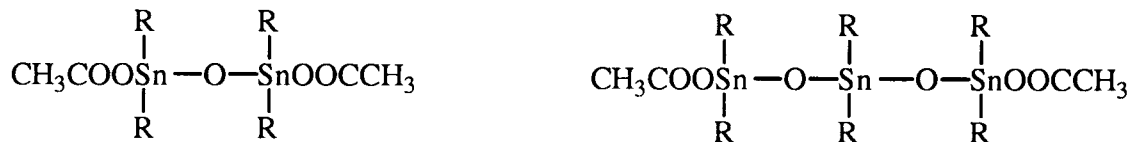Hydrated monobutytin oxide

The oxides precipitate out of aqueous solutions.

The trialkyltin oxides are distillable liquids or low melting solids which are readily soluble in organic solvents. Diorgano- and monoorganotin oxides are polymeric solids which are insoluble in all solvents except by reaction. Although exact structures for these oxides have not been determined due to their intractability, they are known to be extensive networks of -Sn-O-Sn- bonds.

Organotin oxides react with inorganic and organic acids, alcohols, mercaptans, etc., with ligand exchange.

$$[R_3Sn]_2O + 2R'OH \rightleftharpoons 2R_3SnOR' + H_2O$$

$$R_2SnO + 2CH_3COOH \rightleftharpoons R_2Sn(OOCCH_3)_2 + H_2O$$

$$RSnOOH + 3HCl \rightleftharpoons RSnCl_3 + 2H_2O$$

These reactions are equilibrium reactions which are driven to completion by removal of water, often by azeotropic distillation with toluene. They may also be formed using acid anhydrides. With the di- and monoorganic tins, intermediate stannoxanes may be isolated from either the forward or reverse reaction.

$$
\begin{array}{cc}
R & R \\
| & | \\
CH_3COOSn-O-SnOOCCH_3 \\
| & | \\
R & R
\end{array}
\qquad
\begin{array}{ccc}
R & R & R \\
| & | & | \\
CH_3COOSn-O-Sn-O-SnOOCCH_3 \\
| & | & | \\
R & R & R
\end{array}
$$

Other organotin-oxygen compounds are prepared either by the reactions shown above or by reaction of an organotin halide with the sodium salt of the oxy compound.

$$(C_4H_9)_2SnCl_2 + 2C_7H_{15}COONa \rightleftharpoons (C_4H_9)_2Sn(OOCC_7H_{15})_2 + 2NaCl$$
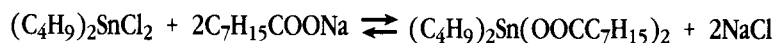
Besides these replacement reactions, organotin oxides undergo addition reactions with unsaturated compounds such as CO_2, SO_2, cyanides, and isocyanates.

$$[(C_4H_9)_3Sn]_2O + CO_2 \rightarrow (C_4H_9)_3SnOCOOSn(C_4H_9)_3$$
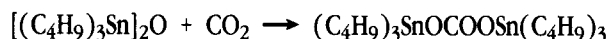
Organotin sulfates, phosphates, nitrates, and metallostannoxanes are also known.

Besides their applications in stabilization of PVC and as catalysts, organotin carboxylates and alkoxides may be used in exchange reactions to form other metal alkoxides and as intermediates for acylation and alklation of hydroxy groups, etc.[7]

Organotin Compounds with Tin-Sulfur Bonds

Tin mercaptides, $R_xSn(SR)_{4-x}$ are much less susceptible to hydrolysis than tin alkoxides or carboxylates. They are readily prepared from an organotin oxide and mercaptans.

$$R_2SnO + 2R'SH \rightarrow R_2Sn(SR')_2 + H_2O$$
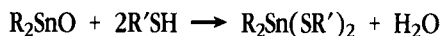
Alternatively they may be prepared from an organotin chloride and mercaptan in a stoichiometric amount of aqueous NaOH or in non-aqueous solution in presence of an amine to remove the HCl by-product.

$$R_2SnX_2 + 2NaOH + 2R'SH \rightarrow R_2Sn(SR')_2 + 2NaX + 2H_2O$$
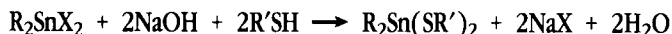
Although relatively stable to hydrolysis in neutral solution, the tin-sulfur bond is cleaved in aqueous caustic; it is also readily cleaved by halogens.

