772. *Reactions of Triethyltin Chloride with Amines.*

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Vapour-pressure and freezing-point measurements have been made on the binary systems formed by triethyltin chloride, Et_3SnCl, with dimethylamine, diethylamine, and trimethylamine. In all cases a 2 : 1 ($2Et_3SnCl$: 1 amine) compound is formed as a solid (m. p. 14·8°, 0·9°, and 8·3° respectively); this is accompanied, for dimethylamine, by the appearance in the liquid of an absorption band at 300 mμ, whilst the electrical conductance shows that some ionic species must be present. A 1 : 1 compound also exists for Me_2NH (m. p. 14·7°), and is detectable for Et_2NH (m. p. −4·0°) but undetectable for Me_3N. No 1 : 2 compounds are formed. Pyridine probably forms only the 1 : 1 compound.

Amongst the addition compounds formed from tin(IV) halides and donor compounds, those containing one molecule of tin(IV) halide to two molecules of donor are perhaps the most important and were regarded by Werner and Pfeiffer [1] as indicating a co-ordination number of six for tin. (For recent views see Bannister and Fowles.[2]) Some compounds containing a greater proportion of the donor have been described,[3] and some containing less, principally the 1 : 1 compounds formed by trialkyltinhalides.[4] However, only one case appears to have been recorded of a 2 : 1 compound in these systems, that formed by stannic chloride and anisole, as indicated by the solid–liquid equilibrium studies by Sisler and his co-workers.[5] This compound was highly dissociated in the liquid phase and could be explained by crystal packing. Our present work shows that this 2 : 1 type of compound occurs in triethyltin chloride systems, where it has some significance in the liquid phase.

Compounds of triethyltin chloride and some common amines could not at first be prepared by precipitation from solution, but a freezing-point investigation showed that 2 : 1 and 1 : 1 compounds do exist, melting just below room temperature. In view of the characteristic absorption spectra and conductances observed in the dimethylamine system, it seems that fuller investigations of this kind may prove worthwhile in other tin(IV) systems.

Freezing-point and vapour-pressure measurements are here recorded for the binary systems formed by triethyltin chloride with dimethylamine, diethylamine, trimethylamine, and pyridine. The dimethylamine system has been investigated more fully, as an example, by spectrophotometric and conductance measurements. Supplementary cryoscopic results are also quoted where relevant.

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[1] Werner and Pfeiffer, *Z. anorg. Chem.*, 1898, **17**, 82.
[2] Bannister and Fowles, *J.*, 1958, 751.
[3] Trost, *Canad. J. Chem.*, 1952, **30**, 834, 842; Ephraim and Schmidt, *Ber.*, 1909, **42**, 3856.
[4] Kraus and Greer, *J. Amer. Chem. Soc.*, 1923, **45**, 2946, 3078.
[5] Sisler, Wilson, Gibbins, Batey, Pfahler, and Mattair, *J. Amer. Chem. Soc.*, 1948, **70**, 3818.

EXPERIMENTAL

Since it was necessary to protect the tin compounds from hydrolysis, all cells for physical measurements were modified for attachment to a vacuum line. This was of standard design,[6] built in this laboratory under the direction of Dr. R. C. Cass, whom we thank. Freezing-point and vapour-pressure measurements were carried out in a small cryoscope of 5 ml. capacity, similar to that used for sulphuric acid.[7] The contents were stirred with a single-armed magnetic stirrer and temperatures were measured with a calibrated single-junction copper–constantan thermocouple. The cryoscope was surrounded by a glass jacket immersed in a bath at 1·2° below the freezing-point and solidification was induced usually by touching the supercooled cell with solid carbon dioxide. Since great accuracy was not sought, the temperature was only recorded to ±0·1° and no supercooling corrections were made. This cryoscope could also be connected through a tap to a mercury manometer for the vapour-pressure measurements. (These are recorded for 20°, but vapour pressures were also determined at the freezing-points of the mixtures, since the quantity of amine in the vapour phase often necessitated a significant correction to the liquid composition, which was different for the freezing-point and 20°.) In carrying out a series of measurements, successive quantities of amine were condensed on a weighed quantity of the tin compound in the evacuated cryoscope, either from a calibrated gas reservoir or, for liquids, from a graduated glass tube of narrow bore sealed to the vacuum line. With pyridine a slight modification was made so that all parts of the cryoscope could be submerged in the bath, since there was a tendency for condensation on the cooler parts during measurements above room temperature. In this case also, our freezing-point technique proved unsuitable, but a rough indication was obtained by cooling and observing the temperature at which a cloudiness first appeared.

When freezing-points of greater accuracy were required, as in the determination of the molecular weight of triethyltin chloride in benzene, a large cryoscope was used, together with a 10-junction thermocouple, Cambridge Vernier potentiometer, and photoelectric amplifier.[8]

The conductance cell (of cell constant $0{\cdot}28_3$ cm.$^{-1}$) had dip-type electrodes and was immersed in water at 25°. Readings were made on a Mullard conductance bridge.

