# The Characterisation of Triorganotin Hydroxides and of Bis(triorganotin) Oxides by Infrared and Mössbauer Spectroscopy

By **J. M. Brown, A. C. Chapman, R. Harper,** and **D. J. Mowthorpe,** Research Department, Albright & Wilson (Mfg) Ltd., Oldbury, Worcs.

Alwyn G. Davies * and **Peter J. Smith,** Christopher Ingold Laboratories, University College, 20 Gordon Street, London W.C.1

Bis(trialkyltin) oxides react with water at 0—5° to give the corresponding trialkyltin hydroxides. The oxides are characterised by a strong band in the i.r. spectra at 740—770 cm^{-1} [ν_{as}(SnOSn)] and by a Mössbauer quadrupole splitting of 1·18—1·63 mm s^{-1}, whereas the hydroxides show i.r. bands at 3610—3630 [ν(OH)] and 880—920 cm^{-1} (δOH), and quadrupole splittings of 2·78—2·99 mm s^{-1}. Trimethyl- and triphenyl-tin hydroxide are stable at room temperature, but triethyl-, tripropyl-, and tributyl-tin hydroxide, which are low-melting solids, are in equilibrium with the corresponding bis(trialkyltin) oxides and water.

TRIALKYLTIN hydroxides and bis(trialkyltin) oxides can be interconverted [equation (1)], but the relative stabilities of the two compounds, and the degree to which they have been characterised, vary greatly with the nature of the alkyl group.[1]

$$2R_3SnOH \rightleftharpoons R_3Sn \cdot O \cdot SnR_3 + H_2O \qquad (1)$$
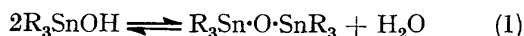
For example, trimethyltin hydroxide can be de-hydrated with sodium in benzene, but the oxide fumes in air as it is rehydrated back to the hydroxide. Bis-(tributyltin) oxide, on the other hand, is less readily hydrated, and, although it is the most common organotin oxide, its corresponding hydroxide has never been characterised; the reports that it is an infusible solid,[2] or a liquid b.p. 186—190° at 5 mmHg,[3] probably refer to dibutyltin oxide and bis(tributyltin) oxide respectively. Usually, both triaryltin hydroxides and the corresponding bis(triaryltin) oxides are available, but they are readily interconvertible,[4] and may be difficult to dis-tinguish.

Although the i.r. spectra of the bis(trialkyltin) oxides have been extensively studied, and most of the bands assigned, there is relatively little information about the related hydroxides.[5] A few Mössbauer spectra of organotin oxides and hydroxides have been recorded,[6] but the identity of the compounds, and particularly their freedom from carbonate, was sometimes question-able.

We have attempted to clarify this situation by study-ing the i.r. and Mössbauer spectra, and, to a lesser extent, the ^{1}H n.m.r. spectra of these compounds.

EXPERIMENTAL

Preparation of Organotin Compounds.—Bis(trimethyltin) oxide was prepared by treating trimethyltin hydroxide with sodium in benzene.[7] The samples of triphenyltin hydroxide and bis(triphenyltin) oxide which were used were those described by Bloodworth.[8] Triethyl-, tripropyl-, tributyl-,

and trioctyl-tin hydroxides were prepared by grinding or stirring together the oxide and water at 0—5°; the pre-paration of tributyltin hydroxide, which has not been described before, is typical.

Bis(tributyltin) oxide was slowly added dropwise into a large excess of water which was rapidly stirred at 4—5°. After 1 or 2 min, a sticky white solid separated. This was removed, dried rapidly between filter papers at *ca.* 0°, then loaded into the spectroscopic cells at low temperature. If the hydroxide was allowed to warm to room temperature, it separated into an upper layer of water and a lower layer of the oxide.

The bis(trialkyltin) carbonates, $(R_3SnO)_2CO$, R = Et, Pr, and Bu, were prepared by adding solid carbon dioxide, or passing carbon dioxide gas, into a solution of the corre-sponding oxide in light petroleum.

Melting or boiling points of the oxides and hydroxides are given in the Table, and are in general agreement with values in the literature.

