Solvolysis of Methyltin Chlorides by Strong-acid Solvents †

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The solvolysis of methyltin chlorides $Me_{4-x}SnCl_x$ in highly acidic media has been followed by means of n.m.r. and Mössbauer spectroscopy. Spectral data for the solvated $[Me_3Sn]^+$, $[Me_2Sn]^{2+}$, $[MeSnCl_2]^+$, and $[MeSnCl]^{2+}$ cations in solution are reported and discussed.

ALKYLTIN SULPHONATES have been prepared by solvolysis of the parent chloride.[1-4] Ligand-exchange reactions involving alkyltin sulphonates have been used to obtain compounds such as $MeSnCl_2(SO_3F)$ and these reactions are dependent on acid strength.[3] These compounds have been well characterised by i.r., Raman, and Mössbauer spectroscopy, and in one case by *X*-ray crystallography.[5] While much is known about the compounds isolated from these solvolysis reactions, relatively little is known about the mechanism, or about the nature of the species in solution prior to crystallisation. Cryoscopic and conductimetric evidence have suggested that $H_2Sn(HSO_4)_6$ and $Me_3Sn(HSO_4)$ are the species present in solution when Ph_4Sn and Me_4Sn, respectively, are dissolved in 100% sulphuric acid.[6] However, no other spectroscopic evidence for the species present was given and no compounds were isolated from the solutions.

Since the species present in these solutions may be different from those isolated, it was of interest to investigate the nature of the solutions further. We here present the results of n.m.r. and Mössbauer studies on the $Me_{4-x}SnCl_x$–H_2SO_4 and –HSO_3F systems.

EXPERIMENTAL

All the organotin compounds were obtained from Alfa Inorganics. Sulphuric and fluorosulphuric acids were obtained from Allied Chemicals. 100% Sulphuric acid was prepared as previously described [7] and fluorosulphuric acid was purified by distillation.[8]

Solutions were prepared by rapid addition of the organotin compounds to the appropriate acid, which had been degassed on a vacuum line. The acid temperature was not allowed to rise above 10 °C and stirring continued until all of the solutes had dissolved. When dissolution was complete, samples were transferred to n.m.r. tubes and Mössbauer cells. N.m.r. spectra were recorded on a Varian A-60 instrument at 37 °C within *ca.* 15 min, while Mössbauer samples were

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[1] P. A. Yeats, B. F. E. Ford, J. R. Sams, and F. Aubke, *Chem. Comm.*, 1969, 791.

[2] P. A. Yeats, J. R. Sams, and F. Aubke, *Inorg. Chem.*, 1971, **10**, 1877.

[3] L. E. Levchuk, J. R. Sams, and F. Aubke, *Inorg. Chem.*, 1972, **11**, 2634.

[4] P. A. Yeats, P. L. Pok, B. F. E. Ford, J. R. Sams, and F. Aubke, *J. Chem. Soc.* (*A*), 1970, 2188.

[5] F. H. Allen, J. A. Lerbscher, and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 2507.

[6] R. J. Gillespie, R. Kapoor, and E. A. Robinson, *Canad. J. Chem.*, 1966, **44**, 1197.

[7] R. J. Gillespie, J. V. Oubridge, and C. Solomons, *J. Chem. Soc.*, 1957, 1804.

[8] J. Barr, R. J. Gillespie, and R. C. Tompson, *Inorg. Chem.*, 1964, **3**, 1149.

quick frozen to a glass and spectra recorded at 80 K as previously described.[9] Solute concentrations were the same as in the more concentrated solutions used to carry out cryoscopic measurements,[6] *i.e.* 0·15 mol kg^{-1}. For Mössbauer measurements, the cell thickness was adjusted to give 15 mg Sn cm^{-2}. Spectra were computer fitted to Lorentzian line shapes [10] and all Mössbauer isomer shifts are reported relative to SnO_2 at room temperature.