Attempts to use spectrophotometric cells with optically flat silica faces were unsuccessful, owing to cracking on immersion in liquid nitrogen during the preparation of the mixtures. Finally a simple (cylindrical) silica tube of external diameter 12 mm. (i.d. 10 mm.) was used, and to its upper end were attached, through a graded seal, a glass 4 mm. vacuum tap and a B14 cone. Stirring was accomplished magnetically (iron-in-glass stirrer). The comparison cell contained water and was made from similar silica tubing. These cells were always placed in the spectrophotometer (Unicam SP.500) with the same orientation to minimize the errors inherent in their design. Colours appeared in many of the mixtures investigated, and our results, though limited to the dimethylamine system and not of great precision, suggest that a more extensive spectrophotometric investigation of these systems would be fruitful.

Materials.—Triethyltin chloride, prepared from tetraethyltin and a slight excess of stannic chloride,[9] followed by fractionation twice *in vacuo*, was collected at 68—72°/0·9—1·2 mm. (Found: C, 30·3; H, 6·4; Cl, 15·0. Calc. for $C_6H_{15}ClSn$: C, 29·9; H, 6·3; Cl, 14·7%), m. p. 15·3° (lit.,[10] 15·5°).

The gaseous amines were obtained from commercial cylinders or ampoules and purified by passage through a potassium hydroxide column and fractionation in the vacuum system. Diethylamine and pyridine were fractionated in the vacuum system and stored in ampoules over mercury-shielded stop-cocks. "AnalaR" benzene was twice recrystallized and then distilled over sodium wire.

RESULTS AND DISCUSSION

The results are in the Tables and the Figure, which summarizes all the data for the dimethylamine system. (Preliminary, more approximate, freezing-point determinations extending beyond $r = 2$ gave no indication of further solid phases.) Compositions are expressed

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[6] Sanderson, "Vacuum Manipulation of Volatile Compounds," Wiley, New York, 1949.

[7] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900; Gillespie, Hughes, and Ingold, *J.*, 1950, 2473.

[8] Kirkbride and Wyatt, *Trans. Faraday Soc.*, 1958, **54**, 483.

[9] Kozeschkow, *Ber.*, 1933, **66**, 1661.

[10] Grüttner and Krause, *Ber.*, 1917, **50**, 1803.

in terms of *r*, the ratio of moles of amine to moles of triethyltin chloride. There is clear evidence for the existence of solid compounds containing two triethyltin chloride molecules to one of amine for all the bases studied except pyridine, which seems to form only the 1 : 1 compound as in the Me_3SnCl system.[4] Favourable crystal-packing arrangements are not sufficient to explain these observations, for the spectrophotometric results show that the composition $r = 0{\cdot}5$ corresponds to the maximum absorption by the liquid at the new peak near 300 mμ. (A further, very weak, absorption at 400 mμ became detectable at $r = 1$.) The low vapour pressures of amine at small values of *r* also strongly indicate chemical reactions, a conclusion which may be strengthened by the observation that in the methylamine–tetraethyltin system, where no compound occurs, there are marked *positive* deviations from Raoult's law[11] (cf. also Greenwood and Wade[12]). Amongst the aliphatic amines, the 2 : 1 and 1 : 1 compounds are more stable for dimethylamine than for diethylamine and trimethylamine, and with the last there is no indication of a 1 : 1 compound in the freezing-point diagram. The extents of the reactions in the liquid cannot be very different for Et_2NH and Me_3N, however, since the vapour pressures of the amine in the two systems at given *r* values are almost in the same ratio as the vapour pressures of the pure bases at 20°, which are 19·2 (Et_2NH)[13] and 141·5 cm. (Me_3N).[14]

TABLE 1. *Vapour pressures* (*cm.* Hg *at* 20°) *and freezing-points in the triethyltin chloride–amine systems.*

