PART - I

A SHORT REVIEW ON THE NATURE OF BONDING AND OTHER RELATED PROPERTIES OF ORGANOTIN COMPOUNDS.

1.A. Introduction:

Organotin compounds are substances in which at least one tin-carbon bond is present. 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. By studying the alkyl derivatives of group IVA metals, the accurate atomic weights of these elements were determined. A comparison of the organometallic derivatives of silicon, tin and lead formed part of the basis of Mendeleeff's famous prediction of new element, eka- silicon (germanium). The discovery of industrial applications of organotin compounds e.g. as stabilisers of polyvinyl chloride plastics, as rubber antioxidants, Ziegler type catalysts in the polymerisation of olefins, agricultural fungicides, as active ingredients in certain veterinary medicinns (4) and an increased general interest have produced a striking renaissance of organotin chemistry starting about 1949 and continuing to the present day.

1.B. Bonding in organotin compounds:

Before going to describe the organotin compounds in detail, it would be useful to discuss briefly the nature of bonding in these compounds.

Tin is a member of group IVA of periodic table. The fifty electrons of the tin atom are arranged as follows: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^2$, the ground state of which is a ^3P state derived from s^2p^2 configuration (5). The common tetra-covalent 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 occours much more frequently than divalent state and a great number of organotin compounds contain tetra valent tin atom. The stable nature and relative low reactivity of the organo derivatives of group IVA metals may be attributed to the sp^3 hybridisation they possess. Thus, tetramethyltin is unreactive towards air and water but trimethylindium and trimethylantimony have a strong affinity towards those reagents. The marked increase in stabilities of R_4Sn compounds over R_2Sn types also demonstrate the effect of increased hybridisation.

1.C. <u>Catenation properties of tin in organotin compounds</u>:

Some excellent reviews on tin-tin compounds are made by various authors in recent years (31-35).

The ditin compounds may be prepared by a number of routes (33), the alkyl derivatives are generally liquid whereas aryl compounds tend to be solid at room temperature. A good number of compounds with chain length varying from 2-6 have been described (33).

Reactions of Me_2SnCl_2 with sodium in liquid ammonia produces linear molecules $\left[Me_2Sn\right]_n$ with chain length n = 12-20 and may be more, as well as at least one cyclic compound, $\left[Me_2Sn\right]_6$. There is no evidence for branching in chains in these compounds (78). Williamsens and Van der Kerk (36,37) have reported the formation of a branched chain compound, $(Ph_3Sn)_4Sn$ by the reaction of Ph_3SnLi with $SnCl_4$. Many a coloured products reported in the synthesis of dialkyltin compounds is due to the partially branched tin chains (38). N.M.R studies indicate the formation of polytin hydrides during the thermal decomposition of butyltin trihydride (33).

Carboxylate and halide derivatives of di and polytin compounds have also been reported (39,40).

Comparison of catenation properties among group IVA elements have shown that there is a decrease in the tendency to catenation in the order $C \ggg Si > Ge \approx Sn \ggg Pb$. This general, if not smooth, decrease in the tendency to catenation may be ascribed to diminished strength of the C-C, Si-Si, Ge-Ge, Sn-Sn and Pb-Pb bonds, which are approximately 83, 42, 40 and 37 K.Cal/mole for C-C, Si-Si, Ge-Ge and Sn-Sn bonds respectively (6).

1.D. <u>The ionic nature of organotin compounds and the effect of bond polarity upon reactions</u>:

The general feature that the electropositivity character increases with atomic number in a group, is also strikingly pronounced among the metals of group IVA. Some properties of the

elements are given in table -I (6).

Table -I

Element	Electronic structure	Ionisation potentials in e.v. First	Second	Electro-negativities(a)	Covalent Radius(b) in $^{o}_{A}$
C	$[He]2s^2 2p^2$	11.3	24.4	2.50	0.77
Si	$[Ne]3s^2 3p^2$	8.1	16.3	1.74	1.17
Ge	$[Ar]3d^{10} 4s^2 4p^2$	7.9	15.9	2.02	1.22
Sn	$[Kr]4d^{10} 5s^2 5p^2$	7.3	14.6	1.72	1.40
Pb	$[Xe]4f^{14} 5d^{10} 6s^2 6p^2$	7.4	15.0	1.55	1.54

a- According to Allred and Rochow; b- tetrahedral i.e. sp^3 radii.

