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Methyltin Hydrides in Fluorosulphuric Acid

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Stannane or the methylstannanes $SnMe_{4-n}H_n$ (n = 1—4) react in fluorosulphuric acid at low temperature (−90 °C) to produce $SnMe_{3-n}H_n^+$ (n = 0—3) and ^1H, ^{13}C, and ^{119}Sn n.m.r. spectroscopy have been used in their characterisation. Hydrogen-evolution, ^{119}Sn n.m.r., and Mössbauer evidence is presented to show that at higher temperatures these species decompose to Sn^{2+}, Sn^{2+} plus $SnMe_2^{2+}$, and $SnMe_2^{2+}$ depending on the starting hydride.

Stannane and the methylstannanes have been well studied by a variety of spectroscopic techniques. Flitcroft and Kaesz[1] reported n.m.r. data, and a correlation between $J(^{119}Sn-^1H)$ and the tin–hydrogen stretching frequency ν(Sn–H) has been made.[2] Tin-119 Mössbauer spectra of stannane and some organotin hydrides have been recorded.[3] May and Spijkerman[4] correlated Mössbauer and n.m.r. parameters for the methyltin hydrides.

Sawyer and co-workers[5–7] have studied the reactions of organotin hydrides with acids. Di-n-butyltin dihydride reacts with HCl in dioxane to produce di-n-butyltin chloride hydride, with the evolution of 1 mol of H_2. This tin chloride hydride reacts further with an excess of acid to form $SnBu^n{}_2Cl_2$ and a further mol of H_2. An exchange reaction between $SnBu^n{}_2Cl_2$ and $SnBu^n{}_2H_2$ gives $SnBu^n{}_2ClH$.[8] Stannane reacts with strong acids, under controlled conditions, and Webster and Jolly[9] have shown that SnH_3^+ is produced. They showed that SnH_4 reacted slowly with strong aqueous acids, at low temperature, to produce 1 mol of H_2 for every mol of SnH_4. On warming to room temperature a further 2 mol of H_2 were produced. In HSO_3F solution, at −78 °C, SnH_4 reacted rapidly to produce SnH_3^+ and 1 mol of H_2. However, on warming to room temperature, no further H_2 was evolved. Birchall and Pereira[10] have compared $^1J(Sn-H)$ for the series SnH_3^+, SnH_4, and SnH_3^-.

Similar behaviour is observed for $SnMe_4$ in HSO_3F, when solvated $SnMe_3^+$ and $SnMe_2^{2+}$ are produced together with the evolution of CH_4.[11] To our knowledge no one has studied the solvolysis of the methyltin hydrides in strong acids. In this paper we report our results on such reactions and provide n.m.r. spectroscopic evidence for the $SnMe_3^+$, $SnMe_2H^+$, $SnMeH_2^+$, and SnH_3^+ cationic species in solution and evidence for the decomposition process.

Experimental

The tin hydrides were produced by standard literature methods,[1,12,13] their purity being checked by vapour-pressure measurements at fixed temperatures and by gas-phase i.r. spectroscopy. Solutions of the hydrides, in either organic solvents or fluorosulphuric acid, were prepared by condensing the hydride into the appropriate quantity of frozen, degassed solvent or acid, in the correct sized n.m.r. tube which was attached to a vacuum line. The n.m.r. tubes were sealed, the solvent allowed to melt, and, in the case of the acid solutions, the temperature was maintained at −90 °C until the n.m.r. spectra were recorded. The organic solutions were allowed to warm to room temperature. N.m.r. spectra of the acid solutions were recorded at a variety of temperatures beginning at −90 °C and warming to room temperature, using the following instrumentation. Proton and ^{13}C n.m.r. spectra were recorded (unlocked) at an external applied field strength of 5.87 T on a Bruker WM.250 spectrometer using n.m.r. tubes of outside diameter 5 mm (^1H) and 10 mm. The observing frequencies were 250.13 MHz (^1H) and 62.89 MHz (^{13}C). Tin-119 n.m.r. spectra were recorded at an external applied field strength of 2.11 T on a Bruker WH-90 spectrometer using 8-mm n.m.r. tubes which were inserted concentrically into a tube of outside diameter 10 mm; $(CD_3)_2CO$ was used as a lock solvent in the outer tube. The operating frequency was 33.56 MHz. Proton and ^{13}C chemical shifts were referenced using $SiMe_4$ in $(CD_3)_2CO$ as an external standard, and ^{119}Sn was referenced using pure $SnMe_4$ as the external standard. Tin-119 Mössbauer spectra of solutions frozen at 77 K were recorded on equipment which has already been described.[14] These spectra were fitted using the program written by Ruebenbauer and Birchall.[15]