RESULTS AND DISCUSSION

Sulphuric and fluorosulphuric acids lend themselves very well to the rapid-freeze technique. Both become very viscous on cooling and tend to form a glass rather than crystallise at their freezing points and solutes dissolved in these acids are trapped in the glasses formed. Mössbauer spectra obtained from tin compounds dissolved in these glasses are characteristic of the species in solution and analysis of such spectra yields useful information about the tin environment.

TABLE 1

N.m.r. and Mössbauer data for solutions of $Me_{4-x}SnCl_x$ in strong acids

	δ * p.p.m.		J(^{117,119}Sn–C–H) Hz		δ p.p.m.	J(^{117,119}Sn–C–H) Hz		δ p.p.m.	Isomer shift † mm s^{-1}	Quadrupole splitting mm s^{-1}
95% H_2SO_4										
Me_3SnCl		1·78	87·6	92·1	1·02	61·1	63·6	0·33		
Me_2SnCl_2		1·67	85·7	88·9						
100% H_2SO_4										
Me_4Sn	3·43	1·80	87·6	90·2	1·00	61·0	63·4	0·28		
Me_3SnCl	3·43	1·81	88·7	90·6				0·28	1·54	4·57
Me_2SnCl_2		1·79	86·4	89·8					1·73	5·12
$MeSnCl_3$		1·96	112·6	117·7					1·00	2·62
									1·32	2·00
5% Oleum										
Me_3SnCl	3·45	1·88	87·6	90·2				0·25		
30% Oleum										
Me_3SnCl	3·46	1·97	84·6	87·2						
HSO_3F										
Me_3SnCl		1·68	85·6	88·9					1·61	4·95
Me_2SnCl_2		1·70	84·6	88·0					1·89	5·41
$MeSnCl_3$		1·92	122·1	127·7					1·17	3·10

* N.m.r. chemical shifts are to low field of external Me_4Si at 37 °C. † Mössbauer chemical isomer shifts are relative to SnO_2 at room temperature.

N.m.r. and Mössbauer data obtained from solutions of the methyltin compounds in sulphuric and fluorosulphuric acids are summarised in Table 1. Solutions of Me_4Sn in 100% H_2SO_4 clearly contained four methyl species. Two of these are Me–Sn compounds since ^{117,119}Sn–C–^{1}H coupling was visible in the n.m.r. spectrum. One peak arises from dissolved CH_4 produced in the solvolysis and the fourth is due to $MeSO_3H$. The latter was identified by addition of $MeSO_3H$ to the solutions when the peak at $-3·43$ p.p.m. increased in intensity. Gillespie *et al.*[6] followed this solvolysis and reaction (1) fitted their cryoscopic and conductimetric

$$Me_4Sn + H_2SO_4 \longrightarrow [Me_3Sn]^+ + HSO_4^- + CH_4 \quad (1)$$

data reasonably well. Deviations of their results from ideality were attributed to the presence of small amounts of $MeSO_3H$, but they made no allowance for the possible presence of dissolved CH_4. In our solutions, one of the methyltin species must be the $[Me_3Sn]^+$ cation. (Throughout the following discussion the methyltin species present in solution are, for convenience, referred to as cations. However we recognise, and subsequently show, that these are solvated tin species with co-ordination numbers of five and six.) The other Me–Sn species cannot be unreacted Me_4Sn because (*a*) the n.m.r. parameters did not correspond to those for tetramethyltin, (*b*) solvolysis was rapid and went to completion,[6] and (*c*) the same tin species were observed in solutions of Me_3SnCl in 95% H_2SO_4 (Table 1). Aubke and his co-workers [1-4] showed that dimethyltin sulphonates can be isolated from solvolysis of tetramethyltin, or tri- or di-methyltin chlorides in sulphonic acids. Only in cases where an excess of Me_4Sn or Me_3SnCl over acid was used could the appropriate $Me_3Sn(SO_3X)$ compound be isolated.[2] These workers found that the conductivity of $Me_3Sn(SO_3F)$ in HSO_3F drifted with time, suggesting that the $[Me_3Sn]^+$ cation is not very stable in these solutions. This was confirmed by our n.m.r. data where an increase in intensity of the peak at $-1·80$ p.p.m. occurred at the expense of that at $-1·00$ p.p.m. This suggests that the absorption at $-1·00$ p.p.m. is due to the trimethyltin cation.

