

THE EFFECT OF ORGANIC SUBSTITUENTS ON THE ACCEPTOR PROPERTIES OF TIN(IV) CHLORIDES

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ABSTRACT : *The equilibrium constant of adduct formation between some triorganotin chloride of the type R_3SnCl ($R=C_6H_5$, $p-CH_3C_6H_4$, $n-CH_3(CH_2)_3$, $C_6H_5-CH_2$) and Lewis bases Cl^- , Br^- , and I^- , were measured in 50% v/v ethanol-water solvent spectrophotometrically. The average equilibrium constant values for the systems studied shows the following acceptor trend of tin(IV) in the triorganotin chlorides:*

p -tolyl > n -butyl > phenyl > benzyl

The influence of the organic moieties on the acceptor property of tin(IV) is discussed.

KEY WORDS : *Triorganotin chloride, Adduct compounds, Stannane chlorotriaryl, Mixed solvent, Acceptor property.*

INTRODUCTION :

Recent studies [1-4] have shown that triorganotin halides form predominantly 1:1 adduct in solution with a variety of monodentate bases. The results provide evidence that in triaryltin compounds $d_\pi - p_\pi$ bonding exists

between the empty d-orbital of the Sn atom and the π electrons of the phenyl ring [5]. While the tin tetraorgano show no evidence of Lewis acidity, the tin(IV) halides are strong Lewis acids forming 1:1 and 1:2 adducts with Lewis

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bases. The organotin halides R_nSnX_{4-n} are intermediate in Lewis acidity between R_4Sn and SnX_4 . The acidity generally increasing as the proportion of the halide increases [6].

This paper reports the equilibrium constants for adducts formation of Ph_3SnCl , $(p\text{-tolyl})_3SnCl$, $(benzyl)_3SnCl$ and $(n\text{-butyl})_3SnCl$ with chloride, bromide and iodide bases in 50% v/v binary mixture as solvent as a quantitative measures of the acidity character of tin(IV) in its triorgano compounds.

EXPERIMENTAL :

Bromobenzene, p- bromotoluene, magnesium turnings and anhydrous tin tetrachloride, ethanol, diethyl ether, acetone and benzyl chloride were obtained from *Merck* (Darmstadt, Germany) and *Fluka* (Switzerland). Solvents used in Grignard reagents were dried and distilled before use but other materials were used without further treatments. For spectroscopy measurements pure NaCl, NaBr and NaI and extra pure ethanol was used as obtained from *Merck*.

Synthesis of the Triorganotin Compounds

The most widely used method for the preparation of organotin compounds is the exchange reaction between tin tetrachloride and organomagnesium halide [7]. Triphenyltin chloride and tri-p-tolytin chloride were prepared according to the method of K.A. Kocheshkov, et al. [8] from the reaction of anhydrous stannic tetrachloride (1 mole) with tetraphenyltin (3 mole) and tetra-p-tolytin (3 mole), respectively.

Tribenzyltin chloride was prepared by *Smith and Kipping* [9] method: From anhydrous stannic tetrachloride and magnesium benzylchloride (Grignard reagent).

Tri-n-butyltin chloride (*Aldrich*, Milwaukee, WI, U.S.A) was used without further treatment. Melting point and the solubility of the prepared compounds in this work were in accord with the previous available data in the literature [10,11]. Some physical constants of the compounds

prepared are shown in Table 1.

General Methods

The ultraviolet absorption spectra of all the triorganotin compounds prepared were measured in 50% ethanol-water solvent using *Unicam* double beam spectrophotometer (*Philips* PU8750, England) fitted with a thermostated cell compartment (0.1°C). Solutions were made with especially purified solvents (spectrosol grade, *Merck*); dried and distilled before use. Conductivity water was prepared from redistillation of distilled water in the presence of sodium hydroxide and potassium permanganate.

The thermodynamic stability constants and the molar extinction coefficients of each adduct formed between a given concentration of the triorganotin chloride and the halides (in excess) were measured in a range of wavelengths (Table 2) using *Ketelaar's* [12] modification of *Benesi-Hildebrand* [13] equation of the form:

$$\frac{LC_a^{\circ}C_d^{\circ}}{A - A_a^{\circ} - A_d^{\circ}} = \frac{1}{K(\epsilon_c - \epsilon_a - \epsilon_d)} + \frac{C_a^{\circ} + C_d^{\circ}}{\epsilon_c - \epsilon_a - \epsilon_d}$$

where C_a° , C_d° are the initial concentrations of the acceptor and the donor; respectively; A is the optical density of the solution. A_a° and A_d° are the optical densities of the pure acceptor and pure donor in solutions of concentration C_a° and C_d° (molar unit); ϵ_c , ϵ_a , ϵ_d ($\text{mol}^{-1}\cdot\text{cm}^{-1}\cdot\text{L}$ unit) are the molar extinction coefficients of the complex, the acceptor, and the donor, respectively, L is the cell optical path length (cm unit) and K is the stability constant of the 1:1 addition compound formed.