(*a*) Dimethylamine			(*b*) Trimethylamine			(*c*) Diethylamine			(*c*) *contd.*		
r	p	F. p.	r	p	F. p.	r	p	F. p.	r	p	F. p.
0·000	0·06	15·3°	0·049	0·90	14·5°	0·062	0·20	13·0°	0·969	9·29	—
0·034	0·03	14·5	0·112	3·27	8·4	0·129	0·57	8·8	1·042	—	−4·4°
0·094	0·06	12·3	0·189	5·31	5·3	0·200	1·03	3·8	1·020	9·88	—
0·180	0·09	7·6	0·258	9·45	−0·4	0·298	1·81	−3·0	1·196	—	−5·4
0·238	0·25	6·4	0·312	10·30	+1·7	0·356	2·49	−1·7	1·164	10·75	—
0·352	0·42	10·1	0·368	16·94	—	0·418	3·10	−0·4	1·307	—	−6·9
0·431	0·61	13·7	0·409	20·05	7·3	0·453	3·44	+0·5	1·273	11·52	—
0·461	0·69	13·9	0·435	22·29	7·9	0·484	3·78	+0·9	1·378	—	−8·5
0·500	0·89	14·8	0·474	25·48	8·2	9·511	4·11	+0·7	1·342	12·12	—
0·534	1·14	14·3	0·500	27·94	8·3	0·533	4·43	−0·2	1·473	12·82	
0·593	1·37	12·8	0·534	30·46	7·8	0·564	4·71	—	1·595	13·32	
0·665	1·94	11·1	0·566	33·56	7·0	0·662	—	−4·6	1·778	—	−11·5
0·801	3·78	8·9	0·611	37·48	—	0·645	5·84	—	1·737	13·83	—
0·869	5·25	13·3	0·662	—	5·6	0·764	—	−4·8	1·920	—	−12·3
0·929	7·18	14·6	0·685	41·78	—	0·744	7·10	—	1·878	14·16	—
0·977	8·24	14·6	0·747	—	4·6	0·840	—	−4·5	1·956	—	−12·7
1·021	9·67	14·7	0·741	47·48	—	0·814	7·91	—	1·913	14·23	—
1·052	11·12	14·3	0·811	—	2·0	0·907	—	−4·5	1·996	—	−12·9
1·083	12·61	13·8	0·815	54·31	—	0·882	8·54	—	1·953	14·28	—
1·178	18·18	11·3	0·922	—	−1·5	0·933	—	−4·0			
1·280	24·38	9·6	0·903	60·82	—	0·907	8·74	—			
1·384	29·84	6·0	1·043	—	−4·9	0·969	—	−4·1			
1·461	34·65	3·8				0·943	8·88	—			
1·498	36·64					0·996	—	−4·1			

A doubled formula for certain tin(IV) halide compounds (Laubengayer and Smith[15]) might simply explain our 2 : 1 compounds, but since it is difficult to see how the addition of a donor molecule could stabilize a dimer of Et_3SnCl considerably, we regard the following proof of the absence of dimerization of triethyltin chloride in benzene as evidence against such a formulation in this case (see Table 3).

In view of the partially ionic character[16] of triethyltin chloride, we may suppose that it is slightly self-dissociated in the liquid state, yielding the Et_3Sn^+ ion. If the anion can

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[11] Joshi, unpublished work.
[12] Greenwood and Wade, *J.*, 1956, 1527; 1957, 1516.
[13] Pohland and Mehl, *Z. phys. Chem.*, 1933, *A*, **164**, 48.
[14] Swift and Hochanadel, *J. Amer. Chem. Soc.*, 1945, **67**, 880.
[15] Laubengayer and Smith, *J. Amer. Chem. Soc.*, 1954, **76**, 5985.
[16] Anderson, *J. Amer. Chem. Soc.*, 1957, **79**, 4913.

be solvated, as $\mathrm{Et_3SnCl_2^-}$, the existence of 2 : 1 compounds can be explained by attachment of the amine base (B) to the acceptor $\mathrm{Et_3Sn^+}$:

$$\mathrm{2Et_3SnCl + B \rightleftharpoons Et_3SnB^+ + Et_3SnCl_2^-} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

Comparison of the conductance with that of other systems ($\mathrm{H_2SO_4}$,[17] $\mathrm{GaCl_3}$–$\mathrm{POCl_3}$ [12]) indicates that the concentration of free ions may not exceed a few units per cent., so that extensive ion-pairing would also have to be supposed and would indeed be expected. It may therefore be significant that at higher *r* values ($r > 0{\cdot}8$) the partial pressures of diethylamine and trimethylamine approximate to the fraction $(2r - 1)/2r$ of the pure amine vapour pressure, which is what would be expected for an ideal solution of ion-pairs of the type, $\mathrm{Et_3SnB^+,Et_3SnCl_2^-}$.

TABLE 2. *Freezing-points in the triethyltin chloride–pyridine system.*

r	0·029	0·058	0·101	0·116	0·159	0·25
F. p.	14·8°	12·9°	11·1°	9·6°	21·7°	36°
r	0·37	0·53	0·73	1·00	1·37	1·78
F. p.	49° *	56°	59°	61°	59°	53°

* Results above 50° were not reproducible to better than 1°.

TABLE 3. *Molecular weight of triethyltin chloride in benzene.*

Weight of benzene in cryoscope 54·60 g. (f. p. 5·445°).

