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THE BEHAVIOUR OF ORGANOTIN CHLORIDES AS CHLORIDE-ION ACCEPTORS IN NON-AQUEOUS SOLVENTS

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SUMMARY

The behaviour in solution of the adducts $[Ph_4As][R_{4-n}SnCl_{n+1}]$ ($R = Me$, Et, Pr, Bu, Ph; $n = 2$ and 3) has been studied by means of conductometric measurements in acetonitrile and molecular weight determinations in acetone.

It has been shown that the adducts are strong 1–1 electrolytes. The formation constants of the anionic species $R_{4-n}SnCl_{n+1}^-$ have been determined by spectrophotometric methods.

INTRODUCTION

Although much information is now available on the stability of individual organometallic complexes[1], very few systematic studies[2] have been carried out on homologous series of organometallic species whose complex-forming ability depends on the nature of both the metal and the organic groups bonded to the metal. Furthermore, most of the previous work has been done in aqueous solution and little attention has been paid to the behaviour of organometallic complexes in non-aqueous solvents.

Earlier articles from this laboratory[3,4] described the potentiometric titrations of organotin chlorides ($R_{4-n}SnCl_n$, $R = Me$, Et, Pr, Bu, Ph; $n = 2$ and 3) with halogen donors in acetonitrile, and it was shown that acid–base reactions of the type shown in eqn. (1) had to be taken into account:

$$R_{4-n}SnX_n + X^- \rightleftarrows R_{4-n}SnX_{n+1}^- \tag{1}$$

The adduct corresponding to the anionic species of the general character $R_{4-n}SnCl_{n+1}^-$ could be precipitated with tetraphenylarsonium chloride in aqueous concentrated HCl solution[5].

The present report describes the behaviour in acetone and in acetonitrile of the $[Ph_4As][R_{4-n}SnCl_{n+1}]$ adducts. Measurements of the formation constants of equilibrium (1) in acetonitrile are also reported. From these constants it is possible to estimate quantitatively the effects which determine the order of stability of this class of complexes as the number and the nature of the organic groups bonded to the tin atom are changed.

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EXPERIMENTAL

Materials and solutions

Phenyltin and butyltin trichlorides (Fluka AG) were distilled before use. All the other organotin compounds were prepared and purified by the methods reported in the literature[6].

Tetraphenylarsonium chloride and triphenylmethyl chloride (KK Labs. Inc., New York) were purified further. The former was precipitated from an ethanolic solution by the addition of absolute ether (m.p. 260°). The triphenylmethyl chloride was recrystallized from petroleum ether (b.p. 40–70°) and dried under vacuum at 60° (found m.p. 110–112°).

Commercial acetonitrile and acetone (C. Erba, Milan) were purified by methods previously described in the literature[7]. The specific conductance of the purified acetonitrile varied from 0.8 to 1.0×10^{-7} $ohm^{-1} \cdot cm^{-1}$.

The preparation of the $[Ph_4As][R_{4-n}SnCl_{n+1}]$ adducts has already been reported[5]. The adduct with R = Me and $n=2$ is new; its m.p. is 174–176°.

Solutions of organotin compounds, tetraphenylarsonium chloride and triphenylmethyl chloride were prepared by adding weighed quantities to a known volume of solvent. All operations were carried out in a dry-box under a nitrogen atmosphere.

Molecular weight

Molecular weights of some representative adducts were determined in acetone solution with a Mechrolab vapour phase osmometer model 301A. Table 1 lists the observed molecular weights at different adduct concentrations. Values of the ratio

TABLE 1

MOLECULAR WEIGHT OF SOME $[Ph_4As][R_{4-n}SnCl_{n+1}]$ ADDUCTS IN ACETONE AT 25°

Adduct	Concn. (g/l)	Mol. wt. exp.	Mol. wt. theor.	i^a
$[Ph_4As][Me_2SnCl_3]$	23.82	408	638.00	1.56
	11.91	384		1.66
	5.95	344		1.85
	2.98	334		1.91
$[Ph_4As][Et_2SnCl_3]$	24.95	425	666.50	1.56
	12.47	390		1.70
	6.23	380		1.75
	3.11	337		1.97
$[Ph_4As][EtSnCl_4]$	16.70	411	672.90	1.63
	8.35	377		1.78
	4.17	354		1.90
	2.09	341		1.97
$[Ph_4As][BuSnCl_4]$	22.62	431	700.95	1.62
	11.31	411		1.71
	5.65	383		1.83
	2.83	360		1.95

[a] i = Mol. wt. theor./Mol. wt. exp.

of the theoretical to the experimental molecular weight are also given; the symbol *i* is used.

