An Investigation of the Hydrolysis Products of Monoalkyltin Trichlorides by ^{119m}Sn Mössbauer, and ^{1}H and ^{119}Sn NMR Spectroscopy

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*^{1}H 400 MHz NMR studies on the MeSnCl$_3$/D$_2$O system at various concentrations have established the presence of the following species: MeSn(OH)Cl$_2$·2H$_2$O, MeSn(OH)$_2$Cl·nH$_2$O and {MeSn(OH)-(H$_2$O)$_4$}$^{2+}$, the latter being the first reported example of a cationic monoalkyltin aquo-species. The availability of high field NMR has enabled the solution of a problem previously not possible, on account of overlapping signals. ^{119m}Sn Mössbauer and ^{119}Sn NMR data for a number of hydrolysis products of monoalkyltin trichlorides are presented.*

Introduction

Studies of the structure of organotin compounds in aqueous solution have generally been limited to methyltin derivatives, since other organotins do not have a sufficiently high solubility in water to permit spectroscopic investigation.

It has been well established, using Raman and ^{1}H NMR spectroscopy, that, in aqueous solution, tri- and di-methyltin compounds, Me$_3$SnX and Me$_2$SnX$_2$, exist as the hydrated cations (I, R = Me) [1, 2] and (II, R = Me) [1, 3, 4] respectively

(I)   (II)
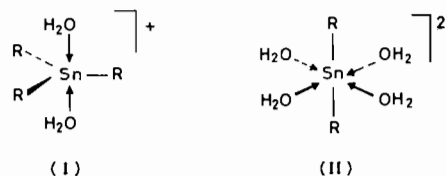
and a salt containing (I), {Me$_3$Sn(H$_2$O)$_2$}$^+$BPh$_4^-$, has been isolated in the solid state [5]. Additionally, ^{119}Sn NMR studies [6] on an aqueous solution of the rather soluble (0.05 *M*) Bu$_3$SnO$_3$SEt [7] indicate that the organotin species present in solution has structure (I, R = Bu).

In contrast, however, very little work has been carried out on the partial hydrolysis products of the monoalkyltin derivatives [8] and Tobias has suggested [1] that these exist in solution only as the hydrated oxides. The current interest in the environmental methylation of organotin compounds [9], and, in particular, the behaviour of the monoorgano-

TABLE I. Analytical, Physical and ^{119m}Sn Mössbauer Data (mm s^{-1}) for RSn(OH)Cl$_2$·nH$_2$O Compounds.

Compound	M. Pt. (°C)	Analyses % [a]			δ [b,c]	ΔE_Q [c]
		C	H	Cl		
MeSn(OH)Cl$_2$·2H$_2$O	69–77	3.96 (4.65)	3.10 (3.10)	27.60 (27.51)	0.84	2.13
EtSn(OH)Cl$_2$·H$_2$O	96–128 (94–96)[d]	9.37 (9.44)	3.05 (3.15)	27.60 (27.95)	0.96	2.23
BuSn(OH)Cl$_2$·H$_2$O	73–120 (80–87)[d]	16.57 (17.05)	3.68 (4.25)	25.57 (25.16)	0.89	2.38
OctSn(OH)Cl$_2$·H$_2$O	102–5 (45–56)[d]	28.33 (28.04)	5.66 (5.91)	21.60 (21.00)	0.89	2.33

[a]Calcd. values in parentheses.   [b]Relative to Ba^{119m}SnO$_3$.   [c]±0.05 mm s^{-1}.   [d]J. G. A. Luijten, *Rec. Trav. Chim.*, 85, 873 (1966).

tins, $RSnX_3$, in dilute aqueous systems [6, 10], has prompted us to report the results of our present study. The use of ^{1}H NMR at 400 MHz has resolved some ambiguities present in previous work at lower frequencies.

Experimental

The first hydrolysis products of the monoalkyltin trichlorides, $RSn(OH)Cl_2 \cdot H_2O$, where R = Et, Bu or Oct, were prepared by allowing the liquid organotin trichloride to hydrolyse in air, as described previously [8]. $MeSn(OH)Cl_2 \cdot 2H_2O$ crystallised as colourless needles from a solution of methyltin trichloride in methanol/light petroleum (b.p. 60–80 °C) when left to stand in air for 2–3 days and was filtered, washed with petroleum ether and dried at room temperature. This compound has not been reported previously.