Hydrogen-evolution experiments were carried out on a standard glass vacuum line equipped with a Toepler pump. Tin hydride (*ca.* 0.3 mmol) was condensed, at 77 K, into a glass vessel containing HSO_3F (35.0 mmol) which had been previously degassed. This solution was warmed to −78 °C (acetone–solid CO_2 bath) when hydrogen evolution occurred. The quantity of hydrogen evolved was measured. Raising the solution temperature to 21 °C resulted in further evolution of hydrogen when the starting hydride was $SnMeH_3$, but not when $SnMe_2H_2$ was used. Amount (mmol) of H_2 evolved: with $SnMeH_3$ (0.305 mmol), 0.285 at −78 °C, 0.344 at 25 °C, total 0.629; (0.258 mmol), 0.252 at −78 °C, 0.246 at 25 °C, total 0.498; with $SnMe_2H_2$ (0.293 mmol), 0.292 at −78 °C, 0.08 at 25 °C, total 0.300. All of the hydrides liberate 1 mol of hydrogen for every mol of hydride dissolved in fluorosulphuric acid at −78 °C. Webster and Jolly[9] had demonstrated this for solutions of stannane. The significance of these observations is discussed below.

Results and Discussion

Table 1 summarises the n.m.r. data of the parent hydrides and their reaction products in fluorosulphuric acid. Literature data have also been included and the agreement between our data and the earlier results is generally good. The tin-119 chemical shift for SnH_4, −493 p.p.m., had not previously been reported, nor had some of the $^1J(^{119}Sn-^{13}C)$ coupling constants.

Webster and Jolly[9] showed, by ^{119}Sn n.m.r. spectroscopy, that when stannane reacts with fluorosulphuric acid, at low temperature, SnH_3^+ is produced. They also suggested that this cation decomposed at room temperature into a tin(II) species having a ^{119}Sn chemical shift of −1 780 p.p.m. We have re-examined this reaction and can confirm these results (Table 1). The ^1H and ^{119}Sn resonances for SnH_3^+ occur at higher frequencies than those of SnH_4, indicating considerable deshielding. Figure 1 shows the ^{119}Sn n.m.r. spectra of SnH_4

Table 1. N.m.r. data for $SnMe_{4-n}H_n$ (n = 1—4) and their solutions in fluorosulphuric acid