Conductance measurements

Conductance measurements were carried out by means of a LKB 3216B Conductivity Bridge. The two conductivity cells used have cell constants 0.0104 cm^{-1} and 0.862 cm^{-1}. All measurements were made at $25 \pm 0.01°$ in an oil thermostat.

TABLE 2

LIMITING MOLAR CONDUCTANCES OF TETRAPHENYLARSONIUM CHLORIDE AND SOME $[Ph_4As][R_{4-n}SnCl_{n+1}]$ ADDUCTS IN ACETONITRILE AT 25°, AND THEORETICAL AND EXPERIMENTAL SLOPES OF THE $\Lambda-\sqrt{c}$ PLOTS

Compound	Λ_0	Onsager slope[b]	Experimental slope	Exp. slope/ theor. slope
Ph_4AsCl	147.0	334.2	348	1.040
	151.2[a]	338.0	252	0.745
$[Ph_4As][Me_2SnCl_3]$	137.5	327.5	338.7	1.035
$[Ph_4As][Et_2SnCl_3]$	131.2	323.0	316.0	0.977
$[Ph_4As][Ph_2SnCl_3]$	118.4	313.7	321.0	1.025
$[Ph_4As][EtSnCl_4]$	135.2	325.7	281.0	0.864
$[Ph_4As][BuSnCl_4]$	133.8	324.6	339.0	1.045
$[Ph_4As][PhSnCl_4]$	132.5	324.0	423.0	1.305

[a] See ref. 8. [b] Calculated on the basis of eqn. (2).

Table 2 shows the limiting equivalent conductances (Λ_0) of tetraphenylarsonium chloride and of several of the adducts in acetonitrile at 25°. The Onsager slope Δ_{th} comes from the relation

$$\Lambda = \Lambda_0 - \Delta_{th}\sqrt{c} \tag{2}$$

In acetonitrile Δ_{th} is equal to $229 + 0.716\ \Lambda_0$ (ref. 8). The Table also shows the experimental slopes Δ_{exp} (taken from Fig. 1) and the ratios Δ_{exp}/Δ_{th} for the various adducts.

Spectrophotometric measurements

The reactions between triphenylmethyl chloride and the $R_{4-n}SnCl_n$ compounds were studied in acetonitrile at 35° by means of spectrophotometric method. An UNICAM SP 800 Spectrophotometer (Cambridge, England) was used.

There are equilibria between triphenylmethyl ions and A^- anions and the ion pairs $Ph_3C^+A^-$ ($A^- = R_{4-n}SnCl_{n+1}^-$). The spectra in acetonitrile are very similar to those found for Ph_3COH in 98 % sulfuric acid and for the system $Ph_3CCl + HgCl_2$ in nitromethane, so that we have assumed, as did other workers[9,10], that the molar extinction coefficients of the Ph_3C^+ and the ion pair $Ph_3C^+A^-$ are the same in acetonitrile as well.

Triphenylmethyl chloride in acetonitrile solutions in the presence of a large excess of tin(IV) chloride gives a molar extinction coefficient for the ion of 4.0×10^4 at 402 mμ. This is in good agreement with the value obtained from triphenylmethanol in 98 % H_2SO_4 at the same wavelength[9].

Solutions containing various concentrations of reactants were prepared by mixing the acetonitrile solutions of $R_{4-n}SnCl_n$ compounds and triphenylmethyl

