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ORGANOTIN HALIDE EQUILIBRIA
II. ARYLTIN TRICHLORIDES WITH AROMATIC AMINES IN ETHER SOLUTION

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INTRODUCTION

In a recent study[1], equilibrium constants were determined for the interactions of phenyl-, methyl- and n-butyltin trichlorides with some nitroaniline and nitrophenylenediamine donors in diethyl ether solution at 25°. The order of decreasing acceptor strengths was established as $PhSnCl_3 > MeSnCl_3 > n\text{-}BuSnCl_3$ and the acidities to be in the ratio of 12 : 3 : 1. This sequence is in accord with the electronegativities of the organic substituents[2].

In the present study, the same donors were used with three other aryltin trichlorides with the object of investigating not only the relative acceptor strengths of these aryl compounds but also some aspects of the carbon–tin bond. The aryl compounds were (4-chlorophenyl)-, 4-tolyl- and 4-biphenylyltin trichlorides. The same approach as used previously was adopted[1].

EXPERIMENTAL

Materials

The solvent and the donors were purified as described[1].

Aryltin trichlorides

The trichlorides were prepared by the treatment of the tetraaryltin compounds with stannic chloride[3,4]. The desired product was initially distilled from the reaction mixture under reduced pressure and subsequent purification was either by sublima-

TABLE 1

PHYSICAL DATA OF ARYLTIN TRICHLORIDES

Tin trichloride	*M.p. or b.p.*	*Ionizable Cl[a] (%)*	
		Calcd.	*Found*
(4-chlorophenyl)-	38–40°	31.64	31.50
4-tolyl-	120° at 10 mm	32.14	32.17
4-diphenylyl-	64–66°	28.13	28.04

[a] Cl determined by potentiometric titration of a hydrolysed sample[1].

tions or distillations also under reduced pressure. Physical data of the trichlorides are given in Table 1.

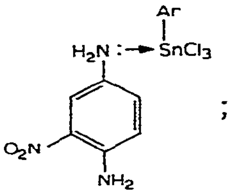
The tetraaryltin compounds were prepared either by Gilman and Rosenberg's method[5] or that of Luijten and Van der Kerk[4].

The experimental method and calculation of the equilibrium constants at 25±0.1°

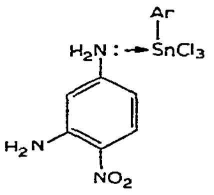
This has been described[1]. Each pK determination was repeated at least twice, with different samples of $ArSnCl_3$ and each determination involved at least five different acceptor–donor compositions. The overall reproducibility was within ±0.03 units.

RESULTS AND DISCUSSION

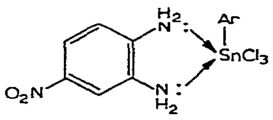
The adduct stoichiometries were 1 : 1; no other was evident. The spectra of the diamine adducts were exactly as described previously[1], indicating that again 1,2-diamino-4-nitrobenzene formed chelates involving both amine groups, while only the more basic group was used in the co-ordination for the other two diamines. The types of diamine adducts were thus,



(I) ;



(II) ;



(III)

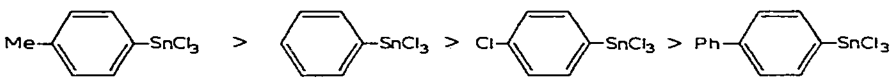
No reductions in the intensities of the adducts' visible bands [of (I) and (II)] were caused by the most concentrated solutions of $ArSnCl_3$, indicating that the free amine group remained un-co-ordinated. The monoamine adducts, as with the corresponding anilinium ions, showed no visible absorption. There were no charge-transfer absorption bands as have been found for some similar adducts of the monoamines[1,6].