			Chemical shift (p.p.m.)			Coupling constant (Hz)			
Compound	Solvent	θ_c/°C	$\delta(^{1}H)$[a]	$\delta(^{13}C)$[a]	$\delta(^{119}Sn)$[b]	$^{1}J(^{117/119}Sn-^{1}H)$	$^{2}J(^{117/119}Sn-C-^{1}H)$	$^{2}J(^{117/119}Sn-^{13}C)$	Ref.
SnH_4	Neat	−50	3.85			1 846/1 931			1
	C_6H_{14}	−65	3.9		−493	1 848/1 933			
						1 929 ± 6[c]			
$SnMeH_3$	C_5H_{12}	40	0.27, 4.14			1 770/1 852	62.0		1
	C_6H_5Me	−35			−346				*d*
	C_6H_{14}	−50	0.33, 4.46	−17.8	−355	1 770/1 850	62.0	370	
						1 856 ± 10[c]	61.0[c]		
$SnMe_2H_2$	C_5H_{12}	40	0.17, 4.76			1 682/1 758	58.0		1
	C_6H_{12}	−20			−225				*e*
	C_6D_6	25	0.20, 4.63	−14.8		1 705/1 782	58.5	361	
$SnMe_3H$	C_6H_6				−104				*f*
	C_5H_{12}	40	0.18, 4.73			1 664/1 744	56.5		1
				−11.8				352	*g*
SnH_4	HSO_3F								
SnH_3^+		−78	7.5			2 787/2 916			10
			7.8		−192.4	2 780/2 910			
					−186	2 960[c]			9
		−30			−193.6	2 775/2 904			
						2 913 ± 10[c]			
Sn^{2+}		25			−1 780				9
					−1 601				
$SnMeH_3$	HSO_3F								
$SnMeH_2^+$		−78	0.51, 8.2	−7.0	−29.3	2 593/2 710	73.0	463	
						2 698 ± 5[c]	73.2[c]		
		−60				2 690 ± 6[c]			
$SnMe_2^{2+}$			1.25				86		
		−30	1.27	10.1	−222		82		
		25	1.6	14.5	−185		88.5	600	
$SnMe_2H_2$	HSO_3F								
$SnMe_2H^+$		−85	0.57, 8.4	−0.8	+156	2 494/2 606	68.0		
						2 460 ± 150[c]			
$SnMe_2^{2+}$		25	1.60		−183		85.5		
$SnMe_4$	HSO_3F								
$SnMe_3^+$		−60	0.75	+6.8	+322		60, 63	388	
$SnMe_2^{2+}$		25	1.68	13.2	−185		88.0	600	

[a] Referenced to external $SiMe_4$ in $(CD_3)_2CO$. [b] Referenced to external neat $SnMe_4$. [c] Measured by ^{119}Sn n.m.r. spectroscopy. [d] J. D. Kennedy and W. McFarlane, *Rev. Silicon, Germanium, Tin, Lead Compd.*, 1974, **1**, 235. [e] C. Schumann and H. Dreeshamp, *J. Magn. Reson.*, 1970, **3**, 204. [f] A. P. Tupciauskus, N. M. Sergeyer, and Yu. A. Ustynzuk, *Org. Magn. Reson.*, 1971, **3**, 655. [g] T. N. Mitchell, *J. Organomet. Chem.*, 1973, **59**, 189.

and SnH_3^+. As the temperature of the SnH_3^+ solution is raised the signal due to the cation slowly disappears. At room temperature the only tin signal present in the spectrum is at −1 601 p.p.m. This value is close to that for a solution of $Sn(SO_3F)_2$ in fluorosulphuric acid. That this signal is due to a tin(II) species was confirmed by recording a ^{119}Sn Mössbauer spectrum of this solution after freezing it at 77 K. The Mössbauer parameters are very close to those of $Sn(SO_3F)_2$ (Figure 2, Table 2). In the ^1H n.m.r. spectrum a weak signal at 4 p.p.m. was attributed to H_2, dissolved in HSO_3F, which was produced in the initial reaction. These observations can be explained by reactions (1) and (2). It is most likely that the

$$SnH_4 + HSO_3F \longrightarrow SnH_3^+ + SO_3F^- + H_2 \quad (1)$$

$$SnH_3^+ + 5HSO_3F \longrightarrow Sn^{2+} + 2H_2SO_4 + 2SO_2 + 4HF + SO_3F^- \quad (2)$$

SnH_3^+ cation will be solvated by SO_3F^- anions to give the tin a five-co-ordinate environment. Evidence for the presence of SO_2 is indirect, but the pale blue colour of these solutions is indicative of the production of polycations of sulphur from the reaction of SO_2 and HSO_3F in the presence of hydrogen.[9]

