CHAPTER I

A Short Review of Organo tin Chemistry

IA Introduction

Organotin compounds are substances containing at least one carbon tin bond. The first chemist to report an organotin compound seems to have been E.Frankland (1,2). But his work appears to have remained unknown to most of his contemporaries as well as to later authors. The work of C.Lowig (3) in 1852 has usually been considered to represent the beginning of organotin chemistry. Apart from the compounds described by lowig, many significant contributions were made in this field during the next few decades.

The vast majority of organotin compounds fall within the four classes :

$$R_4Sn,\ R_3Sn\ X\ ,\ R_2Sn\ X_2\ ,\ R\ Sn\ X_3$$

R can be identical or different, substituted or unsubstituted, aliphatic or aromatic groups. X can be negative groups such as OR, $-SR$, $-OCOR$, $-OSnR_3$, $-NR_2$, or halogen or some other acid radicals or neutral ligands such as $-H$, or electropositive ones such as Li or Na. The three series of organotin hydrides R_3SnH, R_2SnH_2 and RSnH (4,5,6,7) have recently assumed considerable importance.

Stannyl metal compounds of the type R_3SnM and R_2SnM_2(8-9), $Ph_3SnSiph_3$, $Ph_3SnSi(Geph_3)_3$, $R_3Sn - SnR_3$(8), $Ph_3SnZnSnPh_3$and $Ph_3SnCdSnPh_3$ are also known where R may be aliphatic or aromatic, M may be Li,Na or K.

The discovery of industrial applications of organotin compounds as stabilisers of polyvinyl chloride plastics, rubber antioxidants, catalyst in the polymerisation of olefins, agricultural fungicides and as active ingredients in certain veterinary medicine (10) and also an increased general scientific interest produced a striking renaissance of organotin chemistry starting from about 1949 and continuing to the present day.

IB Bonding in Organotin compounds

The electronic configuration of tin is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$; the ground state being 3p state derived from $s^2p^2$of configuration (11) the common tetracovalent state is derived from the sp^3 hybridisation by promoting one of the paired S electrons to the next higher P level. The tetra covalent state occurs much more frequently than divalent state and a great number of organotin compounds contain tetravalent tin atom. Organo derivatives of group IVA metals are generally more stable and less reactive than the corresponding compounds of group III or V metals. The increased stability may be attributed to the Sp^3 hybridisation Thus, tetravalent tin is unreactive towards air and water but trimethyl Indium and trimethyl antimony have a strong affinity towards these reagents. The marked increase in stabilities of R_4Sn compounds over R_2Sn types also demostrate the effect of increased hybridisation on the stability. Metal - Carbon bond strengths have been reviewed by Skinner (12) who noted that mean bond dissociation energies ($\bar{D}$) fall as the subgroup is descended so that $\bar{D}$ (C-R) $\bar{D}$ (Si-R) $\bar{D}$ (Ge-R) $\bar{D}$ (Sn-R) $\bar{D}$ (Pb-R). The mean values of the bond dissociation energies are C-C : 87, C-Si : 70, C-Ge:60, C-Sn : 50, C-Pb : 31-37 K cal/mole. These values are, ofcourse, further dependent on the nature of the alkyl group i.e. on the stabilisation of the corresponding alkyl radicals by hyperconjugation etc.

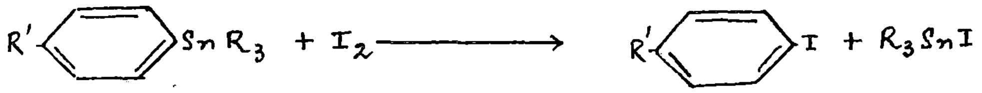
The covalent radius of Sn atom is 1.40 Å and is surprisingly independent of the nature of the ligands. Only when there is an accumulation of strongly negative ligands round the tin there is some decrease in bond lengths. The bonding of the tin would thus appear to be almost entirely covalent at least in crystalline solids, in non polar media and in the vapour. However, the electronegativity of tin being less than most of the common ligands, e.g., carbon, nitrogen, oxygen, halogen and even hydrogen, the bonds are expected to be sufficiently polar. The dipole moment of various Sn - X bonds have also been estimated. The dipole moment of alkyl tin bond, mostly estimated as 0.45 - 0.6D (13 - 15) depends both in magnetude and direction on the nature of alkyl group (16 - 17).

