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 such compound was described by Löwig[1] in 1852. Many significant contributions were made in this field during the next few decades. The assignment of the first accurate atomic weights of the group IVA metals was facilitated by the study of their alkyl compounds. 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). In the recent years organotin chemistry appears to be on the threshold of large-scale commercial development. Organotin compounds have been successfully utilised in the stabilisation of polyvinyl chloride plastics, as rubber antioxidants, Ziegler type catalysts in the polymerisation of olefins, agricultural fungicides, and as active ingredients in certain veterinary medicines[2].

1.B. Bonding in organotin compounds:

Before going to describe the organotin compounds in detail, a brief discussion on the nature of bonding in these compounds would be useful.

Tin, the element of atomic number 50, is a member of group IVA of the periodic Table. In the atom of any element of this group there are four electrons in the valence level. The ground state for these atoms is a 3P state derived from an s^2p^2 configuration[3]. There are two electrons in the s subshell with

spins coupled and in this state only two unpaired electrons in the p sub-shell should be available for bonding. A covalence of two would be expected arising from this ground state of the atom. The common four-covalent state is derived from the sp^3 hybridisation by promoting one of the paired s electrons to the next higher p level. Covalences of two and four would then be expected for these elements in neutral molecules. However, four-covalent state occurs far more frequently than the two covalent state and the great majority of organotin compounds possess a four-covalent tin atom. Because of the sp^3 hybridisation, the organometallic compounds of group IVA are relatively stable and possess relative low chemical reactivity; thus, tetramethyl tin is unreactive towards air and water, in strong contrast to trimethylindium and trimethyl antimony. The marked increase in stabilities of R_4Sn compounds over R_2Sn types also demonstrate the effect of increased hybridisation. All R_2Sn compounds except where R= C_5H_5 (cyclopentadienyl) are usually Sn(IV) compounds since they contain Sn-Sn bonds, although genuine Sn(II) compounds also do exist[4].

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

The tendency to catenation in group IVA appears to vary irregularly. Silicon forms a series of hydrides, Si_nH_{2n+2} and halides Si_nX_{2n+2} (X = F, Cl) which contain Si-Si bonds, while for germanium only the hydrides are known. For tin, catenated hydrides or halides are unknown, but an extensive series of $(R_2Sn)_n$ compounds,

both cyclic and linear, in the latter the mode of chain termination is not certain, are known[4]. For example, the reaction of sodium in liquid ammonia with Me_2SnCl_2 gives $[Me_2Sn]_n$ which consists mainly of linear molecules with chain lengths n = 12-20 and perhaps more, as well as at least one cyclic compound, $[Sn(Me_2)]_6$. There is no evidence for branching of chains[5]. Similar results have been obtained with other alkyl and aryl groups[6] e.g. the cyclic hexamer and monomer of Et_2Sn, the cyclic pentamer and hexamer of Ph_2Sn and the cyclic tetramer of $(t\text{-}Bu)_2Sn$ have been isolated as well as linear species. It has been reported that in some cases the terminal groups of the linear species are $-SnR_2H$. The structure of $[Ph_2Sn]_6$ is known, it contains an Sn_6 ring in a chair configuration, with the Sn - Sn bonds about the same length as those in grey tin[7]. Lead is not known to form any catenated compounds except in alloys such as Na_4Pb_9 which contain distinct poly atomic lead anions. On the whole, however, there is a decrease in the tendency to catenation in the order C $\ggg$ Si $>$ Ge $\gtrsim$ Sn $\ggg$ Pb. This general, if not entirely smooth decrease in the tendency to catenation may be ascribed partly to diminish strength of the C - C, Si - Si, Ge - Ge, Sn - Sn and Pb - Pb bonds, which are approximately 83, 42, 40 and 37 KCal/mole for C - C, Si - Si, Ge - Ge and Sn - Sn bonds respectively[4].

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

The increase in the electropositive character with increasing atomic number, which is found in several groups is

strikingly evident in group IVA. Some propeties of the elements are given in Table-1[4].