Methylstannane is also solvolysed in fluorosulphuric acid and can be monitored by n.m.r. spectroscopy and hydrogen evolution. At low temperature (−78 °C) 1 mol of hydrogen per mol of hydride is evolved. N.m.r. spectroscopy [Table 1, Figure 3(*a*)] shows that the species in solution is $SnMeH_2^+$. Like the SnH_3^+ cation, $SnMeH_2^+$ is also presumably solvated. One notes the deshielding in the ^{119}Sn resonance and the large increases in coupling constants on going from the neutral hydride to the cationic species. As this solution is warmed, new signals appear: Figure 3(*b*) shows the ^{119}Sn n.m.r. spectrum at −60 °C. The signals due to the $SnMeH_2^+$ cation are reduced in intensity and a new multiplet is observed at −228 p.p.m. By −30 °C all of the $SnMeH_2^+$ has decomposed. The spectrum of the resulting species [Figure 3(*c*)] is a septet having a chemical shift of −185 p.p.m. and a coupling constant of 88 Hz. These changes are mirrored in the ^1H spectrum, with the only proton species remaining at room temperature having $\delta(^1H)$ = 1.24 p.p.m. and $^2J(Sn-C-H)$ = 86 Hz. These n.m.r. parameters are characteristic of $SnMe_2^{2+}$, which has been identified as the stable species when $SnMe_4$ is solvolysed in HSO_3F.[11] Scanning the region of the ^{119}Sn spectrum at low frequency revealed a peak at −1 600 p.p.m. due to Sn^{2+}. A ^{119}Sn Mössbauer spectrum of this solution, frozen at 77 K, is shown in Figure 2(*b*). This spectrum has been fitted by two overlapping multiplets, the parameters for which are summarised in Table 2. They are very similar to those for solid $SnMe_2(SO_3F)_2$[11] and $Sn(SO_3F)_2$:[16] the small differences are undoubtedly due to the fact that here the species are in a frozen-solution matrix rather than the pure solids. These observations are satisfied by equation (3). The mechanism of methyl transfer from $SnMeH_2^+$ to produce $SnMe_2^{2+}$ is not clear, but presumably occurs *via* a ditin intermediate. Organoditin compounds are produced from organotin hydrides in acidic solution.[6]

$$2SnMeH_2^+ + 4HSO_3F \longrightarrow SnMe_2^{2+} + Sn^{2+} + H_2SO_4 + SO_2 + 2HF + 2H_2 + 2SO_3F^- \quad (3)$$

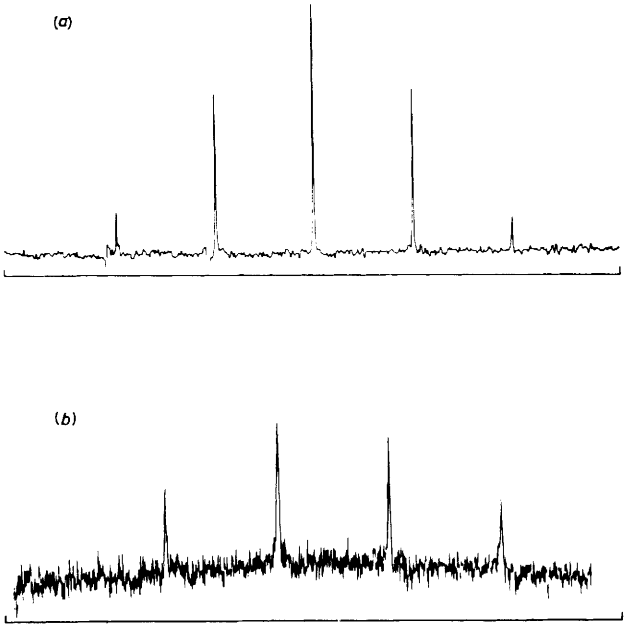

Figure 1. ^{119}Sn N.m.r. spectrum of (*a*) SnH_4 [$\delta(^{119}Sn) = -493$ p.p.m., $^1J(^{119}Sn-^1H) = 1\,928$ Hz] and (*b*) a solution of SnH_4 in fluorosulphuric acid at −78 °C [$\delta(^{119}Sn) = -192$ p.p.m., $^1J(^{119}Sn-^1H) = 2\,910$ Hz]