TABLE 3

EQUILIBRIUM CONCENTRATIONS OF REACTANTS IN ACETONITRILE AT 35°

Compound	$10^5([Ph_3C^+]+[Ph_3C^+R_{4-n}SnCl^-_{n+1}])$ (mole/l)	$10^4[Ph_3CCl]$ (mole/l)	$10^4[R_{4-n}SnCl_n]$ (mole/l)
$PhSnCl_3$	3.70	1.95	7.56
	3.00	1.71	5.89
	2.56	3.00	2.84
	2.08	1.14	5.11
	1.71	2.16	1.93
	1.23	0.88	2.70
	1.22	0.88	2.70
Ph_2SnCl_2	2.38	51.90	16.50
	1.72	38.90	12.30
	1.32	26.00	11.72
	1.15	25.90	8.24
	1.10	26.00	8.52
	1.00	26.00	6.40
	0.40	6.47	4.12
$EtSnCl_3$	3.96	8.44	39.30
	3.00	5.46	39.30
	2.85	1.45	144.00
	2.50	4.07	39.35
	2.02	5.56	22.00
	1.95	2.69	39.40
	1.42	2.26	28.20
	1.27	2.75	19.50
	1.05	1.62	23.90
$BuSnCl_3$	2.37	4.75	108.00
	1.66	2.30	108.00
	1.95	3.35	108.00
	1.62	4.45	53.80
	1.31	3.42	43.10
	0.57	2.83	10.55
	0.97	1.63	52.90
	0.67	1.70	25.00
	0.74	3.48	14.80
	0.70	2.78	17.10
Me_2SnCl_2	1.98	198.30	68.40
	1.33	132.20	45.60
	1.03	101.40	36.00
	0.89	99.00	27.30
	0.675	85.80	18.25
	0.550	66.10	16.00
	0.425	46.30	13.70
	0.238	25.30	9.00
Et_2SnCl_2	2.00	227.00	155.00
	1.42	165.20	128.60
	1.10	132.30	96.40

(*continued on next page*)

TABLE 3 (*continued*)

Compound	$10^5([Ph_3C^+] + [Ph_3C^+R_{4-n}SnCl_{n+1}^-])$ (mole/l)	$10^4[Ph_3CCl]$ (mole/l)	$10^4[R_{4-n}SnCl_n]$ (mole/l)
	1.02	101.40	95.60
	0.825	99.00	64.30
	0.725	64.30	76.10
	0.575	66.10	51.40
	0.475	64.80	35.40
	0.475	50.70	42.80
Pr_2SnCl_2	1.70	101.30	363.00
	1.32	76.10	242.00
	0.90	50.70	181.50
	0.625	40.60	121.00
	0.350	20.20	74.10
	0.325	20.20	60.50
	0.275	20.20	42.40

chloride in different ratios. Equilibrium concentrations of the reactants and products were evaluated from the measured absorbance at 402 mμ. These are given in Table 3.

RESULTS AND DISCUSSION

From the i values of Table 1, the following equilibrium can be written for the four adducts in the concentration range studied:

$$Ph_4As^+R_{4-n}SnCl_{n+1}^- \rightleftarrows Ph_4As^+ + R_{4-n}SnCl_{n+1}^-$$

It seems likely that in acetone the anionic species is very stable. This is in good

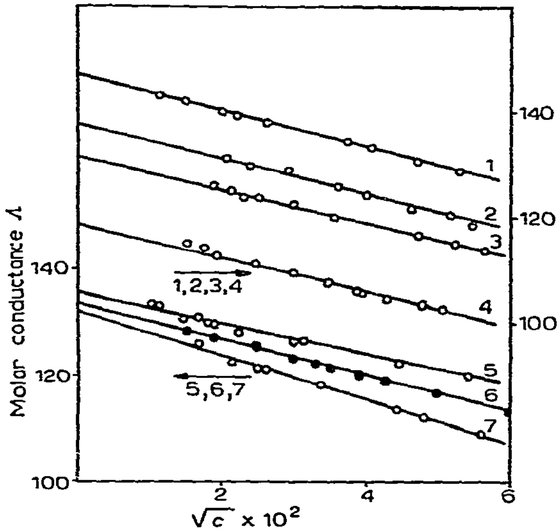

Fig. 1. Phoreograms of tetraphenylarsonium chloride and some adducts in acetonitrile at 25°. (1) Ph_4AsCl, (2) $[Ph_4As][Me_2SnCl_3]$, (3) $[Ph_4As][Et_2SnCl_3]$, (4) $[Ph_4As][Ph_2SnCl_3]$, (5) $[Ph_4As][EtSnCl_4]$, (6) $[Ph_4As][BuSnCl_4]$, (7) $[Ph_4As][PhSnCl_4]$.