Sampling Techniques.—The i.r. spectra were recorded of capillary films for liquids, or Nujol mulls for solids. The trialkyltin oxides and hydroxides readily absorb carbon dioxide from the air, and samples were handled in an atmosphere of dry nitrogen.

Mulls of tripropyltin hydroxide and of tributyltin hydr-oxide were prepared at low temperature. The mulling apparatus was placed in a dry glove-box, and the tempera-ture of the box lowered to *ca.* 2°. The mull was then pre-pared and quickly loaded into a low-temperature cell of conventional design, refrigerated with a mixture of alcohol and solid carbon dioxide.

Samples in sealed polyethylene cells were prepared simi-larly for Mössbauer spectroscopy.

Spectroscopy.—I.r. spectra were recorded using Perkin-Elmer 257, 337, or 457 instruments, calibrated as necessary with polystyrene. The Mössbauer spectrometer has been described;[9] spectra were recorded at 80 K using a stannic oxide source. N.m.r. spectra were recorded on an AEI RS2 spectrometer operating at 60 MHz.

DISCUSSION

Bis(trimethyltin) oxide and bis(triphenyltin) oxide were prepared by dehydrating the corresponding hydr-

[1] 'Organotin Compounds,' ed. A. K. Sawyer, Marcel Dekker, New York, 1971, ch. 4.

[2] Z. M. Manulkin, F. A. Yakubova, A. B. Kuchkarev, and A. M. Rashkis, *Uzbek. khim. Zhur.,* 1962, **6,** 52 (*Chem. Abs.,* 1963, **59,** 3942).

[3] R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.,* 1960, **60,** 459.

[4] R. West, R. H. Baney, and D. L. Powell, *J. Amer. Chem. Soc.,* 1960, **82,** 6269.

[5] T. Tanaka, *Organometallic Chem. Rev.,* 1970, **5,** 1.

[6] P. J. Smith, *Organometallic Chem. Rev.,* 1970, **5,** 373.

[7] T. Harada, *Sci. Papers Inst. Phys. Chem. Res., Tokyo,* 1940, **38,** 115.

[8] A. J. Bloodworth, *J. Organometallic Chem.,* 1970, **23,** 27.

[9] A. G. Davies, H. J. Milledge, D. C. Puxley, and P. J. Smith, *J. Chem. Soc.* (A), 1970, 2862; P. J. Smith, Ph.D. Thesis, University of London, 1970.

oxides, and triethyl-, tripropyl-, tributyl-, and trioctyl-tin hydroxides by hydrolysing the corresponding oxides with water between 0° and 5°. Triethyl-, tripropyl-, and tributyl-tin hydroxides were soft waxy solids with low melting points, and readily reverted on melting into the corresponding oxides and water, which separated into two layers; trioctyltin hydroxide was obtained as a thick milky-white oil, indicating partial separation of water even at 0°. Tripropyl-, tributyl-, and trioctyl-tin hydroxides were stored and handled at low temperature.

Precautions must also be taken to exclude carbon dioxide, or the bis(trialkyltin) carbonates, which are characterised by strong i.r. bands at 1360—1370 $[\nu_s(CO_2)]$ and 1530—1550 cm^{-1} $[\nu_{as}(CO_2)]$, are quickly formed. An i.r. spectrum reported earlier for trimethyltin hydroxide [10] is in fact that for bis(trimethyltin) carbonate,

that the crystal contains a chain of Me_3Sn and OH groups, with the oxygen almost equidistant between the tin atoms, and the Me_3Sn groups nearly planar, the plane being inclined at about 15° to that at right angles to the chain (I; R = Me); the whole chain is coiled into a distorted helix.