Similarly, organotin sulfides, $[R_3Sn]_2S$, R_2SnS, may be prepared from H_2S or a metal sulfide. Diorganotin sulfides are usually cyclic trimers with six-membered-Sn-S-rings. Monoorganotin sulfides, $R_2Sn_2S_3$, are oligomeric.

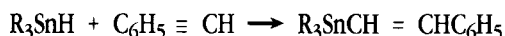Many organotin-sulfur compounds have been developed for application in stabilization of PVC.[8]

Organotin Hydrides

Organotin hydrides are extremely useful in the laboratory as intermediates in organic synthesis. Preparatory methods include reaction of an organotin halide with lithium or sodium aluminum hydride, alkylaluminum hydrides or sodium borohydride in an ether, transfer of hydrogen from a silicon hydride to an organotin oxide or alkoxide, and decarboxylation of a triorganotin formate. Reviews of organotin hydride chemistry are found in references 7 and 9.

Stannane, SnH_4, is an unstable gas which decomposes at room temperature into hydrogen and tin. The stability of organotin hydrides increases in the sequence $SnH_4 < RSnH_3 < R_2Sn_2 < R_3SnH$. Alkyltin hydrides are more stable than aryl. Because of its stability and ease of preparation, the most commonly used organotin hydride in tributyltin hydride.

Reactions of organotin hydrides include:

1. Hydrostannation, addition of Sn-H across a double or triple bond;

$$R_3SnH + CH_2 = CHX \longrightarrow R_3SnCH_2CH_2X$$

$$R_3SnH + C_6H_5 \equiv CH \longrightarrow R_3SnCH = CHC_6H_5$$

Alkynes react more readily than alkenes. The addition reactions frequently follow a free radical mechanism which may be initiated by AIBN. Carbonyl groups add organotin hydrides leading to tin alkoxides and subsequently through protonolysis to alcohols.

$$R_2C = O + R'_3SnH \longrightarrow R_2CHOSnR'_3 \longrightarrow R_2CHOH$$
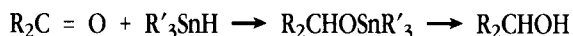
Addition of organotin hydrides to thiocarbonyl and -C=N is also known.

2. Reduction of organic halides;

$$R_3SnH + R'X \longrightarrow R'H + R_3SnX$$
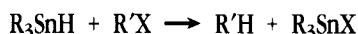
Halogen reduction is generally believed to occur through a free radical mechanism and is often carried out in the presence of an initiator such as AIBN. The ease of the reaction increases in the sequence $RCl < RBr < RI$; alkyl halides react more readily than aryl halides. Reduction of tertiary and secondary alkyl bromides with organotin hydrides is an important use of this technology.[10]

Organotin Compounds with Tin-Tin Bonds

Catenated organotin compounds have been prepared with up to nine Sn-Sn bonds and with 4- and 6-membered cyclic rings. However the most common Sn-Sn compounds are hexaorganotins, R_3SnSnR_3. The major preparatory method for hexaorganodistannanes is through reaction of an alkali metal tin derivative with a tin halide or an in situ reaction of the organotin halide with Na.

$$(CH_3)_3SnNa + (CH_3)_3SnCl \longrightarrow (CH_3)SnSn(CH_3)_3 + NaCl$$
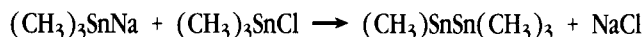
The reactions of hexaorganoditins primarily involve Sn-Sn bond scission with halides, oxygen, peroxides, other oxidizing agents, and alkali metals.

