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An investigation of the base hydrolysis of methyl- and butyl-tin trichloride in aqueous solution by ^1H and ^{119}Sn NMR spectroscopy

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Abstract

The aqueous chemistry of monoalkyltin trihalides is not yet fully understood. This work has elucidated, by ^1H and ^{119}Sn NMR spectroscopy, the hydrolysis products present in aqueous solutions of monomethyl- and monobutyl-tin trichloride containing various mole ratios of NaOH. The initial product upon dissolution of $RSnCl_3$ in water (0.5 M) is $RSn(OH)Cl_2 \cdot 2H_2O$. At a mole ratio of $RSnCl_3$:NaOH of 1:1–2, two additional species are formed, $RSn(OH)_2Cl \cdot 2H_2O$ and $[RSn(OH)(H_2O)_4]^{2+}$. At a mole ratio of 1:3 short chain oligomers are produced, containing Sn–O–Sn linkages and pendant OH groups. At a mole ratio of 1:4, dehydration occurs between oligomers to form a cross-linked or branched polymer. At a ratio of 1:6 or above, depolymerisation has occurred to afford a monomer $RSn(OH)_3 \cdot 2H_2O$. In the case of R=Me the final hydrolysis product is unstable and undergoes disproportionation to yield $R_2Sn(OH)_2 \cdot 2H_2O$ and ultimately $Sn(OH)_6^{2-}$.

Introduction

Although organotin compounds have achieved a wide range of commercial applications [1], few of these involve monoorganotin derivatives. A number of such compounds have been found to be active hydrophobic agents [2–4] for building materials (limestone, bricks and concrete) and for cellulosic substrates [5] (cotton, paper and wood), but have not yet reached commercialisation. In addition, an aqueous mixture of a monoorganotin compound with an alkylglycoside has been shown to be effective as an ore flotation agent [6]. Both of these potential applications involve hydrolysis products of monoorganotin trihalides but the aqueous chemistry of these species is not well understood. In this work we report the results of an NMR spectroscopic study of the species formed following base hydrolysis, in aqueous solutions of methyl- and butyl-tin trichloride.

Experimental

Methyl- and butyl-tin trichloride were commercial samples and were used without further purification.

Solutions for NMR studies were prepared by adding, dropwise with vigorous stirring, the organotin trichloride to aqueous solutions (5 cm^3) containing the appropriate number of mole equivalents of NaOH. The overall concentration with respect to the organotin derivatives was 0.5 M. ^1H NMR spectra were recorded on a Bruker WH400 instrument at 400.13 MHz. Field frequency lock was to 10% wt./wt. internal D_2O. Chemical shifts are relative to external Me_4Si and are accurate to ±0.02 ppm. Proton–tin coupling constants, $^2J(^1H-^{117,119}Sn)$, are accurate to ± 1 Hz. The ^{117}Sn and ^{119}Sn satellites were, in most cases, unresolved and so average values are reported. ^{119}Sn NMR measurements were made on either a JEOL FX60Q or a Bruker WH400 instrument at 22.24 and 149.20 MHz, respectively under nuclear Overhauser suppressed conditions. Field frequency lock for the former instrument was to external D_2O and for the latter to 10% wt./wt. internal D_2O. Chemical shifts are relative to external Me_4Sn and are accurate to ±0.5 ppm.

Results and discussion

The results of the ^1H and ^{119}Sn NMR study of the 0.5 M aqueous solutions of $MeSnCl_3$ containing 0–6 mole equiv. of NaOH are given in Table 1. It should be noted that all of the ^{119}Sn chemical shifts, $\delta^{119}Sn$, are indicative of a six-coordinate tin atom geometry [7]. Thus, all species present in solution