agreement with earlier measurements[3] on the interaction of $R_{4-n}SnCl_n$ compounds ($R=Bu$ and Ph, $n=2$ and 3) with LiCl. Similar conclusions may be reached by considering the conductivity in acetonitrile for the same adducts as well as several others. Fig. 1 shows that the experimental equivalent conductances are a linear function of the square root of the adducts concentrations in the concentration range 4×10^{-4} to 4×10^{-3} M. At concentrations lower than 4×10^{-4} M there is a deviation from linearity. This is probably due to the dissociation of the anionic complex:

$$R_{4-n}SnCl_{n+1}^{-} \rightleftharpoons R_{4-n}SnCl_n + Cl^{-}$$

Furthermore, there is good agreement between the experimental slopes of Λ against $\sqrt{c}$ and the theoretical slopes calculated from the Onsager equation (eqn. 2) for 1–1 electrolytes in acetonitrile at 25°. The ratios $\Lambda_{exp}/\Lambda_{th}$ (*cf.* Table 2) show that the adducts are strong electrolytes except for $[Ph_4As][PhSnCl_4]$, whose ratio is 1.3.

Molecular weight determinations in acetone and conductivity measurements in acetonitrile of the examined adducts, show no evidence of dimerization for the species $R_{4-n}SnCl_{n+1}^{-}$ (presumably by the formation of hexacoordinated chloro-bridge species). The same conclusion had been reached earlier on the basis of potentiometric titrations[4].

Assuming a value of Λ of 58.6 for the Ph_4As^+ ion in acetonitrile[8], a scale of increasing conductivities for the anionic species is given below:

$Ph_2SnCl_3^-$ <	$Et_2SnCl_3^-$ <	$PhSnCl_4^-$ <	$BuSnCl_4^-$ <	$EtSnCl_4^-$ <	$Me_2SnCl_3^-$
59.8	72.6	73.9	75.2	76.6	78.9

It appears that the ionic conductances of these species are largely a function of the effective ionic hydrodynamic radius, and that the extent of solvation of the anions by ion-dipole interactions is substantially the same for all members of the series.

From the spectrophotometric measurements it is possible to calculate the formation constants of the anionic complexes. The following equilibria describe the interactions of organotin chlorides and triphenylmethyl chloride in acetonitrile:

$$R_{4-n}SnCl_n + Cl^{-} \rightleftharpoons R_{4-n}SnCl_{n+1}^{-}$$
$$R_{4-n}SnCl_n + Ph_3CCl \rightleftharpoons Ph_3C^{+}R_{4-n}SnCl_{n+1}^{-}$$
$$Ph_3C^{+}R_{4-n}SnCl_{n+1}^{-} \rightleftharpoons Ph_3C^{+} + R_{4-n}SnCl_{n+1}^{-}$$
$$Ph_3CCl \rightleftharpoons Ph_3C^{+}Cl^{-}$$
$$Ph_3C^{+}Cl^{-} \rightleftharpoons Ph_3C^{+} + Cl^{-}$$

the equilibrium constants of which are K_1, K_2, K_3, K_4 and K_5 respectively. It can be shown that the formation constant K_1 is related to the others in the following way:

$$K_1 = \frac{K_2 \cdot K_3}{K_4 \cdot K_5}$$

From the above relations the following final equation can be written:

$$\frac{[Ph_3C^{+}] + [Ph_3C^{+}R_{4-n}SnCl_{n+1}^{-}]}{[Ph_3CCl]\cdot[R_{4-n}SnCl_n]} = K_2 + \sqrt{\frac{K_2 \cdot K_3}{[Ph_3CCl]\cdot[R_{4-n}SnCl_n]}}$$