Table-1

Element	Electronic structure	Ionisation potentials in e.v.		Electrone-gativities[a]	Covalent Radius[b] in ^{o}A .
		First	Second		
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 can be seen from Table-1, there is considerable difference in electronegativity between carbon and the other elements of group IVA. As such metal-carbon bonds should be expected to be quite polar. In fact, Pauling, using his well known relationship between percentage ionic character of bond and the electronegativity[8] 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 accordingly.

The polarity of a bond not only influences the physical properties of the compound in accordance with the well known characteristics of ionic and covalent compounds, but also influences markedly the chemical reactivity of the compound. 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

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

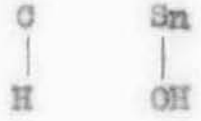
Thus, if an organotin compound is exposed to water, it is to be expected that an H-O dipole will be attracted to C-Sn dipole and oriented in the appropriate direction.

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

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

The approach of dipoles will continue, with corresponding loss of potential energy, until repulsion of the electron shells

equalises the attraction. We then have an active intermediate which may either break apart into the original components or reallign its bonds to form new substances. If the change in free energy favours the latter action, the products will be:



However, due to the low polarity the carbon tin bond as in the tetra-alkyls or tetra-aryls of tin are not actually hydrolysed by water. Hydrolysis requires increase of temperature and pressure or the use of catalysts such as acids or bases which attacks the carbon or tin. An unusual feature of the organotin compounds is the ionisation of some of the R_3SnX and R_2SnX_2 compounds in water[4]. The organotin halides also do not hydrolyse in water without the action of any base because of the stronger bond strength of the tin halogen bond than the tin-oxygen bond. The strength of single covalent bonds between group IVA atoms and other atoms generally decrease in going down the group, as can be seen from Table-2[4].

Table-2

Element[a]	Energy of bond, KCal/mole, with						
	H	C	F	Cl	Br	I	O
C	99	83	116	79	66	57	82
Si	70	69	129	86	69	51	88
Ge	74	71		85	68	50	
Sn	71	68		82	65	47	

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

In case of organosilicon compounds the reverse is the case. In the R_3MOH series, the basicity increases from silicon to lead. The metal carbon bond strengths decrease and the distances increase as going down the group IVA, resulting in progressive decrease in the melting points; Ph_4Si - 233°, Ph_4Ge - 230°, Ph_4Sn - 225° and Ph_4Pb - 225°. 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[2].

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

Silicon, germanium, tin and lead do not form $p\pi$ multiple bonds either to themselves or to other elements where as carbon has a profound 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[4] . For example with the four acids of the type $p\text{-}R_3MC_6H_4COOH$, where M represents carbon, silicon, germanium, or tin, carbon is the most electronegative of four elements and should enhance the acid strength to the greatest extent. Actually, the carbon compound shows the lowest acid strength, indicating that $d\pi - p\pi$ bonding is operative in the other three compounds[9]. The tendency to use d orbitals for π-bonding seems to decrease from Si to Sn, since in $(GeH_3)_2O$ and $(GeH_3)_2S$, the Ge-O-Ge and Ge-S-Ge groups appear to be highly bent[10] where as in $(SiH_3)_2O$ the Si-O-Si

angle is around 150° [11]. Also Ge-X bond lengths seem to be less shortened relative to the sum of the covalent radii of the bond partners than are Si-X bond lengths[12], the shortening is considered to be due at least in part, to $d\pi - p\pi$ bonding. 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 $(SiMe_3)_3N$, $(GeMe_3)_3N$ and $(SnMe_3)_3N$ due to hydrogen bonding. Whereas the silicon compound is virtually non-basic, the germanium compound is about as basic as an organic amine, while the tin compound is more basic than any organic amine[4]. 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 thought to be partly responsible for higher values of Sn-Cl stretching frequency in certain tin compounds[13] and Sn-O frequency in $(Ph_3Sn)_2O$[14].