A plot of the left hand side of the *Ketelaar's* equation versus $(C_a^{\circ} + C_d^{\circ})$ produces a straight line if only 1:1 complex is formed; while a mixture of 1:1 and 2:1 or only 2:1 complex in a system would lead to a curve [2]. The stability constants were calculated from the ratio of the slope to the intercept, both graphically and by the linear least square method. In all the systems studied straight lines were obtained but for $(PhCH_2)_3SnCl\text{-}Cl^{-}$ system where a curve was obtained. Therefore, K values for the latter

Table 1 : Physical constants of the Triorganotin compounds.

Compound	m.p.(°C)	Solubility
Ph ₃ SnCl	106(lit. 106) ^[8]	soluble in organic solvents insoluble in water, soluble in hot benzene.
(p-tolyl) ₃ SnCl	98(li. 97.5) ^[8]	slightly soluble in alcohol, benzene, and ether.
(benzyl) ₃ SnCl	147(lit. 148) ^[16]	soluble in acetic acid, benzene, ether, chloroform, and pyridine, insoluble in alcohol.
(n-butyl) ₃ SnCl	lit.b.p. 145/175mm ^[17]	soluble in organic solvent and insoluble in water.

system were found by the graphical method only, by drawing a tangent to the Ketelaar's plots at the point of intercept.

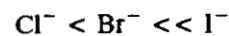
Since all the complexes studied show no isolated charge transfer band; therefore, the stability constants are calculated mostly from plots in the region of wavelengths where the donor show no absorption, but the acceptor and the complex formed show absorption in the same region. Only in a few systems (iodide used as donor) the calculation are made in the region where the complex, acceptor and donor show absorption in the same region. In all the systems studied in this work, the concentration of the acceptors were kept constant; while the concentration of the donors (halide ions) were varied. The spectrum of the acceptor shows a considerable change when the donor concentration is varied. The stability constants evaluated for the systems studied showed little wavelength dependence, with the exception of iodide systems where wavelength dependence is observed [14]. The solvent used for all the systems studied was 50% v/v ethanol-water, and the measurements were carried out at 25±0.1°C. Since the value of K was greatly affected by the slope and the intercept, a small variation in both or either may lead to a substantial change in the K value. In order to avoid such graphical error which may lead to erroneous K values, a much more reliable results were obtained from least square method.

The molar extinction coefficients for the complexes formed at various frequencies were calculated from the value of the slope obtained from the least square method, and the molar extinction coefficients of pure donor and acceptor.

RESULTS AND DISCUSSION :

The average graphical and least square stability constants of the organotin chlorides with the halide donors are listed in Table 2. Since the stability constants are slightly wave dependent, therefore the average K values are used as a quantitative measures for the acidity behaviour of tin in these organo compounds.

Comparison of the average K values in Table 2 shows that the order of basicity of the halide donors toward the triphenyltin, tri-p-tolytin, and tri-n-butyltin chloride is as follow:



This trend shows that I⁻ forms the most stable adduct with each given compound. Since I⁻ is known to behave as a soft base therefore one can conclude that the above given triorganotin chlorides are soft acids (Pearson's rule [15]). The above order of base strengths is consistent with the increasing polarizability on going from chloride to iodide.

The presence of a methyl group in tri-p-

Table 2 : Average graphical and least square K values for the triorganotin chloride- halide systems in 50% ethanol-water at $25 \pm 0.1^\circ\text{C}$.

System	Wavelength region(cm^{-1})	C_d^0/C_a^0	$(K_{av})_{Gr}/M^{-1}$	$(k_{av})_{LS}/M^{-1}$
$\text{Ph}_3\text{SnCl}-\text{Cl}^-$	42800-43600	10-90	41.2 ± 3.6	41.8 ± 5.5
$\text{Ph}_3\text{SnCl}-\text{Br}^-$	42800-44600	10-100	54.8 ± 4.6	52.7 ± 2.9
$\text{Ph}_3\text{SnCl}-\text{I}^-$	39800-41200	6-20	730.4 ± 54.5	798.5 ± 87
$(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{SnCl}-\text{Cl}^-$	41400-43200	10-90	-	-
$(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{SnCl}-\text{Br}^-$	41400-43000	20-80	36.8 ± 4.4	35.7 ± 5.2
$(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{SnCl}-\text{I}^-$	39800-41200	6-18	1006.8 ± 29.6	1030.7 ± 27.3
$(\text{PhCH}_2)_3\text{SnCl}-\text{Cl}^-$	46200-47400	10-70	235.2 ± 8	-
$(\text{PhCH}_2)_3\text{SnCl}-\text{Br}^-$	45600-46800	20-90	212.7 ± 11.7	212 ± 19.0
$(\text{PhCH}_2)_3\text{SnCl}-\text{I}^-$	39600-41000	6-20	-	-
$[\text{n-CH}_3(\text{CH}_2)_3]_3\text{SnCl}-\text{Cl}^-$	45200-46600	10-90	28.6 ± 2.5	28.9 ± 5.6
$[\text{n-CH}_3(\text{CH}_2)_3]_3\text{SnCl}-\text{Br}^-$	44600-45800	30-90	42.8 ± 2.9	44.4 ± 8.5
$[\text{n-CH}_3(\text{CH}_2)_3]_3\text{SnCl}-\text{I}^-$	39800-41200	6-20	878.7 ± 44.4	887.6 ± 45.6

$(K_{av})_{Gr}$ = Average graphical stability constant.