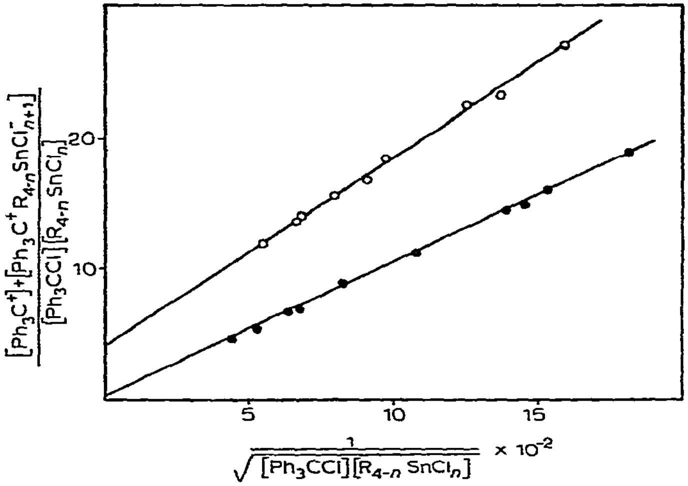

Fig. 2. Plots of $\frac{[Ph_3C^+]+[Ph_3C^+R_{4-n}SnCl_{n+1}^-]}{[Ph_3CCl]\cdot[R_{4-n}SnCl_n]}$ against $\frac{1}{\sqrt{[Ph_3CCl]\cdot[R_{4-n}SnCl_n]}}$.

○ $EtSnCl_3$, ● $BuSnCl_3$.

TABLE 4

STABILITY CONSTANTS OF THE HALO COMPLEXES $R_{4-n}SnCl_{n+1}^-$ IN ACETONITRILE AT 35°

Complex	10^4 $K_2 \cdot K_3$	10^{-6} K_1 (l/mole)	Relative stability
$PhSnCl_4^-$	46.3	6.6	5400
$EtSnCl_4^-$	2.11	0.30	246
$BuSnCl_4^-$	1.21	0.17	140
$Ph_2SnCl_3^-$	0.58	0.083	68
$Me_2SnCl_3^-$	0.028	0.004	3.3
$Et_2SnCl_3^-$	0.010	0.00143	1.2
$Pr_2SnCl_3^-$	0.0087	0.00124	1

Both K_2 and the product $K_2 \cdot K_3$ can be evaluated graphically. Examples of these plots are shown in Fig. 2.

Table 4 lists the values of K_1 which were calculated from the products $K_2 \cdot K_3$, assuming that $K_4 \cdot K_5 = 7 \times 10^{-10}$ ($mole \cdot l^{-1}$). The latter value is derived from our measurements in acetonitrile at 35°.

The relative stabilities of the anionic species are also given in Table 4. The following decreasing order of stability may be written:

$$PhSnCl_4^- > EtSnCl_4^- > BuSnCl_4^- > Ph_2SnCl_3^- > Me_2SnCl_3^- > Et_2SnCl_3^- > Pr_2SnCl_3^-$$

The anionic complex species become less stable as the number of R groups on the tin atom is increased. This is a reasonable result since a decrease in acceptor power must occur when chlorine atoms are replaced by the same number of less electronegative organic groups.

Our previous paper showed qualitatively that electronic effects of the R

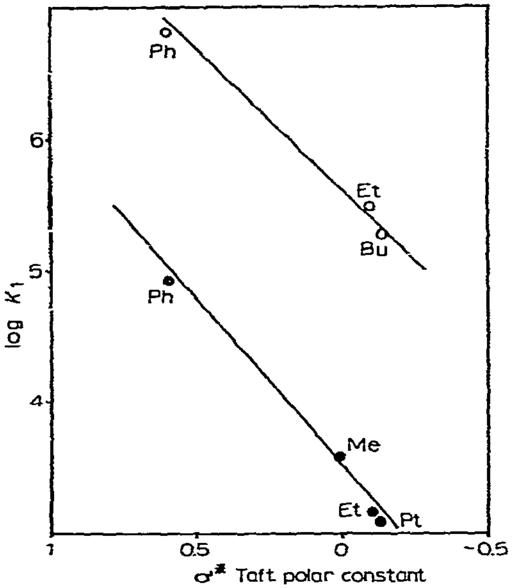

Fig. 3. Correlation of log K_1 against the σ^* Taft polar constant of the R group. ○ $RSnCl_3$, ● R_2SnCl_2 compounds.

groups rather the steric ones play an important role in determining the order of stability of these complexes[4]. Quantitative evidence can now be presented: Fig. 3 shows that there is a linear relationship between the logarithms of the formation constants of the various complexes and the σ^* Taft polar constants[11].

We conclude that the decrease in the stability order Ph > Me > Et > Pr is associated with the decreasing electronegativity of these groups.

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