The electronegativities of the elements of group IV have been investigated extensively by different workers (20 - 23). The results, a selection of which is given in Table 1, always differ according to the method of measurement and the compounds selected. This is not surprising since the electronegativity, not being a uniquely defined parameter, depends on the method of measurement and the surrounding of the atom in question. In practice, therefore, one generally works not with an 'electronegativity of tin' but with a value for tin in a particular combination i.e. allowance will have to made for the influence of all ligands.

Table - 1

	Pauling	Sanderson	Fineman Daignault	Allred Rochow
C	2.5	2.47	2.57	2.60
Si	1.8	1.74	1.90	1.90
Ge	1.8	2.31	2.02	2.00
Sn	1.8	2.02	2.47	1.93
Pb	1.8			2.45

Closely connected with this is the inductive effect which tin atoms or stannyl groups exert on their surroundings. The bond polarisation $C^{\delta -} - Sn^{\delta +}$, which is there in principle, may be changed by substitution at C as well as at Sn. NMR data on organotin compounds (18 - 19) and semiempirical calculations of Majee and Gupta (43) emphasises this. According to Eaborn etal (24) polarisation is increased by electron donor substituents R' in the p - position in a phenyl group, as shown by the increase in the rate of scission of the C - Sn bond by iodine according to reaction (I). The reaction thus belongs to the class of electrophilic aromatic substitution (24 - 25).



(1)

As expected, electron attracting groups R' decrease the rate of lowering the nucleophilicity of the ring carbon attached to tin. The sequence of relative reaction rates is for R' = OMe > - Bu > i - Pr > Et > Me > H > Br > F > Cl > CooH.

Electron donor properties increase in the series (R = Me) : $SiR_3 < GeR_3 < SnR_3$, as may be seen from the relative rates of acidolysis of P - R_3MCH_2CH - SnR_3 . These are for M = Si 1.00, Ge 1.36, Sn 3.21 (26). A similar sequence emerges from I.R and NMR measurements (27) and also from IR studies on esters of the type $MeCOOMMe_3$ which give M = C,Si,Ge (28).

One difficulty which often arises in experiments designed to measure relative inductive effects is that there may be some π- character in a bond between tin and an element possessing p electrons (29 - 30). Thus in a Sn - X bond where X is $C(Sp^2)$, N,O,S or halogen it is possible that, opposing the inductive electron drift in Sn - X, there may be some overlap between a filled p - orbital on X and an empty 5d orbitals on Sn causing a transfer of electron density in the opposite direction. Despite many controversies (31 - 34), it is widely accepted that there are significant (pπ - dπ) contributions to the Sn - N bonds in compounds such as the plannar trisilyl amine (35). There is some evidence that in phenyl tin compounds, interaction occurs between the electrons of the phenyl groups and the 5d orbitals of tin. This conclusion is based on the interpretation of NMR (36 - 37), infrared (38), ultraviolet (38) and dipole moments (39) of phenyl tin compounds and the acid strength of the substituted benzoic acids p-Me_3 M C_6H_4CooH (M = C,Si,Ge,Sn). It can not be assumed that other aromatic groups behave similarly since pKa values for a series of pyridine having Me_3M(M=C,Si,Ge,Sn), substituents in the 2-position indicated the absence of $p\pi - d\pi$ bonding in the tin-pyridine link (40). Calculation based upon nuclear quadrupole resonance measurements indicated π - character in the Sn-I bonds of diethyl tin diiodide whereas it was concluded from the dipole moments of organotin chlorides that the Sn-cl bond order is close to unity (39). There is evidence for $d\pi - P\pi$ interaction in the bonds formed between tin and certain transition metals (41 - 42). On the other hand Gupta and Majee have shown in a series of papers (43) that most of the properties of organotin compounds may be interpreted without assuming any $d\pi - p\pi$ interaction. However in a more recent article (44) Majee has demonstrated that the success of earlier Del Re calculations does not necessarily rule out such interactions.