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TABLE 1. ^{1}H and ^{119}Sn NMR data for aqueous solutions of 0.5 M $MeSnCl_3$ containing x mole equivalents of NaOH

x	pH	δ^1H (ppm)	Relative intensity[a] (%)	$^2J(^1H–^{117,119}Sn)$[b] (Hz)	δ^{119}Sn (ppm)	Compound[c]
0	1.25	0.85	100	128	−482	**1**
1	1.3	0.95	60	125	−482	**1**
		0.79	20	[d]	[e]	**3**
		0.73	20	[d]	−515	**2**
1.5	1.35	1.05	30	126	−481	**1**
		0.85	30	[d]	*c.* −478	**3**
		0.78	30	*c.* 114	−513	**2**
2	1.6	0.90	45	126	−476	**3**
		0.82	55	119	−515	**2**
3	6.6	0.64	[e]	112	−459[f]	**4**
		0.66	[e]	110	−462[f]	
		0.69	[e]	112	*c.* −464[f]	
		0.72	[e]	112	−467[f]	
4	12.5	0.34	100	106	−444	**5**
5	[g]	0.16	100	105	−446[h]	**5**
					−476[i]	**6**
6	13.5	0.10	100	105	−477	**6**

[a] Based on integration of ^{1}H NMR resonances.
[b] ^{117,119}Sn satellites were unresolved and $^2J(^1H–^{117,119}Sn)$ refers to the average value.
[c] For assignments, see Fig. 1.
[d] Not detected.
[e] Not measured, due to overlapping resonances.
[f] The ^{119}Sn resonance cannot be paired with corresponding ^{1}H resonances and are therefore only shown in numerical order.
[g] Not measured.
[h] Relative intensity = 10%, based on integration of ^{119}Sn NMR resonances.
[i] Relative intensity = 90%, based on integration of ^{119}Sn NMR resonances.

should have the required number of associated water molecules to attain this tin atom coordination number.

It has previously been shown[8] that dissolution of $MeSnCl_3$ in H_2O at a concentration of 0.5 M affords $MeSn(OH)Cl_2 \cdot 2H_2O$ as the sole species. Thus, compound **1** (Table 1 and Fig. 1) is ascribed to this. Similarly this earlier work demonstrated that, on lowering the concentration, two other species, i.e. $MeSn(OH)_2Cl \cdot 2H_2O$ and $[MeSn(OH)(H_2O)_4]^{2+}$ are progressively produced. In the present study the addition of the organotin to 1 and 2 mole equiv. of aqueous NaOH resulted in the formation of two additional species of relative amounts shown in Table 1. From the close similarity of NMR parameters, i.e. δ^1H, δ^{119}Sn and $^2J(^1H–^{117,119}Sn)$, between present and past studies, compounds **2** and **3** (Table 1 and Fig. 1) are ascribed to the neutral and cationic species, respectively.

Involved in the earlier assignments [8] of the possible hydrolysis products was a calculation of the magnitude of $^2J(^1H–^{117,119}Sn)$. Holmes and Kaesz [9] reported that the magnitude of the proton–tin coupling, $^2J(^1H–^{117,119}Sn)$, in $[Me_3Sn(H_2O)_2]^+$ and $[Me_2Sn(H_2O)_4]^{2+}$ (69 and 107 Hz, respectively) represents a %s character in each Sn–C bond orbital of 32 and 48%, respectively consistent with sp^2(33%s) and sp (50%s) hybridisation, respectively. Therefore the donation of electrons from the water molecules to tin does not appear to affect the %s character in the Sn–C bonds. If compounds **1** and **2** (Fig. 1) are treated similarly, they can be assumed to be sp^2d(pd) hybridised, with expected proton–tin couplings of approximately 52 Hz [9]. This is much less than the observed average coupling $^2J(^1H–^{117,119}Sn)$, of 128 and 119 Hz (Table 1), and the difference must be due to an increase in %s character of the Sn–C bond caused [10] by the electronegative Cl atoms or OH groups bonded to tin. Additive substituent effects to the proton–tin coupling constant in methyltin compounds have been reported previously [11]. From the couplings observed for $MeSn(OH)Cl_2 \cdot 2H_2O$ and $MeSn(OH)_2Cl \cdot 2H_2O$, increases of 28 and 19 Hz may be ascribed to the Cl atom and OH group, respectively.