The analytical and physical data for the hydrolysis products, together with their [119m]Sn Mössbauer parameters, are listed in Table I. Mössbauer spectra were obtained at 80 K, using a constant acceleration microprocessor Mössbauer spectrometer described previously [11].

^{1}H NMR spectra at 90 MHz and ^{119}Sn NMR spectra at 33.34 MHz were measured on a JEOL FX90Q spectrometer at an ambient temperature of 298 K; 400 MHz ^{1}H NMR spectra were recorded at an ambient temperature of 291 K on a Bruker WH-400 instrument. Field frequency lock was to solvent D_2O in all cases. Chemical shifts to high field are negative in sign.

Results and Discussion

For the first hydrolysis products of monoalkyltin trichlorides, Luijten reported [8] the general formula to be $RSn(OH)Cl_2 \cdot H_2O$, where R = Et, Bu or Oct, and the structure of the ethyl derivative has been established crystallographically [12] to be a hydroxyl-bridged dimer (III, R = Et).

(III)
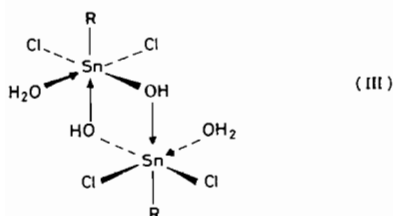
The close resemblance of the [119m]Sn Mössbauer parameters for the first hydrolysis products to those of (III), (Table I), indicates the same 6-coordinate dimeric structure. Elemental analysis is consistent with the presence of two water molecules in the
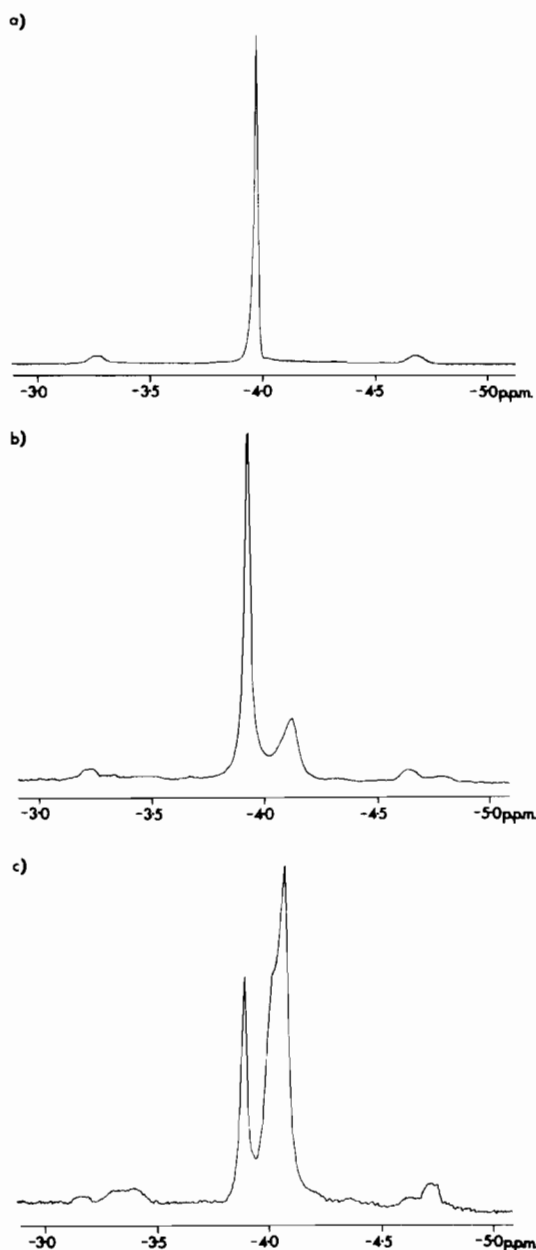
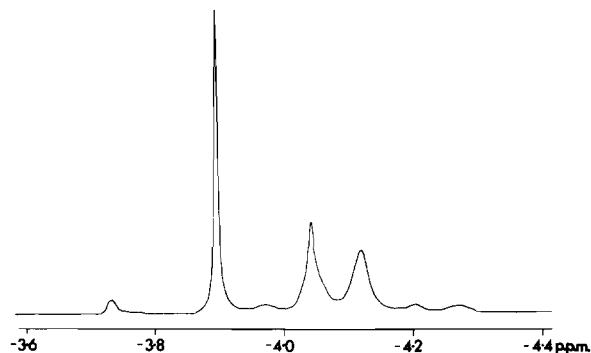Fig. 1. 90 MHz ^{1}H NMR Spectra of Aqueous Solutions of $MeSnCl_3$ (a) 0.5 M (b) 0.25 M (c) 0.05 M.