Solvolysis of Me_3SnCl occurred in 95% H_2SO_4, again giving n.m.r. peaks at $-1·8$ and $-1·0$ p.p.m. and a resonance due to CH_4 (Figure 1). Equation (2) satisfies the data. In more acidic solvents, the rate of the above

$$Me_3SnCl + 2H_2SO_4 \longrightarrow [Me_2Sn]^{2+} + 2HSO_4^- + CH_4 + HCl \quad (2)$$

reaction was faster, so that by the time the n.m.r. spectrum had been recorded the concentration of the

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[9] T. Birchall and B. Della Valle, *Canad. J. Chem.*, 1971, **49**, 2908.

[10] G. M. Bancroft, W. K. Ong, A. F. Maddock, R. K. Prince, and A. J. Stone, *J. Chem. Soc.* (*A*), 1967, 1966.

$[Me_3Sn]^+$ cation was too low to be observed. No methanesulphonic acid was produced in aqueous sulphuric acid, but was formed in larger amounts as the SO_3 concentration increased. In 30% oleum, the production of $MeSO_3H$ over CH_4 was favoured since no methane was observed in this solution. Dimethyltin dichloride was solvolysed to give only the $[Me_2Sn]^{2+}$ cation; no CH_4 or $MeSO_3H$ were observed in any of these solutions and Me_2SnSO_4 can be isolated in a pure form as Aubke and his co-workers [1] have shown. This compound was also obtained from the Me_4Sn– and Me_3SnCl–H_2SO_4 systems on prolonged standing, which further points out the instability of $[Me_3Sn]^+$ in these highly acidic media. In view of this, it seems surprising that Gillespie's cryoscopic data for Me_4Sn [6] should fit equation (1) so closely.

In fluorosulphuric acid, solvolysis was even more rapid and $[Me_2Sn]^{2+}$ was the only species detectable by n.m.r. spectroscopy when Me_4Sn, Me_3SnCl, or Me_2SnCl_2 were added to this acid. Again $Me_2Sn(SO_3F)_2$ was the sole product isolated from this system. No methane was detected by n.m.r. spectroscopy in the first two cases, but was confirmed by i.r. examination of the gaseous products.

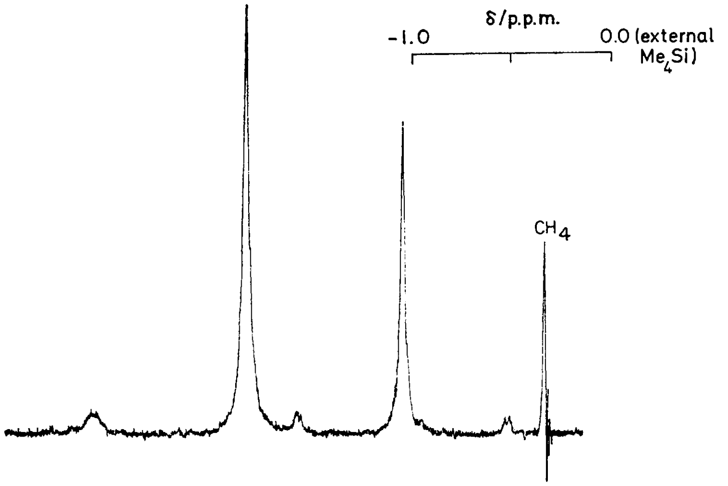

FIGURE 1 N.m.r. spectrum resulting from dissolution of Me_3SnCl in 100% H_2SO_4 at 37 °C