This reasoning does not take into account the presence of oligomers containing Sn–O–Sn linkages, since no data are available to calculate the substituent effect of O–Sn moieties on the proton–tin coupling constant. Although such species containing Sn–O–Sn linkages have been isolated as hydrolysis products of monoalkyltin trihalides [12–14], it is believed that these are not formed by the addition of $MeSnCl_3$

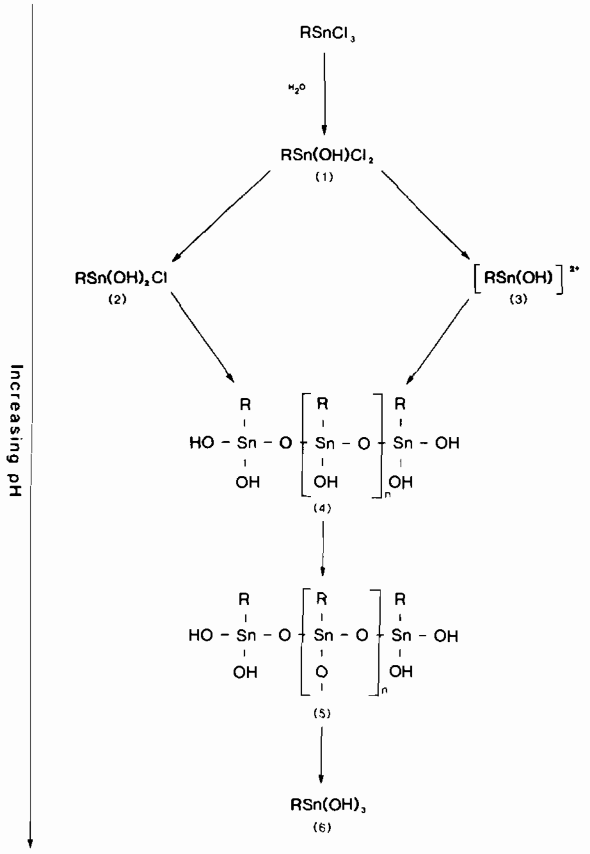

Fig. 1. Species present in aqueous solutions of alkyltin trichlorides/NaOH (0.5 M with respect to organotin compound).

to 2 mole equiv. of NaOH. If oligomers were formed, additional OH groups after 1 mole equiv. would not be removed from solution by bonding to tin and the pH would rise accordingly, whereas very little change is observed. However, the addition of $MeSnCl_3$ to 3 mole equiv. of NaOH produces a large increase in pH which does suggest the formation of oligomeric species. The ^1H NMR spectrum of this solution shows a feature of overlapping peaks consisting of four major resonances (Table 1). Similarly, four main resonances are observed in the ^{119}Sn NMR spectrum. Attempts were made to confirm the presence of Sn–O–Sn linkages by observation of tin–tin coupling interactions, but these were not seen, if present, due to the signal-to-noise ratios of the recorded spectra being of insufficient magnitude. Thus, although oligomers are believed to be present they must consist of short chains, i.e. $n \leqslant 5$ (Fig. 1), since longer chain species would afford simpler NMR spectra, due to the similarity of both Sn and H environments in the repeating unit.

Addition of the organotin trichloride to 4 mole equiv. of aqueous NaOH and subsequent NMR analysis revealed a single peak in both the ^1H and ^{119}Sn spectra. Furthermore, it was noted that the pH of the solution rose drastically (Table 1). These observations may be interpreted in terms of linking of terminal OH groups on the oligomers to form a cross-linked or branched polymer (compound **5**; Figure 1).