As evidenced from table-1, as because there is a considerable difference in electronegativities between carbon and other elements of group IVA, the metal-carbon bonds should be expected to be quite polar. In fact, Pauling (9) has calculated ionic character of C-Si and C-Sn bonds to be 12% and 15% respectively. Use of Allred and

Rochow's electronegativity values would make these values 14.2% and 14.6% almost identical. Since the electronegativity of carbon varies with the nature and number of attached atoms and groups, the ionic character of tin-carbon bond will also vary.

The physical as well as chemical properties of the compounds depend on the bond polarity. In general, bond partners that carry an appreciable difference of electrical charge relative to each other will serve as an electric dipole that attracts and orients neighbouring reagents. Since tin is positive with respect to carbon, the relative polarity of the C-Sn bond may be formally represented as

$$\overset{\delta-}{C}\!\!-\!\!-\overset{\delta+}{Sn}$$

Therefore, when an organotin compound is exposed to water, the H-O dipole, as expected, would be attracted to C-Sn dipole and would orient in the appropriate direction.

$$\overset{\delta-}{C} - \overset{\delta+}{Sn}$$

$$\overset{\delta+}{H} - \overset{\delta-}{O}$$

The approach of dipoles will continue, with corresponding loss of potential energy, until the repulsion of the electron shells is balanced by the attraction. In these circumstances, the formed active intermediate may either break apart into the original components or realign its bonds to form new substances. If the change

in free energy favours the latter possibility, the products will be:

But due to low polarity of C-Sn bonds as in the tetraalkyls and aryl derivatives of tin are not actually hydrolysed by water. Hydrolysis, however, may be brought about by increasing pressure and temperature and using catalysts such as acids or alkalies which attacks the carbon or tin. A rather unusual feature of the organotin compounds is the ionisation of some of the R_3SnX and R_2SnX_2 compounds in water (6). The strength of single covalent bonds between group IVA and other atoms generally decrease in going down the group, as can be seen from table -II(6).

Table -II

Elements(a)	Energy of bonds, K Cal/mole with						
	H	C	F	Cl	Br	I	O
C	99	83	116	79	66	67	82
Si	70	69	129	86	69	51	88

Contd...

Table - II (Contd.)

Element (a)	Energy of bonds, K Cal/mole with						
	H	C	F	Cl	Br	I	O
Ge	74	71		86	68	50	
Sn	71	68		82	66	47	

a - data derived mainly from MX_4 type compounds which are unstable and or non-existent when M = Pb.

The polarity of the metal carbon bond increases with increasing atomic number within the group and the bond becomes more sensitive to attack by polar reagents. This is also evident from the increase in the polar character of the halogens in compounds such as R_3MX (4).

1.3. Multiple bonding and the effect of availability of d-orbitals of tin in organotin compounds.

Multiple bonds involving $p\pi$ orbitals among the metals or to other elements is not known with Silicon, germanium, tin or lead whereas carbon has a great tendency to do so. However, there is good evidence that the d orbitals of the elements, other than carbon are