IC Catenation Properties of Sn in Organotin Compounds

Tin like other members of group IVA shows the tendency to catenation. A number of excellent reviews are now available on tin - tin compounds (45 - 49). The ditin compounds may be prepared by a number of methods (47), the alkyl derivatives are generally liquid and the aryl derivatives tend to be solid at ordinary temperature. A good number of compounds of the type

$[R_2Sn]_n$ with the number of tin ranging from 2-6 have been described (47). The reaction of metallic sodium in liquid ammonia with Me_2SnCl_2leads mainly to the compounds $[Me_2Sn]_n$, which are linear molecules with chain length n = 12-20 and perhaps more, and at least to one cyclic compound $[Me_2Sn]_6$.

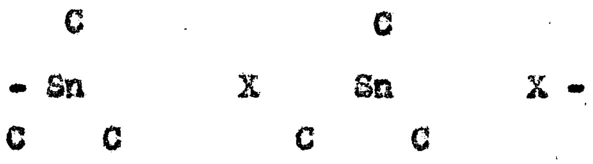
There is no evidence for branching of the chains (50-51). Similar results have been obtained with other alkyl and aryl compounds (51), e;g. cyclic hexamer of Et_2sn, the cyclic pentamer and hexamer of Ph_2sn, the cyclic tetramer of $(t-Bu)_2Sn$ etc. Williamson and Vander Kerk (52-53) have however reported a branched chain compound $(Ph_3Sn)_4Sn$ by the reaction of Ph_3SnLi with $Sncl_4$. Some coloured products reported in the synthesis of dialkyl tin compounds are due to the formation of partially branched tin chains (54). NMR studies indicate the formation of poly tin hydrides during thermal decomposition of butyl tin trihydride (47). Carboxylates and halide derivatives of di and poly tin compounds. have also been reported (55-56).

ID Organotin Complexes

Organotin compounds can form various types of complexes with ligands. The structural aspect of those compounds has been exhaustively reviewed by Ingham etal (8), Poller (57), Gielen and Sprecher (58) and more recently by Ho and Zukermann (58a).

The most interesting example is afforded by $\overset{X}{R_3Sn}$ type compounds which form various types of adducts with Lewis bases (8). These adducts are generally penta co-ordinated (59-60). For X = cl,Br or I, Me_3SnX type compounds are usually tetrahedral but for X = ClO_4^- , F^- , CO_3^- , BF_4^- , No_3^- , AsF_6^- , $OCOR^-$, the compounds are five coordinate about tin where anions are probably either bridging or chelate types (61-62). The aqnoion $Me_2Sn(H_2O)_4^{+2}$ has a linear C-Sn-C group, there being presumably four water molecules weakly co-ordinated in the equitorial plane (63). Similarly R_3SnX and R_2SnX_2 compounds can form organotin chelates with chelating agents such as 8 hydroxy quinoline (64-66), acetyl acetone (67-68), 1,10 Phenanthroline (65,68) etc. which may be five, six or sometimes even eight co-ordinated compounds.

The most general feature of the penta co-ordinated tin is a polymeric structure formed by the bridging of an anionic group to the tin atom from either side of the plane of the trialkyl tin group. This kind of structure is designated as type I. Type I compounds can be devided into three sub groups as shown in the table-2.



$$-\underset{C\quad C}{\overset{C}{Sn}}\quad X\quad \underset{C\quad C}{\overset{C}{Sn}}\quad X-$$

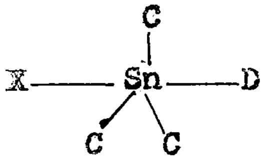
Type - I

Table-2

Sub group	Compound
(a)	$(CH_3)_3SnF$, $(CH_3)_3SnOH$
(b)	$R_3SnOOCR'$, $(C_4H_9)_3Sn$(imidazole), $(CH_3)_3SnNO_3$, $(CH_3)_3SnClO_4$, $(CH_3)_3SnSiF_6$, $R_3Sn\ AlCl_4$
(c)	$(CH_3)_3SnCl$, $(CH_3)_3SnBr$, $(CH_3)_3SnCN$, R_3SnN_3 ,$(CH_3)_3SnNCS$, $(CH_3)_3SnNCO$.