A ^{119}Sn NMR spectrum recorded for a solution containing a mole ratio of organotin to NaOH of 1:5 showed the same peak attributed to compound **5**, as well as a resonance at −476 ppm. The ^1H spectrum, however, showed just a single broad resonance (linewidth approximately 23 Hz) centred at 0.16 ppm. At a mole ratio of organotin to NaOH of 1:6 a single sharp resonance resulted in both the ^{119}Sn and ^1H spectra. The magnitude of the $^2J(^1H-^{117,119}Sn)$ coupling, as measured from the latter spectrum, is 105 Hz.

It was observed that during the mixing of the organotin to 3, 4 or 5 mole equiv. of aqueous NaOH, rapid stirring was required to avoid precipitation of the tin species, which is consistent with the formation of oligomers or polymers. In contrast, addition of the organotin to 6 mole equiv. of NaOH produced a species which was readily soluble. This observation suggests that depolymerisation has occurred and a monomer is produced, as has been reported previously for a dimethyltin species [15]. Possible monomeric species that may be present are $MeSn(OH)_3$, $MeSn(OH)_4^-$ and $MeSn(OH)_5^{2-}$. In the same way that coupling interactions were calculated for the early hydrolysis products, a similar treatment for the above species yields values of 110, 118 and 130 Hz, respectively. Therefore, by comparison with the experimental value of 105 Hz, the preferred final hydrolysis product is $MeSn(OH)_3$. From its ^{119}Sn NMR chemical shift (Table 1), this species should have a six-coordinate tin atom geometry, i.e. $MeSn(OH)_3 \cdot 2H_2O$.

It is of interest to note that the above solution is not stable, since a ^{119}Sn NMR spectrum recorded 2 weeks after preparation showed three distinct resonances (Fig. 2), of which that at −479 ppm is assigned to $MeSn(OH)_3 \cdot 2H_2O$. The peak at −167 ppm is ascribed to a dimethyltin species since a ^{119}Sn NMR spectrum recorded for a 0.5 M aqueous solution of Me_2SnCl_2 affords a single peak with the same chemical shift. On the basis of the work of Tobias *et al.* [15], the dimethyltin derivative present in this solution is $Me_2Sn(OH)_2 \cdot 2H_2O$. Similarly, the peak at −588 ppm (Fig. 2) is assigned to an inorganic tin species, since no line broadening was observed after re-recording the spectrum under conditions of proton coupling and a ^{119}Sn NMR spectrum of a 0.5 M aqueous solution of $Na_2Sn(OH)_6$ gives a similar peak with a chemical shift of −593 ppm. Therefore,

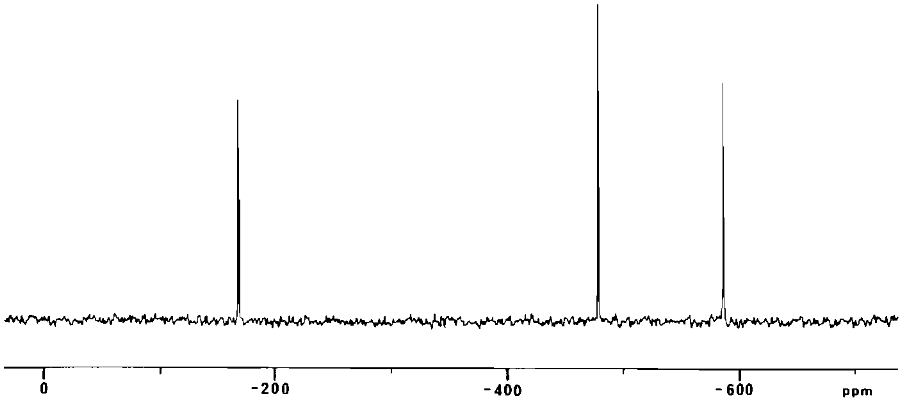

Fig. 2. ^{119}Sn NMR spectrum of 0.5 M aqueous solution of $MeSnCl_3$ containing 6 mole equiv. of NaOH, two weeks after preparation.

it is proposed that these products arise from a disproportionation reaction of the monomethyltin species, i.e.

$$2MeSn(OH)_3 \cdot 2H_2O \longrightarrow Me_2Sn(OH)_2 \cdot 2H_2O + Sn(OH)_4 \cdot 2H_2O$$

$$Sn(OH)_4 \cdot 2H_2O \xrightarrow{2OH^-} Sn(OH)_6^{2-}$$

To our knowledge this is the first observation of a disproportionation reaction involving a monoorganotin derivative.