used in $d\pi - p\pi$ bonding (6). Thus, the consideration of acid strength of the four acids of the type $p\text{-}R_3MC_6H_4COOH$ reveals that the carbon compound which would be expected to have the greatest acid strength because of its most electronegative character, shows the lowest acid strength. This indicates that $d\pi - p\pi$ bonding is operative in the other three compounds (10). However, it seems that the tendency to use d orbitals in π bonding decreases from Si to Sn, since in $(GeH_3)_2S$ and $(GeH_3)_2O$, the Ge-S-Ge and Ge-O-Ge appear to be highly bent (11) where as in $(SiH_3)_2O$ the Si-O-Si angle is around 150^0 (12). Relative to the bond lengths of Si-X, Ge-X bond lengths are less shortened as computed from the sum of covalent radii of the bond partners (13). Further evidence of the lowering, or non existence of $d\pi - p\pi$ bonding in the elements below silicon comes from the relative base strengths of the amines viz. $(SiMe_3)_3N$, $(GeMe_3)_3N$ and $(SnMe_3)_3N$ due to hydrogen bonding. The silicon compound is virtually non-basic, but the germanium compound is as basic as an organic amine, whereas the tin compound is more basic than any organic amine (6). However, the possibility of $d\pi - p\pi$ bonding in tin cannot be completely ignored, at least with elements of higher atomic numbers e.g., Cl, Br, I etc. In fact, $d\pi - p\pi$ bonding is partly responsible for higher values of Sn-Cl stretching frequency in certain tin compounds (14) and Sn-O frequency in $(Ph_3Sn)_2O$ (15). Although, later on, from IR and Raman studies of compounds $R_3SnXSnR_3$ (X = O, S) it was concluded that there was no

π-contribution to the Sn-O and Sn-S bonds (41), similar ideas regarding Sn-O and Sn-S bonds in other compounds were reached by other workers (43 - 45).

Due to the availability of d orbitals, tin can extend its coordination number from 2 to 8 and so organotin compounds can form various types of complexes with ligands. Thus the most interesting example is afforded by R_3SnX type compounds which forms various types of adducts with Lewis bases (4). These compounds are generally penta coordinated (16, 17). When X is Cl, Br or I in Me_3SnX, they are usually tetrahedral. But for X = ClO_4^-, F^-, CO_3^{-2}, BF_4^-, NO_3^-, AsF_6^-, $OCOR^-$ the compounds are five coordinate about tin, where the anions are probably either bridging or chelate types (18,19). The aquo- ion $\left[Me_2Sn(H_2O)_4\right]^{+2}$ has a linear C-Sn-C group, there are presumably four water molecules weakly coordinated in the equitorial plane (20). In alkaline solution of Me_2SnCl_2, there exists trans $\left[Me_2Sn(OH)_4\right]^{-2}$ ion (20). Similarly R_3SnX and R_2SnX_2 compounds can form organotin chelates with chelating agents such as 8-hydroxy quinoline (21,22,41) acetyl acetone (23,24), 1,10 phenanthroline (22,24) etc. which are generally five or six and sometimes seven and eight coordinated compounds.

A penta coordinated intermediate of the type $\geqslant SnX.N$ may be formed when a neucleophilic substitution at tin takes place as follows (26)

$$\geqslant SnX + N \longrightarrow \geqslant SnN + X$$

Eaborn (27) has pointed out that in case of silicon atom such type of intermediate complex formation may decrease substantially the free energy of the transition state. Since complex formation is much more marked with tin than with silicon the facilitation of nucleophilic substitution reactions by this means is correspondingly more important. This facilitation may be pronounced even if the intermediate is very weak to be detected (27).

Nucleophilic assistance influences the cleavage of tin carbon bond by electrophilic attack at carbon atom (28-30). Thus in the halogen cleavage of Sn-C bond the presence of a donor solvent, such as an alcohol or acetic acid, even though it cannot form stable adduct with the tin compound can affect the rate of halogen cleavage by rendering nucleophilic assistance.

$$R_4Sn + Solvent \rightleftharpoons Solvent \longrightarrow SnR_4$$

$$Solvent \longrightarrow \underset{\displaystyle R \quad R}{\overset{\displaystyle R}{Sn}} - R + X_2 \rightleftharpoons \left[Solvent \longrightarrow \underset{\displaystyle R \quad R}{\overset{\displaystyle R}{Sn}} \cdots R \cdots \overset{\delta+}{X} \cdots \overset{\delta-}{X} \right]$$

$$\rightleftharpoons R_3SnX.solvent + RX \text{ (where } X = Br, I).$$

The polarity of Sn-C bond together with the tendency of tin atom to form adducts with Lewis bases (donors) may be successfully utilised to explain a number of reactions, e.g., the cleavage

of Sn-C bonds by some chelating agents studied by Nelson and Martin (25) and the reactions of $R_3SnOCOR'$, $(R_3Sn)_2O$ and some organotin oximates with mercury salts etc.

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