monomethyltin derivative. The second water molecule is, hence, most likely to be loosely bound, possibly by weak hydrogen bonds, cf. $SnCl_4 \cdot 5H_2O$ [13] A single crystal X-ray study of this compound is under way and the results will be reported in a subsequent publication.

It has been noted [14] that a 60 MHz ^{1}H NMR spectrum of an aqueous solution of $MeSnCl_3$, at concentrations greater than 0.21 M, showed just one peak, whereas, at lower concentrations, a second broad resonance appeared, upfield from the main

TABLE II. ^{1}H^a and ^{119}Sn NMR Chemical Shifts, $\delta\,^1$H and $\delta\,^{119}$Sn, and Tin–Proton Coupling Constants, ^{2}J(^{117,119}Sn–^{1}H), for Aqueous Solutions of Methyltin Chlorides and MeSn(OH)Cl₂·2H₂O.

Compound	Concentration (M)	$\delta\,^1$H^b (p.p.m.)	^{2}J(^{117,119}Sn–^{1}H)^c (Hz)	$\delta\,^{119}$Sn^d (p.p.m.)
MeSnCl₃^e	0.5	−3.98	127.9	−481
	0.25	−3.93^f	129.6	−486
	0.05	−3.89	130.2	−498
		−4.04	127.4	^{g}
		−4.12	121.2	−515
	0.005	−3.93	~132^h	^{i}
		−4.04	127.5^j	^{i}
		−4.14	~119^h	^{i}
MeSn(OH)Cl₂·2H₂O	0.1	−3.91	130.8	−487
		−4.04	126.4	^{g}
		−4.11	120.9	^{g}
Me₂SnCl₂	0.05	−3.9	107	−293
Me₃SnCl	0.05	−4.2	69	40^k

^{a}Recorded at 400 MHz, except for Me₂SnCl₂ and Me₃SnCl (90 MHz). ^{b}Relative to H₂O (error = ±0.02 p.p.m., except for Me₂SnCl₂ and Me₃SnCl, where error = ±0.05 p.p.m.). ^{c}^{117,119}Sn satellites were unresolved and ^{2}J(^{117,119}Sn–^{1}H) refers to the average value. ^{d}Relative to Me₄Sn (error = ±0.5 p.p.m.). $^e\delta\,^{119}$Sn = 474–481 p.p.m. {B. K. Hunter and L. W. Reeves, *Can. J. Chem., 46*, 1399 (1968)}. ^{f}Only one peak is reported, due to the coincidence, at 400 MHz, of the ^{117,119}Sn satellites with the minor resonance. ^{g}Peak not detected. ^{h}Approximate value, due to very low intensity. ^{i}Not recorded. ^{j}In this case, where the satellites were resolvable, the ^{119}Sn value is quoted. ^{k}Range of ~23 p.p.m. {B. K. Hunter and L. W. Reeves, *Can. J. Chem., 46*, 1399 (1968)}.

Fig. 2. 400 MHz ^{1}H NMR Spectrum of a 0.05 M Aqueous Solution of MeSnCl₃.

signal. This effect may be seen in Fig. 1, which shows 90 MHz ^{1}H NMR spectra of MeSnCl₃ in water at concentrations of (a) 0.5 M, (b) 0.25 M, and (c) 0.05 M. The spectrum of the 0.05 M solution shows a shoulder on the broad resonance, which was not observed by previous workers [14], indicating the possibility of three species in solution. This is clearly demonstrated by a 400 MHz ^{1}H NMR spectrum of the same solution (Fig. 2).

Associated with each of the three peaks are ^{117,119}Sn satellites, revealing the presence of organotin species. The broadness of both the central and satellite features probably indicates the presence

of chemical exchange, which does not, however, involve breaking of the tin–carbon bond.