Weight of $\mathrm{Et_3SnCl}$ added (g.)	0·9673	2·0750	
Depression of f. p. of benzene	0·377°	0·784°	
Molecular wt. of $\mathrm{Et_3SnCl}$	241	249	(Calc. for monomer, 241·3)

At the end of this experiment additions of diethylamine were made and the further depressions of freezing-point showed clearly that the $\mathrm{Et_2NH}$ and $\mathrm{Et_3SnCl}$ molecules were combining to give fewer particles than would be expected in the absence of any reaction, again confirming that some form of reaction occurs in the liquid.

Several different explanations, all consistent with eqn. (1), are now possible for the 1 : 1 compounds. Kraus and Greer[4] formulated their $\mathrm{Me_3SnCl,C_5H_5N}$ compound as a substituted ammonium halide, which is consistent with (1) if it is supposed that the $\mathrm{Et_3SnCl_2^-}$ ion dissociates to give $\mathrm{Cl^-}$ as the concentration of triethyltin chloride decreases. Such an explanation throws the responsibility for the change from the 2 : 1 to the 1 : 1 ratio on the anion, however, and does not therefore explain the different behaviour of the bases. A more attractive hypothesis is that the relative acid strengths of $\mathrm{Et_3SnB^+}$ and $\mathrm{BH^+}$ are such that reaction (1) is followed by a proton transfer which gives the 1 : 1 ratio at higher *r* value, *e.g.*,

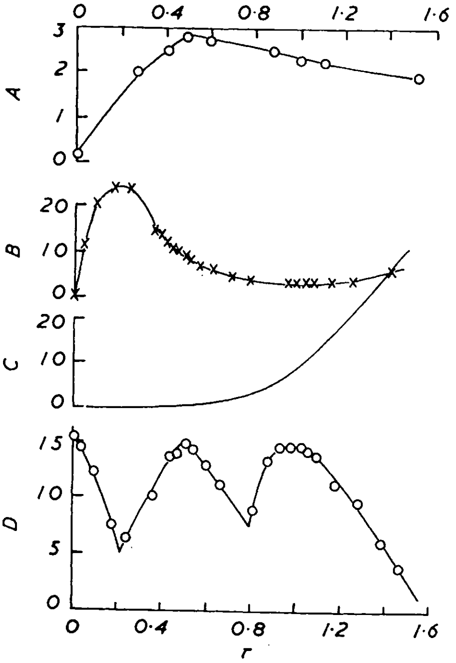
$$\mathrm{2Et_3SnCl + 2Me_2NH \rightleftharpoons Et_3SnNMe_2 + Me_2NH_2^+ + Et_3SnCl_2^-} \quad . \; . \; . \; . \quad (2)$$

Such a reaction would be more important at low *r* values for stannic chloride systems (since $\mathrm{Cl_3SnNMe_2H^+}$ would be expected to be a stronger acid than $\mathrm{Et_3SnNMe_2H^+}$) and could therefore explain the absence of 2 : 1 compounds in those systems. A further advantage of reaction (2) is that $\mathrm{Me_3N}$, which does not form the 1 : 1 " compound," cannot undergo this reaction. But there is then the disadvantage that the same should apply to pyridine.

A simpler explanation of the 1 : 1 compounds is that they are not entirely ionic. Kraus and Greer[4] regarded the undissociated form of their pyridine compound as containing quinquevalent nitrogen. Although such a structure could be reformulated in modern terms as an ion-pair, there is still the possibility that truly non-ionic forms may be present, but with five groups round the tin atom. Bases might then be expected to fall into two

[17] Gillespie and Wasif, *J.*, 1953, 204.

classes in their behaviour towards triethyltin chloride, roughly according to their sizes. Those which are small enough (NH_3,$MeNH_2$) may form 1 : 1 and 1 : 2 co-ordination compounds (with perhaps subsequent reactions [2]) so strongly that any tendency to react according to eqn. (1) is completely masked, whilst larger bases (Et_2NH,Me_3N) react as in (1) because they cannot easily form a fifth group around the tin atom. Pyridine behaves as a relatively small amine [18] and a 1 : 1 compound may also be stabilized in this case by $d\pi$–$p\pi$ bonding (cf. Chatt and Williams [19]).



Properties of the triethyltin chloride–dimethylamine system.

A, Optical density at 300 mμ.
B, Specific conductivity, κ (mmho $cm.^{-1}$).
C, Vapour pressure (cm. Hg.).
D, Freezing point (° c).

Much of the above tentative explanation requires the existence of $Et_3SnCl_2^-$ ions, for which we have no evidence other than the fact that they satisfy the 2 : 1 stoicheiometry [eqn. (1)] and relieve us of the necessity for assuming the presence of $(Et_3SnCl)_2B$ molecules in the solution.

The University, Sheffield, 10.

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[18] Bjerrum, *Chem. Rev.*, 1950, **46**, 381 (see p. 389).
[19] Chatt and Williams, *J.*, 1954, 4403.