The compounds in the (a) subgroup of this classification contain tin atoms bridged by the anionic groups in the manner, -Sn - X - Y - X -, where X represents a halogen, an oxygen or a nitrogen atom and Z represents the reminder of the resulting group. The compounds in both (a) and (b) subgroup compounds are assumed to contain planner SnC_3 moities, but in so far as they have been studied, those in the (c) subgroup have no such planar arrangement.

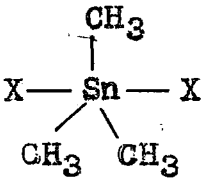
In compounds of structure type II, a donor molecule is co-ordinated to a triorganotin halide to give a trigonal bipyramidal arrangement. The best studied example is the 1 : 1 addition compounds of $(Ch_3)_3$ SnCl and pyridine.



(D = donor molecule)

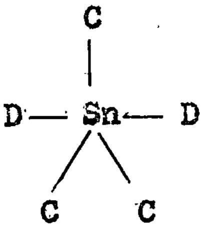
Type II

A halide ion can also act as a Lewis base to trimethyl tin halide, giving a symmetrical bipyramidal configuration of type III



Type III

In cases where the anionic groups have no co-ordinating sites, for example $B(C_6H_5)_4^-$, two molecules of a mono-anionic Lewis base such as water can occupy the co-ordination sphere, giving a planar SnC_3 arrangement with a penta co-ordinated tin atom (type IV)



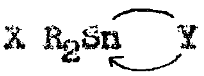
(Type IV)

This finding may well be applied to interpret the structure of 1 : 2 addition compounds of formula $R_3SnX.2D$(8) as that containing a bipyramidal $[R_3SnD_2]^+$ and X anion, and may preclude the existence of hexa-co-ordinated tin atoms in such triorganotin complexes.

If the X group in R_3SnX belongs to a chelating ligand, intramolecular co-ordination can occure as shown in structure (V).

Type V

In the case of di-organotin derivatives, both penta co-ordinated and hexa co-ordinated tin compounds have been reported. Penta co-ordinated tin is observed in dialkyl tin halide, carboxylates, dialkyl tin halide oxinates and dimethyl (1,3-dimethyl triazono) tin halides (69) (type VI)



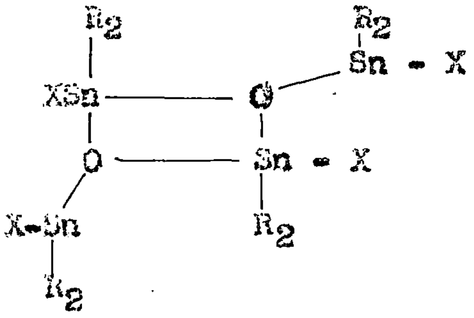
Type VI

The 2 : 1 addition compound of $(C_6H_9)_2Sn(NCO)_2$ and bipyridine is another type of penta co-ordinated di-organotin structure (VII)

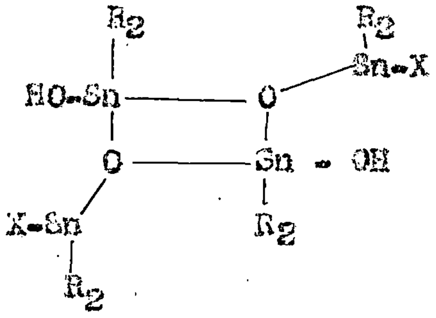
$$X_2R_2Sn \longleftarrow D — D \longrightarrow SnR_2X_2$$

Type VII

The dimeric tetraalkyl distannoxenes $(XR_2SnOSnR_2X)_2$ and $(XR_2SnOSnR_2OH)_2$ are unique because they are believed to contain both tetra-co-ordinated and penta co-ordinated tin atoms (Type VIII and VIII′)

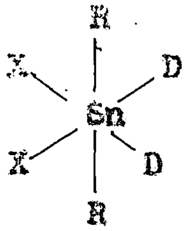


Type VIII



Type VIII

Infrared spectroscopic investigations have shown that the addition compounds of R_2SnX_2 (X = halogen) and monodentate amines in 1 : 2 mole ratio, or bidentate amines in 1:1 mole ratio, are of the type IX