^{1}H and ^{119}Sn chemical shifts, $\delta\,^1$H and $\delta\,^{119}$Sn, and coupling constants, ^{2}J(^{1}H–^{117,119}Sn) are given in Table II. The 400 MHz ^{1}H NMR spectrum of the 0.05 M solution of methyltin trichloride in water consisted of three peaks, whereas the ^{119}Sn spectrum showed only two. Presumably, the third species was either coincident or too weak to be detected in the spectrum, which showed a signal-to-noise ratio of only 6:1 for the major feature.

A 400 MHz ^{1}H NMR spectrum of a 0.1 M aqueous solution of MeSn(OH)₂Cl₂·2H₂O very closely resembled the spectrum shown in Fig. 2 (see also Table II) and a ^{119}Sn NMR spectrum of the same solution revealed a peak at −487 p.p.m. This high field chemical shift is characteristic of a 6-coordinate octahedral species, *cf.* {Me₂Sn(H₂O)₄}$^{2+}$ (Table II), and suggests that the dimeric structure of the monomethyltin derivative (III, R = Me) is preserved in aqueous solution. Again, other ^{119}Sn resonances may have been present, but these were not detected in the spectrum. It was, however, noted that a saturated solution of BuSn(OH)Cl₂·H₂O in D₂O (*ca.* 3% w/v), showed three ^{119}Sn resonances (at −283, −503 and −536 p.p.m.).

From the similarity between the ^{1}H and ^{119}Sn NMR parameters of aqueous solutions of MeSnCl₃ and of its first hydrolysis product, it is therefore suggested that the species formed upon dissolution of

the monoalkyltin trichloride, at higher concentrations, is $MeSn(OH)Cl_2 \cdot 2H_2O$. The same product may be present in aqueous solutions of $\{MeSnCl_5\}^{2-}$, which have been found, by heteronuclear double resonance, to have a ^{119}Sn chemical shift value of —464 p.p.m. [15].

Luijten also prepared some second hydrolysis products of alkyltin trichlorides, by reaction of 1 mol of the organotin trichloride with 2 mols of aqueous sodium hydroxide [8]. The general formula of these compounds was found to be $RSn(OH)_2Cl \cdot nH_2O$, where R = Et, Bu or Oct, and n = 0 or 1. Our attempts to prepare and isolate a pure sample of the second hydrolysis product of methyltin trichloride were unsuccessful. However, a 90 MHz ^1H NMR spectrum of an aqueous mixture of 1 mol of methyltin trichloride and two mols of sodium hydroxide showed a broad peak centred at approximately 4 p.p.m. upfield from the water resonance, with broad $^{117,119}Sn$ satellites (presumably due to overlapping) of approximately 126 Hz coupling. This spectrum very closely resembles the broad resonance seen in the ^1H spectrum of a 0.05 M aqueous solution of methyltin trichloride. It therefore appears that the second species formed upon dilution of an aqueous solution of methyltin trichloride is $MeSn(OH)_2Cl \cdot nH_2O$. The fact that the ^1H chemical shift of this species is upfield from that of $MeSn(OH)Cl_2 \cdot 2H_2O$ presumably results from substitution of the Cl atom by the less electronegative OH groups. The magnitude of the coupling constant, $^2J(^1H-^{117,119}Sn)$, is dependent [16] upon the % s electron character in the tin—carbon bond, and, since according to Bent [17], electronegative groups repel s character, substitution by a less electronegative group will produce a decrease in $^2J(^1H-^{117,119}Sn)$. On this basis, the peak at —4.12 p.p.m. with a smaller coupling is assigned to $MeSn(OH)_2Cl \cdot nH_2O$. This assignment is supported by the behaviour of its relative intensity with dilution: on dilution from 0.5 M to 0.05 M there was an increase, but, on further dilution to 0.005 M, its intensity decreased.

The peak at —4.04 p.p.m. in Fig. 2 must, therefore, be due to a third hydrolysis product. If it is assumed that, as before, this involves substitution of a Cl atom by an OH group, this would result in the formation of $MeSn(OH)_3$. Such a compound would presumably exist in aqueous solution, as do the trimethyl- and dimethyl-tin derivatives [1], in equilibrium with other hydroxy species:

$$MeSn(OH)_3 \rightleftharpoons MeSn(OH)_2^+ \rightleftharpoons MeSn(OH)^{2+} \rightleftharpoons MeSn^{3+}$$
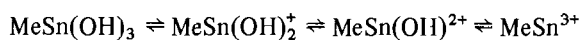
As the pH is reduced, the species to the right are increasingly favoured.