Solutions of $MeSnCl_3$ in either H_2SO_4 or HSO_3F showed only one methyl resonance, with accompanying $^{117,119}Sn$ satellites. This n.m.r. spectrum could arise from either the $[MeSnCl_2]^+$ or the $[MeSnCl]^{2+}$ cations producted in reactions (3) and (4), but it is not possible to

$$MeSnCl_3 + HSO_3F \longrightarrow [MeSnCl_2]^+ + SO_3F^- + HCl \quad (3)$$

$$MeSnCl_3 + 2HSO_3F \longrightarrow [MeSnCl]^{2+} + 2SO_3F^- + 2HCl \quad (4)$$

decide which is present from the n.m.r. spectrum alone. Because the CH_3 resonance was sharp and the $^{117,119}Sn$ satellites clearly resolved, it is unlikely that two species having similar n.m.r. parameters are present together.

Unlike the n.m.r. experiments, the Mössbauer results showed that only one tin species was detectable for either Me_4Sn or Me_3SnCl in these solvents. Because Mössbauer samples were prepared immediately after the solute had dissolved, the quadrupole doublet observed [Figure 2 (*a*)] must arise from the $[Me_3Sn]^+$ cation. The n.m.r. data showed that this cation is further solvolysed to $[Me_2Sn]^{2+}$, but the symmetric nature of the Mössbauer spectrum and the narrow linewidth (0·91 mm s^{-1}) indicate that the concentration of this latter species must be quite low under these conditions. This is reasonable since these frozen samples were prepared immediately dissolution had occurred, at temperatures which did not exceed 10 °C, and preliminary rate data showed that $t_{\frac{1}{2}}$ for this reaction is *ca.* 10 min at 37 °C. Spectra of the Me_2SnCl_2 solutions were clearly different from the above, having both a higher isomer shift and quadrupole splitting, and can only arise from the $[Me_2Sn]^{2+}$ cation. Figure 2 (*b*) shows the spectrum of a solution of $MeSnCl_3$ in sulphuric acid. This can only be reasonably analysed in terms of two overlapping quadrupole doublets indicating the presence of two tin species. However, in fluorosulphuric acid, only one tin species was detectable. These facts are in agreement with solvolysis according to equations (3) and (4) and although the sulphates are not known, $MeSnCl_2(SO_3F)$ and $MeSnCl(SO_3F)_2$ have been prepared.[3] Since these reactions occurred faster at higher temperatures and in a more acidic solvent, it is reasonable to suppose that the cations detected in sulphuric acid are $[MeSnCl_2]^+$ and $[MeSnCl]^{2+}$, while in fluorosulphuric acid only the latter was detectable. The n.m.r. spectrum arising from solutions of $MeSnCl_3$ in both H_2SO_4 and HSO_3F must then correspond to that of the $[MeSnCl]^{2+}$ cation.

Both Me_4Sn and Me_3SnCl were immediately solvolysed in acid solution to give $[Me_3Sn]^+$ which reacted further to $[Me_2Sn]^{2+}$ and CH_4. The rate of this second solvolysis depended on the temperature and acid used. One can see that both n.m.r. and Mössbauer parameters for a particular cation vary depending on the preparative conditions. Variations in *J*(Sn–C–H) for Me_2SnX_2 in aqueous HX solutions have already been observed.[11] The solvolysis of $MeSnCl_3$ also proceeded in a stepwise manner, but did not go to completion and there was no evidence for a $[MeSn]^{3+}$ cation. This may be because the attacking species is the proton and the rate of solvolysis will slow down as the positive charge builds up on the tin atom. Table 2 summarises n.m.r. and Mössbauer data for the various cations produced in these solutions. These data must be regarded as approximate since they were not recorded under identical conditions: concentration studies and extrapolation to infinite dilution would be necessary before precise values could be assigned.