Due to the availability of d-orbitals, organotin compounds can form various types of complexes with ligands. The most interesting example is afforded by R_3SnX type compounds which form 1:1 adducts with various Lewis bases[2]. These are apparently five-co-ordinate trigonal bipyramidal molecules, a structure proved for $Me_3SnCl.Py$ which has equitorial methyl groups[15,16]. Again Me_3SnX type of compounds when X = Cl, Br, or I the compounds are simple tetrahedral, but when X = ClO_4^-, F^-, CO_3^{-2}, BF_4^-, NO_3^-, AsF_6^- the the compounds are five coordinate about tin where the anions are

either bridging or chelate[17,18] types. The aquo-ion $[Me_2Sn(H_2O)_4]^{+2}$ has a linear C-Sn-C group, there are presumably four water molecules weakly coordinated in the equitorial plane[19]. In alkaline solution of Me_2SnCl_2, there exists trans $[Me_2Sn(OH)_4]^{-2}$ ion[19]. Similarly, R_3SnX and R_2SnX_2 compounds can form organotin chelates with chelating agents such as 8-hydroxy quinoline[20,21], acetyl acetone[22,23], 1, 10 phenanthroline[21,23] bipyridyl[21,23,24] etc. which are either five or six coordinate compounds.

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 $(R_3Sn)_2O$ and some organotin oxinates with mercuric halides etc.

B I B L I O G R A P H Y

1. C. Lowig — Ann. 84, 308 (1852)

2. R.K.Ingham, S.D.Rosenberg and H.Gilman — Chem.Review 60, 520-625 (1960)

3. C.E.Moore — Atomic Energy Levels, Circular 467, National Bureau of standards, Vol. I Government Printing Office, Washington, D.C. (1949)

4. F.A.Cotton and G.Wilkinson — Advanced Inorganic Chemistry, 2nd Edition, 1967, Inter Science Publishers, New York.

5. T.L.Brown and G.L. Morgan — Inorg. Chem. 2, 736 (1963)

6. W.V.Farrer and H.A.Skinner — J.Organo-metal Chem. 1, 434 (1964)

7. D.H.Olson and R.E. Rundle — Inorg. Chem. 2, 1310 (1963)

8. E.G.Rochow, D.T. Hurd and R.N.Lewis — The Chemistry of Organometallic compounds- John Wiley and Sons. Inc. 1957, New York.

9. J.Chatt and A.A.Williams — J.Chem. Soc, 4403 (1954)

10. T.D.Goldfrab and S.Sujishi — J.Amer.Chem.Soc. 86, 1679 (1964)

11. R.Verma, A.G.MacDiarmid and J.G.Miller — Inorg.Chem. 3, 1754 (1964)

12. J.E.Griffiths and K.B.McAfee — Proc. Chem. Soc. 456 (1961)

13. W.H.Nelson and D.F.Martin — J.Inorg.Nucl.Chem. 27, 89 (1965)

14. R.C.Poller — J.Inorg.Nucl.Chem. 24, 593 (1962)

15. N.A.Matwiyoff and R.S.Drago — Inorg. Chem. 3, 337 (1964)

16. R.Hulme — J.Chem.Soc. 1524 (1963)

17. H.C.Clark, R.J.O'Brien — Inorg.Chem. 2, 740, 1020 (1963)

18. H.C.Clark, R.J.O'Brien and J.Troller — J.Chem.Soc. 2332 (1964)

19. R.S.Tobias and C.E.Freidline — Inorg.Chem. 4, 215 (1965)

20. D.Blake, G.E.Coates and J.M.Tate — J.Chem.Soc. 756 (1961)

21. T.Tanaka, M.Komura, Y.Kawasaki and R.Okawara — J.Organometal Chem. 1 (6), 484 (1964)

22. A.W.Westlake and D.F.Martin — J.Inorg. Nucl. Chem. 27, 1579 (1965)

23. D.L.Alleston and A.G.Davies — Chem. Ind. 551 (1961)

24. J.E.Ferguson, W.R. Roper and C.J.Wilkins — J.Chem.Soc. 3716 (1965)

25. W.H.Nelson and D.F. Martin — J.Organometal Chem. 4(1) 67 (1965)