$(K_{av})_{LS}$ = Average least square stability constant.

tolytin chloride increases markedly its softness relative to triphenyltin chloride. The electron releasing property of the methyl group increases the electron density on tin atom through d_π - p_π bonding between the empty d-orbital of tin atom and the filled p-orbital of the phenyl group.

The K value for the tri-n-butyltin chloride-iodide system falls between those of triphenyltin and tri-p-tolytin chloride complexes with iodide. The softness of tin in this compound may be attributed to a great extent, to the electron releasing (inductively) property of the butyl group.

However, the order of the stability constants of tribenzyltin chloride with the same halides is reversed, i.e. the base strengths toward tribenzyltin chloride is as follow:

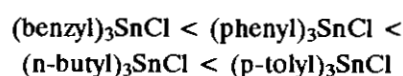


The above order of base strengths shows that chloride ion (hard donor) forms a more stable complex with tribenzyltin chloride, while bromide forms a less stable complex and iodide

forms a complex of very low stability constant (almost zero stability constant). The presence of methylene group in this compound renders the tin atom behaving as a hard acid. The shielding effect of CH_2 group in this compound prevents the formation of d_π - p_π bonding, therefore the net positive charge on the central tin atom remains intact. Furthermore, the marked curvature of Ketelaar's plots for this system (i.e. $(\text{PhCH}_2)_3\text{SnCl}-\text{Cl}^-$) indicates the presence of 2:1 complex showing the preference for six coordination usually exhibited by hard acids [3,6] (Fig. 1).

CONCLUSIONS :

By comparison of K values for all complexes studied with a given donor, for example iodide ion, we arrive at the conclusion that in the case of iodide ion as a soft donor the acceptor property of tin in all the organotin chlorides studied follows the sequence given below:



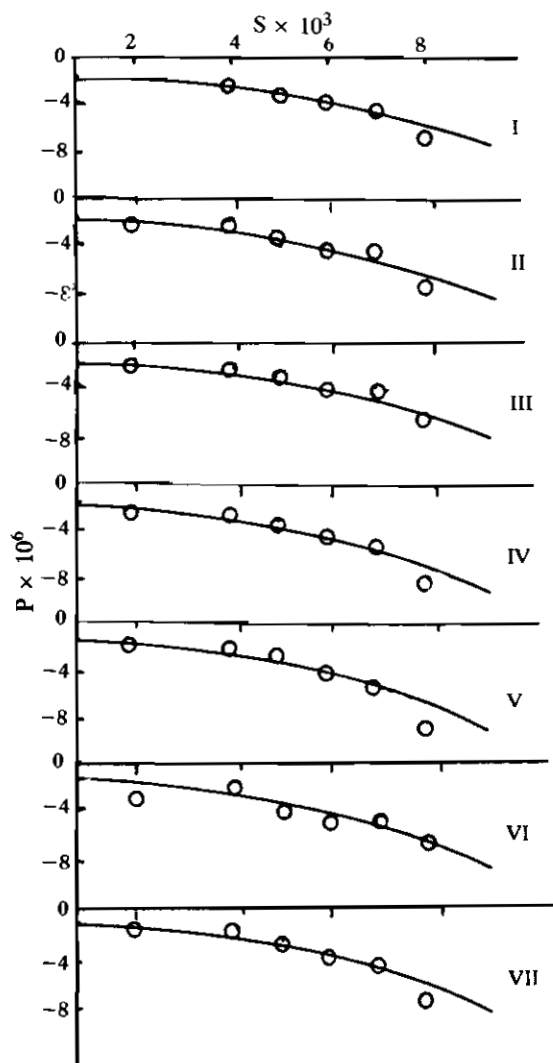


Fig. 1: Ketelaar plots for $(\text{PhCH}_2)_3\text{SnCl-Cl}^-$ system at:

- I 46200 cm^{-1} , V 47000 cm^{-1}
 II 46400 cm^{-1} , VI 47200 cm^{-1}
 III 46600 cm^{-1} , VII 47400 cm^{-1}
 IV 46800 cm^{-1}

$$P = \frac{C_a^\circ C_d^\circ}{A - A_a^\circ}, \quad S = C_a^\circ + C_d^\circ$$

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