The increase in $J(^{117,119}Sn\text{-}C\text{-}^1H)$ from the parent halide to the cations indicates increasing *s* character in the $Sn\text{-}CH_3$ bond. This could be due to changes in the relative electronegativity of X in $Me_{4-x}SnX_x$, as Cl^- is replaced by HSO_4^- or SO_3F^-, causing a redistribution of the *s* character in the sp^3 hybrids. While this might satisfactorily explain the increase for $[Me_3Sn]^+$, changes

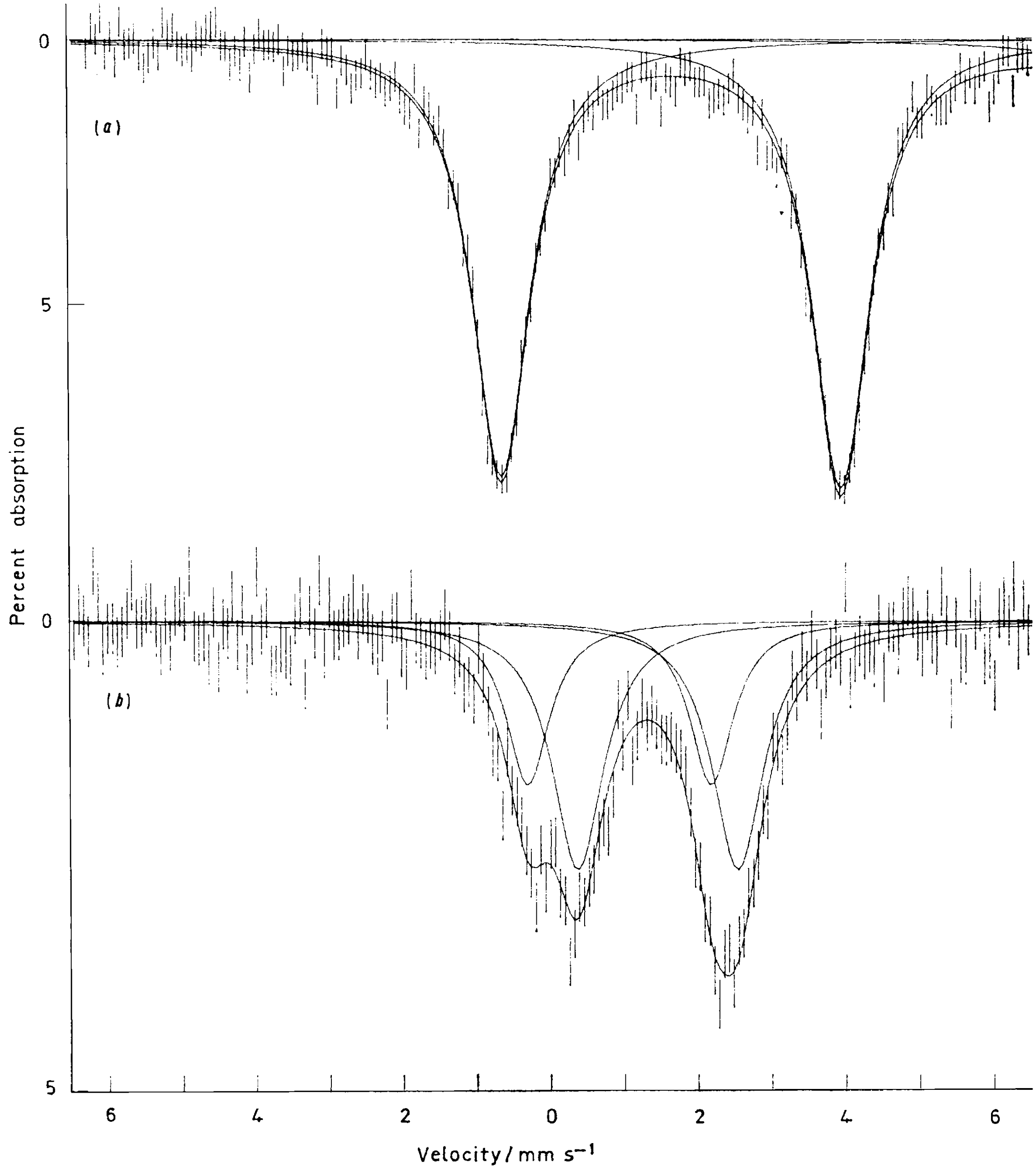

FIGURE 2 Mössbauer spectra in 100% H_2SO_4 of (*a*) Me_3SnCl, (*b*) $MeSnCl_3$

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[11] H. N. Farrar, M. M. McGrady, and R. S. Tobias, *J. Amer. Chem. Soc.*, 1965, **87**, 5019.