(I)
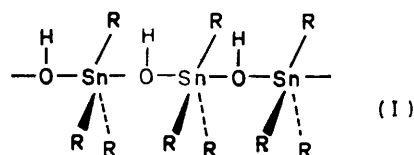
This compound can thus be used as a model for interpreting the spectra. The i.r. spectrum (see Table), which has been discussed before,[14,15] is consistent with

Characterisation of trialkyltin hydroxides and bis(trialkyltin) oxides [a]

		Infrared		Mössbauer				Infrared	Mössbauer	
	M.p.	ν(OH)	δ(OH)	δ	ΔE		B.p. (mmHg)	ν_{as}(SnOSn)	δ	ΔE
Me_3SnOH	117—118° (118—119) [b]	3620	920	1·20 (1·07— 1·19)	2·89 (2·71— 2·91) [f]	$(Me_3Sn)_2O$	86 (24)	740	1·10	1·18
Et_3SnOH	48—50 (49—50) [b]	3630	890	1·30 (1·35)	2·90 (3·00) [f]	$(Et_3Sn)_2O$	76—79 (0·1)	740	1·27	1·32
Pr_3SnOH	30—32 (34—35) [b]	3620 [c]	890/905 [c,e]	1·34	2·96	$(Pr_3Sn)_2O$	104—106 (0·1)	760	1·29	1·27
Bu_3SnOH	15—16	3630 [c]	880 [c]	1·37 (1·46)	2·99 (3·24) [g]	$(Bu_3Sn)_2O$	154—158 (0·25)	770	1·19 (1·10— 1·29)	1·60 (1·15— 2·40)
Oct_3SnOH	Oil			1·35	2·95	$(Oct_3Sn)_2O$	Oil	770	1·21	1·57
Ph_3SnOH	120	3610	898/913 [e]	1·26 (1·16— 1·35)	2·78 (2·70— 2·83) [f]	$(Ph_3Sn)_2O$	M.p. 117·5— 118	770	1·07 (1·08)	1·63 (2·15) [h]
$(PhCMe_2\cdot CH_2)_3\cdot SnOH$ [h]	(145—146)	(3620) [d]		(1·10)	(1·18)					

[a] Data from the literature are given in parentheses, i.r. in cm^{-1}, Mössbauer in mm s^{-1}. [b] J. G. A. Luijten and G. J. M. van der Kerk, ' Investigations in the Field of Organotin Chemistry,' Tin Research Institute, 1959. [c] I.r. spectra at −80°. [d] I.r. spectra on melt. [e] All bands ascribed to δ(OH) were broad, and those for Pr_3SnOH and Ph_3SnOH were split into doublets. R. A. Cummins (*Austral. J. Chem.*, 1965, **18**, 98) has shown that Ph_3SnOD shows a singlet at 673 cm^{-1}, and suggested that the doublet might be caused by Fermi resonance with an out-of-plane C—H vibration. [f] P. J. Smith, *Organometallic Chem. Rev.*, (A) 1970, **5**, 373. [g] V. V. Khrapov, *Cand. Diss. Inst. of Chem. Phys. Acad. Sci. U.S.S.R. (Moscow)*, 1965, quoted in ' Chemical Applications of Mössbauer Spectroscopy,' ed. R. H. Herber and V. I. Goldanskii, Academic Press, New York, 1968. [h] W. T. Reichle, *Inorg. Chem.*, 1966, **5**, 87. R. H. Herber, H. A. Stöckler, and W. T. Reichle, *J. Chem. Phys.*, 1965, **42**, 2447.

and the values in the literature for the Mössbauer parameters of tributyltin hydroxide are close to those which we have obtained for bis(tributyltin) carbonate (isomer shift, δ 1·48; quadrupole splitting, ΔE 3·24 mm s^{-1} see Table). The oxides and hydroxides also react with carbon disulphide,[11] and the spectrum reported for a solution of triethyltin hydroxide in carbon disulphide [12] is rather that for a mixture of bis(triethyltin) sulphide, carbonate, and dithiocarbonate.

The Mössbauer parameters, and the assignments of the significant i.r. bands, are given in the Table.