Attempts to obtain information on the hydrolysis products of $BuSnCl_3$ were limited to studies by ^{119}Sn NMR, due to the complexity of the ^{1}H spectra. In addition, as a result of the reduced solubility of butyltins compared to methyltins [1] NMR spectra could only be recorded for solutions containing organotin to NaOH ratios of 1:0, 4, 5, and 6 (Table 2). The first hydrolysis product of $BuSnCl_3$ has been isolated and shown [16] to be $BuSn(OH)Cl_2 \cdot H_2O$, which exists in the solid-state as an OH-bridged dimer [8]. A ^{119}Sn NMR spectrum of 0.5 M $BuSnCl_3$ in water exhibits a single resonance at -490 ppm and is ascribed to the first hydrolysis product. This chemical shift is 8 ppm to low frequency of the analagous methyltin derivative and presumably reflects the increased electron donor ability of the butyl group. For the same reason, in CCl_4 a chemical shift separation of -12 ppm is observed between $MeSnCl_3$ (0.5 M; $\delta^{119}Sn = 22.3$ ppm) and $BuSnCl_3$ (0.5 M; $\delta^{119}Sn = 10.3$ ppm). Therefore, it would seem that a typical shift change upon substitution of a methyl group by a butyl moiety would be of this order. Consequently comparison of the tin chemical shifts reported in Tables 1 and 2 shows that the same trends are occurring. Therefore, it is believed that the species present in the butyltin solutions are analagous to those described for the methyltins (Fig. 1).

TABLE 2. ^{119}Sn NMR data for aqueous solutions of 0.5 M $BuSnCl_3$ containing x mole equivalents of NaOH

x	δ^{119}Sn (ppm)	Relative intensity[a] (%)	Compound[b]	$\Delta(\delta^{119}Sn)$[c] (ppm)
0	-490	100	1	-8
4	-462[d]	100	5	-18[e]
5	-459	36	5	-13
	-485	64	6	-9
6	-490	100	6	-13

[a] Based on integration of ^{119}Sn NMR resonances. [b] For assignments, see Fig. 1. [c] Chemical shift separation between the ^{119}Sn NMR resonances of aqueous solutions of 0.5 M $MeSnCl_3$ containing xNaOH and 0.5 M $BuSnCl_3$, containing xNaOH, see text. [d] Recorded on an aqueous solution of 0.25 M $BuSnCl_3 + 4$ mole equiv. NaOH, due to poor solubility of organotin product. [e] ^{119}Sn chemical shift separation between aqueous solutions of 0.5 M $MeSnCl_3$ containing 4NaOH and 0.25 M $BuSnCl_3$ containing 4NaOH.

Conclusions

This work has elucidated the species present in aqueous solutions of monoalkyltin trichlorides, upon the addition of various mole ratios of NaOH. The initial hydrolysis product on dissolution of the organotin trichloride in water is $RSn(OH)Cl_2 \cdot 2H_2O$. On increasing the pH, additional hydrolysis products are formed and these have been assigned to various monomeric (neutral and cationic) as well as oligomeric and polymeric (containing Sn–O–Sn linkages) derivatives. The final species formed at pH > 12.5 is $RSn(OH)_3 \cdot 2H_2O$.

In the case of R = Me, the final compound formed is unstable and undergoes disproportionation to form $R_2Sn(OH)_2 \cdot 2H_2O$ and ultimately $Sn(OH)_6^{2-}$.

This work has implications for the future potential use of organotin compounds as hydrophobic agents.

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