in the other cases were too large to be accounted for in this manner. Furthermore, both $[Me_3Sn]^+$ and $[Me_2Sn]^{2+}$ cations gave quadrupole splittings much larger than are possible for tetrahedral species, *e.g.* $Me_3Sn(HSO_4)$, indicating that rehybridisation at the tin nucleus occurred. Trimethyltin fluoride has been shown to have a five-co-ordinate tin atom,[12] and spectral data for $Me_3Sn(SO_3X)$ have been interpreted in terms of five-co-ordinate structures.[2] Similar arguments were used to suggest that $Me_2Sn(SO_3X)_2$ compounds were six-co-ordinate,[1] and *X*-ray analysis subsequently showed this to be the case for $Me_2Sn(SO_3F)_2$, the methyl groups occupying axial positions. The increases in *J*(Sn–C–H) are then due to bonds in the Sn–C unit changing from sp^3 in Me_4Sn, through sp^2 in $[Me_3Sn]^+$, to *sp* hybridised in $[Me_2Sn]^{2+}$. The cations have the remaining co-ordination positions filled by solvent molecules, *i.e.* $[Me_3Sn(H_2SO_4)_2]^+$, $[Me_2Sn(H_2SO_4)_4]^{2+}$, and $[MeSnCl(H_2SO_4)_4]^{2+}$. The further considerable increase in *J*(Sn–C–H) from $[Me_2Sn]^{2+}$ to $[MeSnCl]^{2+}$ reflects the differing electronegativity of CH_3 compared to Cl. A CH_3–Sn bond would have more covalent character, a greater share of the *s* electrons than the more ionic Sn–Cl bond, and hence an increase in coupling.

TABLE 2

N.m.r. and Mössbauer data for solvated methyltin cations

Cation	Solvent	$J(^{117,119}Sn–C–^1H)$ Hz		Isomer shift mm s^{-1}	Quadrupole splitting mm s^{-1}
$[Me_3Sn]^+$	H_2SO_4	61·0	63·4	1·53	4·55
	HSO_3F			1·61	4·95
$[Me_2Sn]^{2+}$	H_2SO_4	86·4	89·8	1·73	5·12
	HSO_3F	84·6	88·0	1·89	5·41
$[MeSnCl_2]^+$	H_2SO_4			1·32	2·00
	HSO_3F				
$[MeSnCl]^{2+}$	H_2SO_4	112·6	117·7	1·00	2·62
	HSO_3F	122·1	127·7	1·17	3·10

The Mössbauer data provide a further indication that these cations are solvated as indicated above. Parameters for these species in solution are similar to those obtained by Aubke and his co-workers [1-4] for solid alkyltin sulphonates and the tin environments are undoubtedly similar. Rapid proton transfer will occur between these solvated tin cations, which will behave as acids, and the free base present, *i.e.* HSO_4^- or SO_3F^-, to give $Me_3Sn(HSO_4),H_2SO_4$, $Me_2Sn(HSO_4)_2,2H_2SO_4$, $Me_2Sn(SO_3F)_2,2HSO_3F$, *etc.* Only relatively minor reorganisation of these co-ordinated unidentate sulphonate anions and solvent molecules will be required before crystallisation occurs in order to give the polymeric solid compounds. The minor differences between the solution and solid-state spectra can be explained in terms of strongly bridging bidentate ligands in the solid-state structures being replaced by weaker unidentate SO_3X^- or HSO_3X ligands.

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[4/741 *Received*, 11*th April*, 1974]

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[12] H. C. Clark, R. J. O'Brien, and J. Trotter, *Proc. Chem. Soc.*, 1963, 85.