A 0.05 M solution of methyltin trichloride in water has a pH of 1.4, and, therefore, $MeSn(OH)_3$ is unlikely to be present under these conditions. In

addition, the ^1H chemical shift value argues against the aqueous species being $MeSn(OH)_3$, since this product would have an even higher field chemical shift than $MeSn(OH)Cl_2 \cdot 2H_2O$ or $MeSn(OH)_2Cl \cdot nH_2O$ on electronegativity grounds. Holmes and Kaesz [16] reported that the magnitude of the proton—tin coupling, $^2J(^1H-^{117,119}Sn)$, in $\{Me_3Sn(H_2O)_2\}^+$ and $\{Me_2-Sn(H_2O)_4\}^{2+}$ (Table II) represents a % s character in each Sn—C bond orbital of 32% and 48% respectively. These values are consistent with sp^2 (33% s) and sp (50% s) hybridisation respectively, supporting the idea [18] that the most stable configuration of the cation in solution is that which maximises the s character in the metal—carbon bonds. In other words, the donation of electrons from the water molecules to tin does not appear to affect the % s character in the Sn—C bonds. If the first and second hydrolysis products of methyltin trichloride are treated similarly, they can be assumed to be sp^3 hybridised, with expected proton—tin couplings of approximately 52 Hz [16]. This is much less than the observed couplings of 130 Hz and 121 Hz (Table II), and the difference must be due to an increase in % s character of the Sn—C bond caused [17] by the electronegative Cl atoms or OH groups bonded to tin. Additive substituent effects to the proton—tin coupling constant value in methyltin compounds have been reported previously [19]. From the couplings observed for $MeSn(OH)Cl_2 \cdot 2H_2O$ and $MeSn(OH)_2Cl \cdot nH_2O$, increases of 29 Hz and 20 Hz may be ascribed to the Cl atom and OH groups respectively.

The coupling of 127 Hz recorded for the third hydrolysis product (Table II), indicates [16] a % s character in the Sn—C orbital of approximately 60%. Hence, if again the electron donating water molecules have little or no effect on the s density in the Sn—C orbital, the peak at —4.04 p.p.m., in Fig. 2, is clearly not due to the $MeSn^{3+}$ cation, for which the % s-character would be 100%. The coupling constant for $MeSn(OH)^{2+}$, predicted by the substituent parameters deduced above, is 123 Hz, which is close to the experimental value of 127 Hz. A similar calculation for $MeSn(OH)_2^+$ yields a much lower value of 109 Hz. The preferred species, $MeSn(OH)^{2+}$, would undoubtedly be hydrated, and it is therefore suggested that the peak at —4.04 p.p.m. (Fig. 2) is due to $\{MeSn(OH)(H_2O)_4\}^{2+}$.

The 400 MHz ^1H spectrum of a 0.005 M aqueous solution of $MeSnCl_3$ indicates the predominance of $\{MeSn(OH)(H_2O)_4\}^{2+}$ (54%), together with $MeSn(OH)_2Cl \cdot nH_2O$ at a lower level (37%), and a much reduced concentration of $MeSn(OH)Cl_2 \cdot 2H_2O$ (9%). The main feature of the spectrum is noticeably narrower, as are the satellites, just allowing resolution of ^{117}Sn and ^{119}Sn couplings. This narrowness is consistent with the final product of hydration under these conditions being $\{MeSn(OH)-(H_2O)_4\}^{2+}$.

Conclusion

^{1}H NMR spectroscopy at 400 MHz has enabled the resolution of peaks which were not resolvable at 90 MHz. These have been assigned to various hydrated methyltin species.

An important conclusion is that, in any environmental studies [20] involving aqueous methylation of tin species. ^{1}H NMR measurements are extremely important, but must be carried out at the highest possible magnetic fields, in order to minimise overlap of resonances. For example, it may be impossible to distinguish between such different species as $\{Me_2\text{-}Sn(H_2O)_4\}^{2+}$ and $MeSn(OH)Cl_2 \cdot 2H_2O$ (see Table II).

Acknowledgements

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