Applications of Organotin Compounds

1. PVC Stabilization

The use of organotin compounds for stabilization of polyvinyl chloride (PVC) was first developed in the 1930's; this application was an impetus to extensive research in the area of organotin chemistry in the following years. Although the number of organotin compounds which are used as PVC stabilizers is very extensive, most are either mono- or diorganotin compounds where the organic group is either methyl, n-butyl or n-octyl. The majority of the derivatives are alkyltin mercaptides or carboxylates such as dibutyltin bis(laurylmercaptide), $(C_4H_9)_2Sn(SC_{12}H_{25})_2$, dimethyltin S-S'-bis(isooctylmercaptoacetate), $(CH_3)_2Sn(SCH_2COOC_8H_{17})_2$, and dibutyltin maleate, $[(C_4H_9)_2SnOOCCH = CHCOO]_n$. Many derivatives including phosphates, oxides, alkoxides, and other types of sulfur derivatives have been patented.

PVC is inherently thermally unstable and would not survive extrusion temperatures without stabilization. degradation occurs through progressive loss of hydrogen chloride leading to a system of conjugated double bonds with resulting color formation and loss of physical properties. The process is accelerated in the presence of HCl and oxygen; thus after the initial loss of HCl, the degradation rate rapidly increases. the organotin stabilizer traps any HCl released and also functions as an antioxidant.[7]

2. Catalysis

Organotin, as well as stannous compounds are used commercially in a variety of catalytic applications.[11] It is notable that in most of these applications one of the reactants contains an OH group, either an alcohol or a silanol. Catalytic mechanisms have been proposed which involve coordination of tin with the OH-containing compound and possibly the other reactant.

The major catalytic use of tins in urethane formation through the reaction of an isocyanate with the active hydrogen of an alcohol.

$$RN = C = O + R'OH \xrightarrow{\text{cat.}} RNHCOOR'$$

Polyurethanes are used in a wide variety of forms and applications, including flexible foams for furniture and bedding, rigid forms for insulation and building materials, coatings, elastomers, etc.
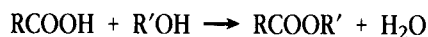
Isocyanates are highly reactive to any active hydrogen atoms present in the system, including water, polyol, amine hydrogens in the urethane group and other side products. Organotins, stannous tins, and t-amines catalyze all these reactions to varying degrees. Combinations of amines and tins are often used to promote these various reactions in order to obtain the desired physical properties, particularly in foams.

Both stannous and diorganotin compounds are used commercially for urethane catalysis. Other organotins are either toxic (triorganotins) or have poor activity (mono- and tetraorganotins). Liquid forms of tin catalysts having fatty acid ligands are usually used in urethane systems so that they will dissolve readily without heating. In many urethane systems the most active type of tin catalyst is a stannous compound such as stannous bis(2-ethylhexoate), $Sn[OOCC_7H_{15}]_2$. However stannous compounds are oxidatively unstable and cannot be used in systems where there is a chance for oxidation prior to carrying out the reaction. Therefore many systems use the more stable organotin compounds; dibutyltin dilaurate is used most frequently, although dimethyl-, dibutyl-, and dioctyl-tin derivatives of various fatty acids or mercaptides have been used. When compared on an equal tin basis, methyltins are slightly more active than butyls and octyls; however greater reactivity differences may be obtained by varying the ligand. Thus dibutyltin diacetate is more reactive than dibutyltin dilaurate, while tin-sulfur compounds such as dibutyltin bis(lauryl mercaptide) or dibutyltin bis(isooctylmercaptoacetate) are less reactive.

The mechanism of tin catalysis in urethane systems is believed to involve either a ternary complex between the isocyanate, alcohol, and tin catalyst or insertion of the tin catalyst into the isocyanate followed by reaction with alcohol.[12]

Related to polyurethane systems are blocked isocyanates in which a polyisocyanate is blocked with a volatile compound containing an active hydrogen. The blocked isocyanate is reacted with a polyol using heat and a catalyst. Dibutyltin dilaurate is frequently used in the reactions of blocked isocyanates, but other diorgano- and monoorganotin catalysts are also active.