Solutions of dimethyltin dihydride in fluorosulphuric acid are much less stable than the other hydrides discussed above. At −78 °C the hydride reacts with fluorosulphuric acid to produce 1 mol of hydrogen gas. We have been unable to obtain a n.m.r. spectrum of $SnMe_2H_2$ in fluorosulphuric acid which contains no $SnMe_2^{2+}$ decomposition product. The transfer of the cold n.m.r. samples to the cold probe, no matter how rapid, is still not fast enough to prevent some decomposition. The ^1H n.m.r. spectrum at −85 °C contains signals due to $SnMe_2H^+$ and $SnMe_2^{2+}$. The chemical shifts and coupling constants are listed in Table 1. The ^{119}Sn n.m.r. spectrum (Figure 4) confirms the presence of these species. The high-frequency doublet is due to $^1J(^{119}Sn-^1H)$ from the $SnMe_2H^+$ cation, while that at low frequency arises from the $SnMe_2^{2+}$ cation. These signals are broad and each should be a septet due to $^2J(^{119}Sn-C-H)$ coupling. At −85 °C we were unable to resolve this coupling. The room-temperature spectrum clearly shows the $^2J(^{119}Sn-C-H)$ coupling for $SnMe_2^{2+}$ but, at this temperature, decomposition of the $SnMe_2H^+$ cation is complete. Confirmation of $SnMe_2^{2+}$ in the room-temperature solution comes from the ^{119}Sn Mössbauer spectrum obtained by freezing this solution. The spectrum is shown in Figure 2(*c*) and the parameters, Table 2, are close to those for $SnMe_2(SO_3F)_2$.[11]

Trimethyltin hydride behaves in the same way as the other hydrides, producing $SnMe_3^+$ and H_2 at low temperature, followed by methane evolution at room temperature to give $SnMe_2^{2+}$. N.m.r. data, some of which have been reported,[11] are included in Table 1. This $SnMe_3^+$ cation can also be produced by solvolysis of $SnMe_4$.[11,17]

In any series of main-group element hydrides MH_x replacement of hydrogen by methyl groups results in a deshielding of the M resonance.[18–20] This has been noted for the tin hydrides[21,22] and our results allow completion of this correlation. The ^{119}Sn chemical shifts for $SnMe_{4-n}H_n$ are plotted *versus* *n* in Figure 5(*a*). The straight line does not pass through zero, the value for $SnMe_4$, probably because the stannane shifts were measured as dilute solutions in organic solvents while $SnMe_4$ was recorded as the neat liquid. A similar trend is observed for the cationic series $SnMe_{3-n}H_n^+$ (n = 0—3), with their ^{119}Sn shifts being more positive than those for the corresponding neutral hydrides. The greater