The only trialkyltin oxide or hydroxide for which an X-ray investigation has been carried out is trimethyltin hydroxide. Kasai, Yasuda, and Okawara [13] showed

this structure. The OH stretching vibration at 3620 cm^{-1} gives a sharp band, confirming the absence of hydrogen bonding; the assignment of the band at 920 cm^{-1} to the OH bending vibration is confirmed below for triethyltin hydroxide. The spectrum has a strong band at 550 cm^{-1} assigned to the asymmetric stretch of the Me_3Sn group, and the absence of the band at *ca*. 510 cm^{-1}, which is strong in the Raman spectrum, confirms that the Me_3Sn group is planar, and the symmetrical stretch of this group is i.r.-inactive. A broad band in the spectrum at 780—800 cm^{-1} does not indicate the presence of bis(trimethyltin) oxide, but is probably associated with the rocking mode of the methyl groups, which gives rise to the strongest band in the i.r. spectrum of trimethyltin chloride.[16]

[10] D. A. Kochkin, L. V. Lukyanova, and E. B. Reznikova, *J. Gen. Chem. (U.S.S.R.)*, 1963, **33**, 1892.
[11] A. J. Bloodworth, A. G. Davies, and S. C. Vasishtha, *J. Chem. Soc.* (C), 1967, 1309.
[12] L. Domange and J. Guy, *Ann. pharm. franç.*, 1958, **16**, 161.
[13] N. Kasai, K. Yasuda, and R. Okawara, *J. Organometallic Chem.*, 1965, **3**, 172.

[14] R. Okawara and K. Yasuda, *J. Organometallic Chem.*, 1964, **1**, 356.
[15] H. Kriegsmann, H. Hoffmann, and S. Pischtchan, *Z. anorg. Chem.*, 1962, **315**, 283.
[16] W. F. Edgell and C. H. Ward, *J. Mol. Spectroscopy*, 1962, **8**, 343.

Values for the Mössbauer quadrupole splitting which have been recorded before for compounds with the structure trans-R_3SnX_2 are in the range ca. 3·0—3·8 mm s^{-1}.[6] The observed value for trimethyltin hydroxide (ΔE 2·89 mm s^{-1}) is in reasonable accord with this, although the effect of tilting the Me_3Sn group out of the equatorial plane is not known.

There appears to be no evidence that bis(trialkyltin) oxides are other than tetrahedral monomers in the solid or in solution. In bis(trimethyltin) oxide, the band arising from the symmetrical stretch of the Me_3Sn group at 508 cm^{-1} is now present alongside that due to the asymmetrical stretch at 532 cm^{-1} in the i.r. spectrum, indicating that the Me_3Sn group is not planar. Bands associated with the OH group are absent, and $\nu_{as}(SnOSn)$ is present at 740 cm^{-1}.

The best model compound for predicting the Mössbauer parameters for tin in a tetrahedral environment R_3SnOR' is probably tris-(2-methyl-2-phenylpropyl)tin hydroxide, $(Me_2PhC \cdot CH_2)_3SnOH$, which, for steric reasons, cannot be dehydrated below 340°,[17] and is almost certainly unassociated. The Mössbauer spectrum shows the values of δ 1·13 mm s^{-1}, ΔE 1·08 mm s^{-1},[18] the quadrupole splitting, which is sensitive to stereochemistry, being different from that for the five-co-ordinate Me_3SnOH discussed above, but close to that for bis(trimethyltin) oxide (ΔE 1·18 mm s^{-1}). This would be compatible with the oxide, like tris-(2-methyl-2-phenylpropyl)tin hydroxide, being approximately tetrahedral and unassociated in the solid state.

The Mössbauer parameters of all the other trialkyltin hydroxides and bis(trialkyltin) oxides which we have investigated (see Table) are similar to those for trimethyltin hydroxide and bis(trimethyl)tin oxide respectively, suggesting that, in the solid state at 80 K, the hydroxides all have the structure (I) with five-co-ordinate tin, and the oxides are simple monomers containing four-co-ordinate tin. However, the i.r. spectra show that there are constitutional, though not structural, differences between the various hydroxides at higher temperatures.

The i.r. spectra of triethyltin hydroxide and of bis-(triethyltin) oxide have been discussed by Lohmann who reported that the band associated with the asymmetric stretching of the SnOSn group at 770 cm^{-1} was also present, though with diminished intensity, in the hydroxide, and suggested that the hydroxide should therefore be regarded as a hydrated oxide.[19] We have shown that this band can almost be made to disappear if a mixture of the oxide and an excess of water is ground together in an inert atmosphere, and the i.r. cell is prepared at low temperature. The band at 770 cm^{-1} can be accounted for adequately on the grounds of the balanced equation (1).