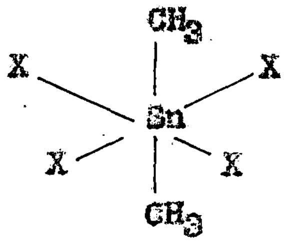


Type IX

Many di-organotin bis (Chelates) have been isolated (64,65,69-75) and found to contain hexa co-ordinated tin atom. Some representative compounds are acetyl acetonates, oxinates, and carboxylates. The alkyl group in these compounds exists predominantly in the trans position (type X), though X-ray crystallography on dimethyl tin dioxinate shows this to have a very much distorted structure (85)

Type X

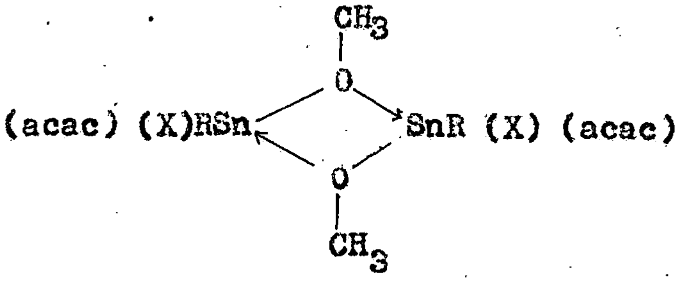
The most symmetric specis is the $(CH_3)_2 SnX_4^{-2}$ anion (X = F,Cl,NCS) where structure is represented by (XI). Tobias etal have shown that there are analogous specis, $[(CH_3)_2 Sn(OH)_4]^{2-}$ as well as cationic hydrated specis in aqueous solution of dimethyl tin compounds (73,76,77)



Type XI

Reports on mono-organotin compounds indicate that some of these might have hexa co-ordinated and even hepta co-ordinated tin atoms. However, little work has been done on their detailed configurations. Mono-organotin halide bis acetyl acetonates (78) and bis oxinates (79) as well as the addition compounds of formula $RSn X_2 .2D$(80) are examples of hexa co-ordinated tin compounds.

The complex compound $[(acac)XRSn(OCH_3)]_2$, obtained by partial alcoholysis from $RXSn(acac)_2$ is unique in that it contains two bridging methoxy groups forming a four membered Sn-O ring as shown in structure XII



Type XII

A hepta co-ordinated tin is observed in phenyl tin tris (tropolonate) and probably in mono organo tin tris (carboxylates).

Several organo tin (IV) complexes with quadri and tetradantate anionic schiff base ligands have been prepared and investigated in the solid state (81 - 83). Mossbauer parameters derived from both zero field and magnetically perturbed spectra suggest that the R_2Sn(salen)*, R = Me, Et, Ph and Me_2Sn(Saldap-2-OH)** complexes have distorted trans octahedral structures. However in Ph_2Sn(H-Saldap-2-O) the ligand appears to be only terdentate leading to a penta-co-ordinate structure similar to those of the $R_2Sn(Sal\text{-}N\text{-}2\text{-}OC_6H_4)$ derivatives (R = Ph,Me).

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* H_2Salen - N,N′ ethylene bis (salicylaldimine)

** H_2saldap-2-OH - N,N′(2-hydrony trimethylene) bis (Salicylaldimine)

Recently organotin complexes of strong π acids of the type Me_3Sn TCNQ, $MeCP_2Sn$.TCNQ, $MeCP_2Sn$.nTCNE(n =1,2) and SnX_4.TCNE.THF(X=cl,Br) (84) have been prepared (TCNQ = Tetra cyano p - quinodimethane, TCNE = tetracyano ethylene). The infrared spectra of the complex Me_3Sn.TCNQ exhibits a single band at 555 cm^{-1} in the tin-carbon streching region which is assigned to the anti-symmetric mode of a planar Me_3Sn moiety, with bridging TCNQ residues resulting in a trigonal bipyramidal configuration at the tin. The intense colouration of the compound is indicative of the formation of $(TCNQ)^{-}$ radical anion on complexation. The complex is therefore best represented by the canonical from $(Me_3Sn)^{+}$. $(TCNQ)^{-}$ and thus provides the first example of an isolable paramagnetic organotin complex.

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