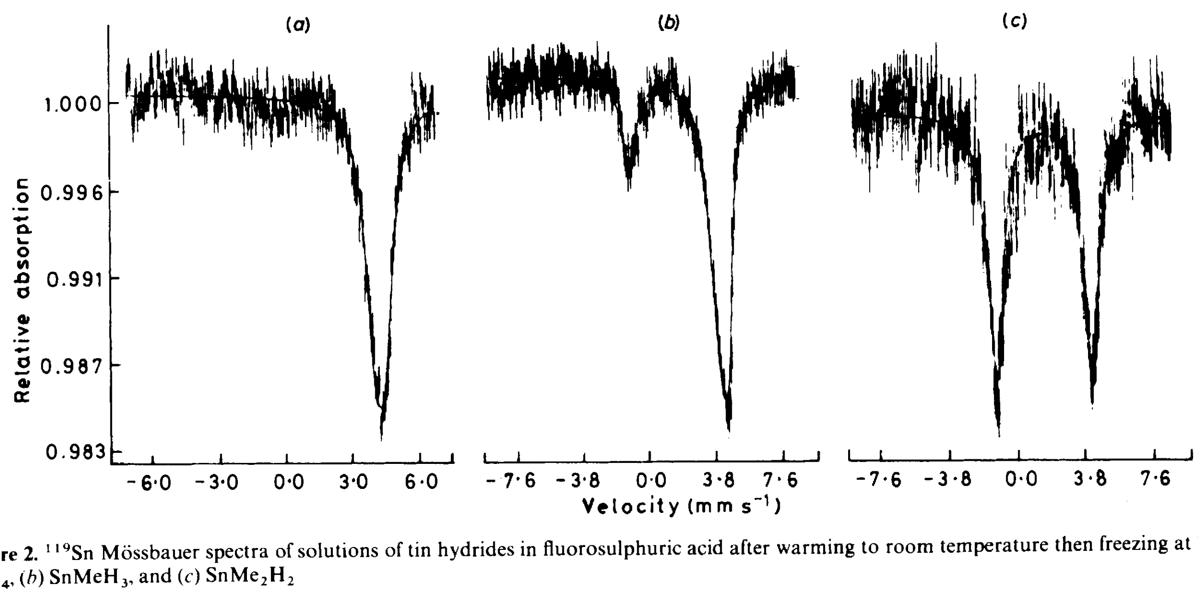

Figure 2. ^{119}Sn Mössbauer spectra of solutions of tin hydrides in fluorosulphuric acid after warming to room temperature then freezing at 77 K: (*a*) SnH_4, (*b*) $SnMeH_3$, and (*c*) $SnMe_2H_2$

Table 2. ^{119}Sn Mössbauer data (mm s^{-1}) for solutions of tin hydrides in fluorosulphuric acid after standing at room temperature, recorded at 77 K

Compound	Medium	Sn^{IV} δ	Δ	Γ	Sn^{II} δ	Δ	Γ
SnH_4	HSO_3F				4.33	0.58	0.88
$SnMeH_3$	HSO_3F	1.86	5.22	0.95	4.42	0.60	0.95
$SnMe_2H_2$	HSO_3F	1.81	5.25	1.07			
$SnMe_3H$[11]	HSO_3F	1.61	4.95				
$Sn(SO_3F)_2$[16]	Solid				4.18	0.68	1.33
$SnMe_2(SO_3F)_2$[11]	Solid	1.89	5.41				
$SnMe_3(SO_3F)$*	Solid	1.52	4.61	0.99, 1.04			

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

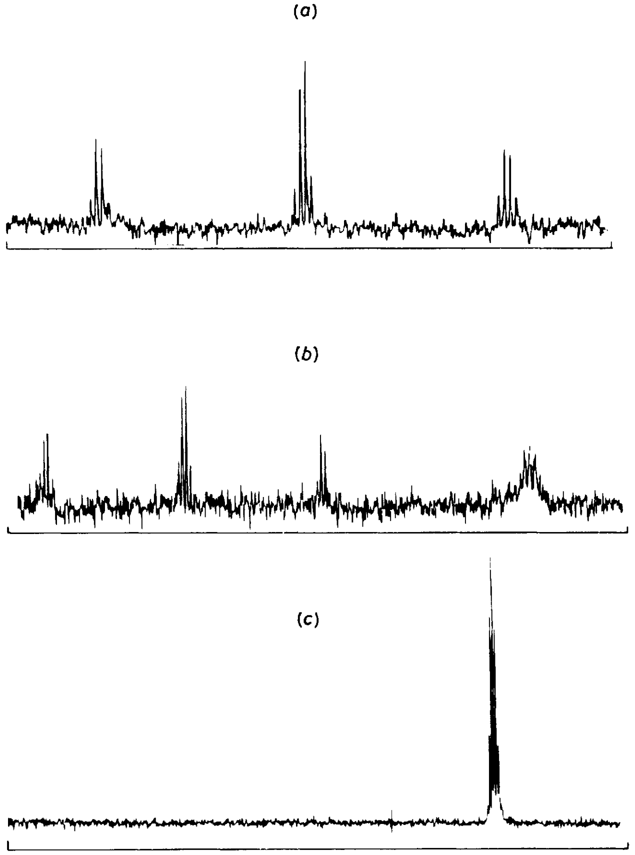

Figure 3. ^{119}Sn N.m.r. spectra of a solution of $SnMeH_3$ in fluorosulphuric acid at (*a*) −78 °C [$\delta(^{119}Sn) = -29$ p.p.m., $^1J(^{119}Sn-^1H) = 2\,710$ Hz], (*b*) −60 °C [$\delta(^{119}Sn) = -28, -228$ p.p.m.], and (*c*) 25 °C [$\delta(^{119}Sn) = -185$ p.p.m.]

influence of methyl-group substitution, on the tin chemical shifts, reflects the tighter C–Sn bonding in the cationic species. The deshielding that the tin nucleus experiences, on removal of a hydrogen from these stannanes, is dramatic, suggesting that any interaction with solvent molecules, or fluorosulphate anions, in solution must be relatively weak, though undoubtedly present.