A second important use of tin catalysts is in the manufacture of esters and polyesters. Esters are formed from the reaction of an alcohol with a carboxylic acid or a carboxylic acid ester.

$$RCOOH + R'OH \longrightarrow RCOOR' + H_2O$$
Direct esterification
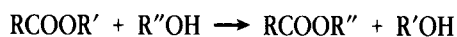
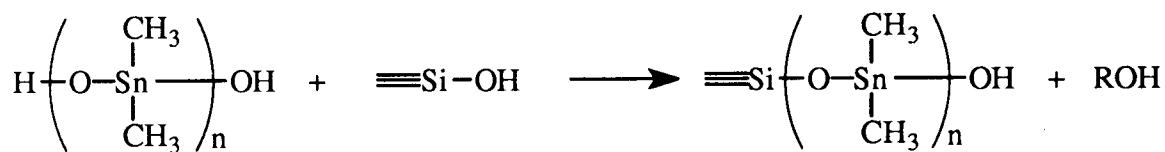$$RCOOR' + R''OH \longrightarrow RCOOR'' + R'OH$$
Transesterification

Both reactions are carried out at elevated temperatures and in the presence of a catalyst. Conventional catalysts are strong acids such as HCl and H_2SO_4 for direct esterification and caustic for transesterification. Stannous and organotin compounds, as well as titanates, are less active catalysts than strong acids and bases, but have the advantage that they do not catalyze side reactions such as dehydration; thus when they are used, product purity is improved. They are limited by reaction temperatures, which in the case of direct esterification is usually greater than 180-200°C and for transesterification is greater than 150°C. An exception is transesterification of methyl methacrylate, which can be carried out at 100°C using dibutyltin oxide as catalyst.

Because of temperature limitations, esters which are prepared using the metal catalysts are limited to high boiling esters such as phthalate and adipate esters and polyesters.

Stannous, monoorganotin, and diorganotin compounds are effective tin catalysts for esterification and transesterification. Tin oxides or salts are added initially and dissolve when heated in the reaction mixture to form carboxylates or alkoxides derived from the reactants. Although the actual catalytic species is not known, the $Sn(II)$, RSn-, or R_2Sn- moieties remain intact, with ligand exchange reactions occurring at the labile end, bringing together the reactants. The tin compounds most frequently used in esterification/transesterification are stannous oxide, stannous oxalate, hydrated monobutyltin oxide, monobutyltin trioctoate, dibutyltin oxide, and dibutyltin diacetate.

Stannous and monobutyltin compounds are excellent for direct esterification. Stannous compounds tend to be insoluble in esters, while the organotins remain in solution; thus the stannous catalysts may be removed by filtration, while the organotin remains dissolved in the product. Diorganotins such as dibutyltin oxide are most frequently used in transesterification reactions.

A third area where tin catalysts find application is in condensation reactions for preparing room temperature vulcanized (RTV) silicones.[11] Crosslinking occurs by reaction between a linear low molecular weight hydroxy functional silicone and a tri- or tetrafunctional crosslinker.

$$H \left(O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Sn}} \right)_n OH \; + \; \equiv Si-OH \; \longrightarrow \; \equiv Si \left(O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Sn}} \right)_n OH \; + \; ROH$$

The catalysts used for silicone condensation reactions are usually tin based; like urethane reactions, these catalysts are stannous or diorganotin compounds, most frequently stannous octoate or dibutyltin dilaurate. It has been proposed that the tin catalyst forms an intermediate with the crosslinker to form a Sn-O-Si bond which subsequently reacts with the silanol.[10]

Other

Other applications include the use of triorganotins for biocidal activity in antifouling paints, wood preservatives, and agriculture[11] and the use of inorganic or organotin compounds deposited on hot glass to form tin oxide coatings. The latter process is used on bottles to reduce breakage on the line and on windows to form heat reflective coatings to reduce heat loss.[13]

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