If deuterium oxide is used instead of water, the band at 3630 cm^{-1} shifts to 2665 cm^{-1}, and that at 890—645

cm^{-1}, whence $\nu(OH)/\nu(OD) = 1\cdot36$, and $\delta(OH)/\delta(OD) = 1\cdot38$, confirming the assignment of these two bands.

The ^1H n.m.r. spectra confirm that equilibration of oxide and hydroxide occurs readily by equation (1). Bis(triethyltin) oxide shows a complex A_3B_2 pattern centred at about τ 9, where $\tau A < \tau B$, and $\tau_B - \tau_A/J = ca.$ 0·6. The spectrum of the solid hydroxide was recorded over a narrow temperature range through the m.p. of 48—50°. As the temperature was increased, the broad bands gradually sharpened until at ca. 50° the spectrum was identical with that of bis(triethyltin) oxide, together with extra singlets at ca. τ 6·5 and 5, due to dissolved water, and dispersed water droplets, respectively, showing that the hydroxide had decomposed to the oxide and water at its m.p. Similar decomposition occurs when triethyltin hydroxide or tripropyltin hydroxide are dissolved in benzene or carbon tetrachloride at room temperature, when water comes out of solution as a separate layer, and the n.m.r. spectrum is identical with that of the corresponding oxide, with an extra peak due to water at about τ 5.

Tripropyl- and tributyl-tin hydroxides have progressively lower m.p.s, and undergo dehydration to the oxide, more readily than triethyltin hydroxide. If the Nujol mulls were prepared and scanned at −80°, the i.r. spectra were principally those of the hydroxides (see Table) with some broad hydrogen bonded OH bands at 3100—3400 and 3600 cm^{-1} respectively, and $\delta(OH_2)$ at 1630 and 1610—1620 cm^{-1} respectively. The $\nu(SnOSn)$ bands at 760 and 770 cm^{-1} respectively, were very weak. If these samples were allowed to warm to room temperature, the spectra obtained were largely those of a mixture of the appropriate oxide and water.

There has been some controversy over the identity of triphenyltin hydroxide and bis(triphenyltin) oxide. West, Baney, and Powell[4] reported that the hydroxide showed an OH band at 3647 cm^{-1} and a water band at 3681 cm^{-1}, but Kushlefsky, Simmons, and Ross[20] found that a band at 3646 cm^{-1} was present in both the hydroxide and the freshly made or intensively dried oxide, and suggested that this band cannot be explained simply as an OH stretching frequency.

More recently Bloodworth[8] has shown by thermogravimetric analysis that the hydroxide is quantitatively dehydrated between 80 and 100°. His initial hydroxide shows the presence of the bands listed in the Table, and none for water or for the $\nu(SnOSn)$ vibration at 770 cm^{-1}. The bands ascribed to the OH group are completely absent from the spectrum of the ultimate oxide, which is characterised by a strong band at 772 cm^{-1}. Apparently the absorption at 3646 cm^{-1} reported by Ross in the oxide must be ascribed to the presence of some impurity.

We conclude that the stability of trialkyltin hydroxide with respect to the corresponding oxides and water, by equation (1), follows the sequence of their m.p.s,

[17] W. T. Reichle, Inorg. Chem., 1966, 5, 87.
[18] R. H. Herber, H. A. Stöckler, and W. T. Reichle, J. Chem. Phys., 1965, 42, 2447.

[19] D. H. Lohmann, J. Organometallic Chem., 1965, 4, 382.
[20] B. Kushlefsky, I. Simmons, and A. Ross, Inorg. Chem., 1963, 2, 187.

i.e. Ph_3SnOH, $Me_3SnOH > Et_3SnOH > Pr_3SnOH > Bu_3SnOH$. In the solid state at 80 K they are probably co-ordinatively associated into linear polymers containing five-co-ordinate tin, and Mössbauer spectroscopy can readily differentiate between this configuration and the bis(trialkyltin) oxides which contain tetrahedral four-co-ordinate tin. When the hydroxides melt, or are dissolved or ground into mulls at room temperature, they disproportionate into oxide and water to an extent described by the above relative stabilities.