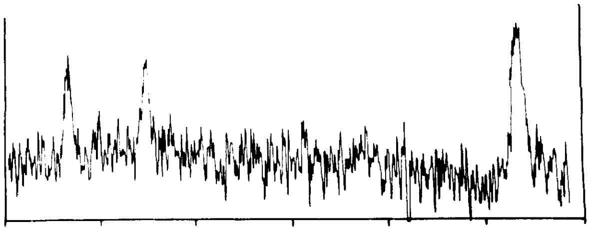

Figure 4. ^{119}Sn N.m.r. spectrum of a solution of $SnMe_2H_2$ in fluorosulphuric acid at −85 °C [$\delta(^{119}Sn) = 156$ p.p.m., $^1J(^{119}Sn-^1H) = 2\,460$ Hz; −223 p.p.m.]

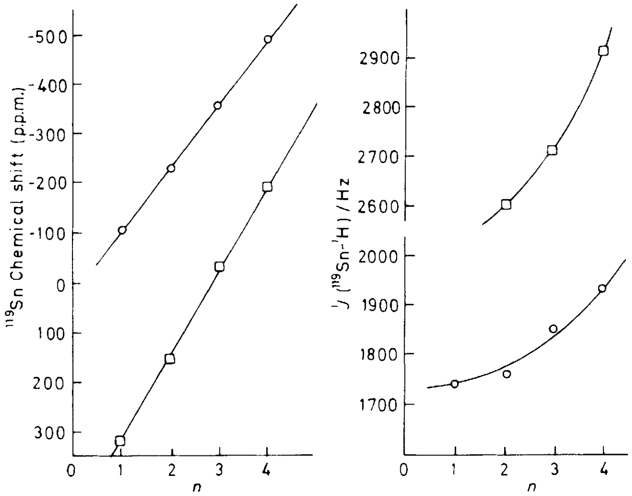

Figure 5. Plots of ^{119}Sn n.m.r. chemical shifts and $^1J(^{119}Sn-^1H)$ coupling constants *versus n* in $SnMe_{4-n}H_n$: parent hydride (○); hydride in fluorosulphuric acid (□)

Examination of the trends in $^1J(Sn-H)$ across these series is also informative. There is a trend to smaller $^1J(Sn-H)$ as the number of methyl groups increases in the hydrides, Figure 5(*b*),[18] but the correlation is not as good as was observed for the chemical shifts. A dramatic increase in $^1J(Sn-H)$ is observed on reaction in fluorosulphuric acid [Table 1, Figure 5(*b*)] and the coupling constant decreases, as before, with methyl substitution. If the spin–spin coupling constant is dominated by the Fermi-contact term then, in simple valence-bond terms, one could attribute these changes to a change in hybridisation at the tin from sp^3 to sp^2. The *s* character of the bond is increased, therefore the tin–hydrogen coupling should increase. We note that all couplings in the cationic species are higher than in the parent hydrides.

Few structures of trialkyltin species have been reported, but trimethyltin fluoride has been shown to contain tin in a five-co-ordinate environment. Spectroscopic evidence has been used to imply five-co-ordination, about the tin, in $SnMe_3(SO_3X)$. Spectral studies, in strong acids, of these trialkyltin sulphates have shown that the environment about the tin is very much the same as in the solid state,[11] *i.e.* trigonal planar. The sulphate groups occupy the positions above and below the plane to complete the trigonal-bipyramidal arrangement about tin. We believe that the tin nuclei in the $SnMe_{3-n}H_n{}^+$ species are similarly co-ordinated.

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