The Table provides the pK values for the equilibria:

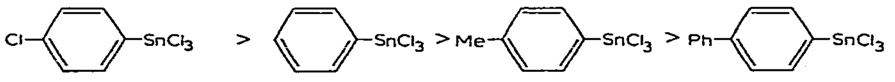
$$ArSnCl_3 + Donor \rightleftarrows ArSnCl_3 : Donor$$

Formation constants for organotin chloride adducts are still scarce; other systems have been studied by Okawara *et al.*[7] (for 2,2'-bipyridine adducts of Me_2SnCl_2, Et_2SnCl_2, n-Pr_2SnCl_2, n-Bu_2SnCl_2 and n-$BuSnCl_3$), by Drago *et al.*[8] ($MeSnCl_3$ with a number of oxygen, nitrogen, sulphur and phosphorus donors; one donor, tetramethylene sulphone, was also studied with Et_3SnCl) and by Satchell and Mohammad[9] ($PhSnCl_3$ with perinaphthenone). The organic substitution as expected greatly reduces the acidity of stannic chloride. The particular donor, as well as the type and the number of the organic substituents, can have some influence on the relative acidities of stannic chloride and the organotin chloride, as shown by the ΔpK values in ether for $SnCl_4$ and $PhSnCl_3$ being 1.25 units and 1.80 units respectively with perinaphthenone[9] and 6-methyl-3-nitroaniline[1].

These two donors are very different. In this study, the two types of donors —the monoamines and the diamines—are structurally similar. Despite this similarity, two distinct acceptor sequences are found for the monoamines as one group and for the diamines as another, and this is irrespective of the use of the additional amine group in the co-ordination to the tin. The two sequences are (*a*) towards the monoamines:



and (*b*) towards the diamines:



It was realised initially that ether could have some influence on these acceptor-donor equilibria, arising from its strong solvating and co-ordinating power. An attempt to measure the importance of this solvent participation has been described for the phenyltin trichloride/4-methyl-3-nitroaniline equilibrium[1]. The p*K* value barely altered from that in ether (−0.93) on moving to a mixed ether/*o*-dichlorobenzene solvent (60:40 by volume), where the value was −0.96. (The adduct was insoluble in *o*-dichlorobenzene alone, and this prevented study in this non-co-ordinating solvent.) It was assumed from the above results that ether had only a very small effect on the acidity of $PhSnCl_3$. It was this fact, plus the almost consistent acceptor strength sequence obtained for $PhSnCl_3$, $MeSnCl_3$ and n-$BuSnCl_3$ towards the donors[1] (the only exception being base no. 4), which led us to expect an equally simple pattern with other aryltin trichlorides.

It has been shown that a powerful co-ordinating solvent can indeed affect the relative strengths of similar acceptors[7]. The formation constants for a series of dialkyltin dichloride/2,2′-bipyridine adducts in the solvent, acetonitrile, gave rise to the following order of acceptor strengths, $Et_2SnCl_2 > Me_2SnCl_2 >$ n-$Pr_2SnCl_2 >$ n-Bu_2SnCl_2. But when the solvent–solute interactions (*i.e.* the heats of mixing the solvent and the acceptors) were taken into account, the order of the heats of formation of R_2SnCl_2 : 2,2′-bipyridine was R = Me > Et > n-Pr > n-Bu, which is in agreement with the electronegativities of the organic groups[2]. The solvation of all adducts were assumed to be similar. As only the one donor was studied, it remains unknown whether such solvent participation would change the acceptor sequence from one similar donor to another.

The conclusion must be drawn that differential solvation effects are probably important for these $ArSnCl_3$ systems and the very small influence by the solvent on the $PhSnCl_3$ equilibrium constant quoted above cannot be simply assumed to apply to all the other chloride systems. The inductive effects of the organic substituents must also have some influence on the $ArSnCl_3$ compounds as found from other equilibrium studies[1,7] and also from such studies as the cleavage reactions of aryltin compounds by electrophilic reagents[10,11,12].

There is an additional aspect of the bonding in aryltin compounds and this is the possibility of $(p \rightarrow d)_\pi$ bonding resulting from an overlap of the aromatic π

TABLE 2

PK VALUES FOR THE INTERACTIONS BETWEEN ORGANOTIN TRICHLORIDES AND THE ANILINE DONORS, D, IN ETHER SOLUTION AT 25°

$K = [ArSnCl_3 : D]/[D][ArSnCl_3]$.

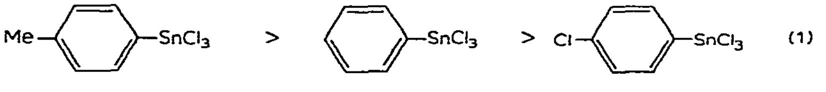
K_a = dissociation constant of DH^+ in water at 25°.

λ_{max}(D) and λ_{max}(DA) are the maxima of the visible absorption of the donor and its adducts respectively in mμ.

No.	*Donor*	*pK_a*	*$\lambda_{max}(D)$*	*$\lambda_{max}(DA)$*	*pK for R of $RSnCl_3$*					
					p-ClC_6H_4	*Ph*[a]	*p-MeC_6H_4*	*p-PhC_6H_4*	*Me*[a]	*n-Bu*[a]
(a) Aniline derivatives										
1	4-Methyl-3-nitro-	2.90	367		−0.70	−0.93	−1.10	+0.06	−0.35	+0.10
2	3-Nitro-	2.50	368		−0.39	−0.62	−0.78	[b]	−0.03[c]	+0.47[c]
3	6-Methyl-3-nitro-	2.32	366		−0.01	−0.21	−0.36	[b]	+0.40[c]	[b]
(b) Benzene derivatives										
4	1,3-Diamino-4-nitro-	1.01	376	398	−1.36	−0.06	−0.21	[b]	−0.75	−0.66
5	1,4-Diamino-3-nitro-	>4	466	396	−2.71	−2.30	−1.98	−1.80	−1.90	−1.62
6	1,2-Diamino-4-nitro-	2.70	380		−3.30	−2.68			−1.95	−1.66

[a] From ref. 1. [b] Insufficient interaction with the most concentrated $RSnCl_3$ solution to measure the pK. [c] Adducts showed charge-transfer absorption, with maximum at ~405 mμ.

electron orbitals with an empty *d* orbital of tin. Among the studies to have shown such bonding are some dipole moment[13,14], spectral[15,16] and dissociation constant[17] studies. Huang and Hui[13] showed this bonding to be more important for a series of *para*-substituted phenyltrimethyltin compounds in the order, Me > H > Cl, which is also that of the increasing electron release by these substituents*. Thus both the $(p \rightarrow d)_\pi$ bonding and the inductive effects increase the electron density on tin in the tin trichlorides in the sequence:


(1)

The reverse order would be expected to be the acceptor strength order in the absence of other factors. Two other factors at least are present here. The first is the ether solvation and also possibly co-ordination to the acceptors. The acceptor–solvent interactions are considered to be much more important than the solvation of the adducts and further the solvation of the adducts of a given donor are assumed to be similar. As the solvation of the acceptor decreases with the increasing electron density on tin, the solvation energy losses on adduct formation should decrease in the reverse of sequence (1).

The second factor is the hybridisation changes and the internal bonding reorganisation, including some changes in the $(p \rightarrow d)_\pi$ character of the aryl–tin bond, which should occur on adduct formation. Energy will be required to bring about these changes.

To account for the sequence obtained with the monoamine donors, it must be assumed that the solvation energy losses are sufficiently large to overcome all other factors; while for the diamine donors, the observed orders could arise from the solvation energy loss not now being so dominant, due to either stronger acceptor–donor interactions or greater bonding reorganisations within the acceptors both relative to the monoamine study.

The 4-biphenylyl compound has not so far been considered. It appeared the weakest of the four aryl acceptors towards all donors. The 4-biphenylyl group can be more, or less, electron releasing than the phenyl group, depending on the electron demand. As some resonance occurs across the rings, $(p \rightarrow d)_\pi$ bonding should be at least as developed as in the phenyl compound. These factors should make the tin in 4-biphenylyltin trichloride more electron dense than that in $PhSnCl_3$. The compensation for the larger electron density on tin, by the reduced solvation loss on adduct formation, as occurs with the 4-tolyl and phenyl compounds and especially with the monoamine adducts, does not seem to be so important for the 4-biphenylyltin trichloride.

Although some interesting results have been obtained, the acceptor sequence of these aryltin trichloride acceptors has not been found. Either a non-co-ordinating solvent has to be used or a detailed analysis of the ether systems has to be performed, before this information is found.

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* No π bonding was actually detected for the (*p*-chlorophenyl)tin compound, but it has been shown to be present in the analogous silicon compound[18].

SUMMARY

Equilibrium constants for the interactions of (4-chlorophenyl)-, 4-tolyl- and 4-biphenylyltin trichlorides with some nitroanilines and nitrophenylenediamines in ether solution have been obtained at 25° in a spectroscopic study. 1:1 complexes were obtained in all cases. Comparison of the acidities of the three aryl acceptors with that of phenyltin trichloride (obtained in a previous study) have been made.

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