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AUTOASSOCIATION OF TRIBUTYLTIN DERIVATIVES OF PHOSPHORUS OXY-ACIDS: A ^{119}Sn , ^{31}P NMR AND $^{119\text{m}}\text{Sn}$ MÖSSBAUER STUDY

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Summary

^{119}Sn and ^{31}P NMR data at 30 and -50°C , together with $^{119\text{m}}\text{Sn}$ Mössbauer parameters, are reported for tris(tributyltin) phosphate, $(\text{Bu}_3\text{SnO})_3\text{PO}$, and two related compounds, $(\text{Bu}_3\text{SnO})_n\text{P}(\text{O})\text{Ph}_{3-n}$ ($n = 1, 2$). The results are discussed on the basis of a proposed common self-associated structure for this type of compound. The tris- and bis-tributyltin derivatives are shown to contain tin in 4- and 5-coordinate environments.

Introduction

Tris(tributyltin) phosphate, $(\text{Bu}_3\text{SnO})_3\text{PO}$, has recently been introduced as a fungicide in commercial organic solvent-based wood preservative formulations [1]. However, the structure of this compound has not been fully investigated, and, to our knowledge, neither tin-NMR nor Mössbauer studies have been carried out. ^{119}Sn and ^{31}P NMR and $^{119\text{m}}\text{Sn}$ Mössbauer data for this and two closely related molecules, $(\text{Bu}_3\text{SnO})_n\text{P}(\text{O})\text{Ph}_{3-n}$ ($n = 1, 2$), are now reported, and the results are discussed in terms of a proposed common structure.

Experimental

The tributyltin compounds, $(\text{Bu}_3\text{SnO})_3\text{PO}$ (I), $(\text{Bu}_3\text{SnO})_2\text{P}(\text{O})\text{Ph}$ (II), and $\text{Bu}_3\text{SnOP}(\text{O})\text{Ph}_2$ (III) have been prepared previously [2–7] and were synthesised in the present case by heating bis(tributyltin) oxide with the required mole ratio of the appropriate phosphorus oxy-acid in toluene, the water being removed azeotropically using a Dean and Stark apparatus. Satisfactory microanalytical data were obtained for all three compounds.

^{119}Sn and ^{31}P spectra were recorded, using 10 mm tubes, at 30 and -50°C , on JEOL FX60Q and JEOL FX90Q instruments respectively. Field frequency lock for the high temperature spectra was to external deuterium oxide, and, for the low temperature spectra, to approximately 20% internal deuteriotoluene. ^1H decoupled ^{119}Sn NMR spectra were measured under nuclear Overhauser suppressed conditions [8]; chemical shifts ($\delta(^{119}\text{Sn})$) are relative to Me_4Sn and are accurate to ± 0.5 ppm. ^{31}P chemical shifts ($\delta(^{31}\text{P})$) are relative to H_3PO_4 and are accurate to ± 0.1 ppm.

NMR spectra of compounds I and II were obtained from approximately 50% w/w solutions in toluene. Those of compound III were obtained from approximately a 10% w/w solution in the same solvent.

$^{119\text{m}}\text{Sn}$ Mössbauer spectra were recorded using a constant acceleration micro-processor spectrometer (from Cryophysics Ltd., Oxford) with a 512-channel data store. A $\text{Ba}^{119\text{m}}\text{SnO}_3$ source was used at room temperature and the samples were packed in perspex discs and cooled to -196°C , using a liquid nitrogen cryostat. The experimental error in the isomer shift (δ), quadrupole splitting (ΔE_Q) and linewidths (Γ) is ± 0.05 mm s^{-1} .

Results and discussion

^{119}Sn and ^{31}P NMR data for compounds I–III are presented in Tables 1 and 2 respectively

For the tris- and bis-triorganotin derivatives, two resonances are observed in the ^{119}Sn NMR spectra, with relative intensities of the high frequency to low frequency peaks of 2/1 and 1/1, respectively.

^{119}Sn NMR chemical shifts are indicative of coordination number [9] and the values recorded for these compounds are consistent with the presence of both 4- and 5-coordinate tin atom environments. Compound III, which has only one tributyltin moiety, shows a single tin resonance, characteristic of a 5 coordinate geometry for the tin atom. ^{119}Sn NMR spectra recorded at 30°C showed evidence of splitting arising from $^2J(^{119}\text{Sn}-\text{O}-^{31}\text{P})$ coupling, but this was poorly resolved, presumably due to dynamic processes. This was confirmed by the spectra recorded at -50°C ,

TABLE 1
 ^{119}Sn NMR DATA FOR COMPOUNDS I–III

Compound	Temperature ($^\circ\text{C}$)	$\delta(^{119}\text{Sn})$ (ppm)	$^2J(^{119}\text{Sn}-\text{O}-^{31}\text{P})$ (Hz)
I	30	88.2	^a
		-106.0	^a
	-50	93.1	66
		-110.0	^a
II	30	104.0	^a
		-85.8	^a
	-50	109.4	85
		-90.5	114
III	30	-65.4	^a
	-50	-70.8	116

^a Couplings were unresolved.

TABLE 2
 ^{31}P NMR DATA FOR COMPOUNDS I–III

Compound	Temperature ($^{\circ}\text{C}$)	$\delta(^{31}\text{P})$ (ppm)	$^2J(^{117,119}\text{Sn}-\text{O}-^{31}\text{P})^a$ (Hz)
I	30	-5.2	^b
	-50	^c	^b
II	30	3.5	^b
	-50	^c	101 (inner) 100–105 (outer) ^d
III	30	14.4	^b
	-50	^c	114 (inner) 114 (outer)

^a ^{117}Sn and ^{119}Sn satellites were unresolved and $^2J(^{117,119}\text{Sn}-\text{O}-^{31}\text{P})$ refers to the average value.

^b Satellites were unresolved. ^c Numerical values of $\delta(^{31}\text{P})$ were not measured. ^d A precise measurement of this coupling was not possible, due to the low intensity of the satellites.

which displayed narrower linewidths, with better resolved splittings (Table 1 and Fig. 1).

There were significant changes in the chemical shift values between 30 and -50°C . On reducing the temperature, the low frequency (5 coordinate) resonances moved to lower frequency and the high frequency (4 coordinate) resonances moved to higher frequency. This indicates that there are exchange processes occurring between different 4 coordinate sites and between different 5 coordinate sites at rates which are comparable to, or faster than, their respective NMR time scales. Exchange between 4- and 5-coordinate sites is slow on that time scale, as evidenced by the observation of separate resonances.

^{31}P NMR spectra of compounds I–III at 30°C did not show resolvable Sn–O–P couplings, although some additional line broadening at the base of the peak, which may be due to this effect, was observed. However, Ridenour and Flagg previously observed [6] $^2J(^{117,119}\text{Sn}-\text{O}-^{31}\text{P})$ couplings in the ^{31}P NMR spectra of $\text{Me}_3\text{-SnOP(O)Me}_2$ (102 Hz) and $(\text{Bu}_3\text{SnO})_2\text{P(O)Me}$ (83 and 110 Hz), in tetrahydrofuran, at -60 and -50°C respectively, and, in the present study, some couplings were

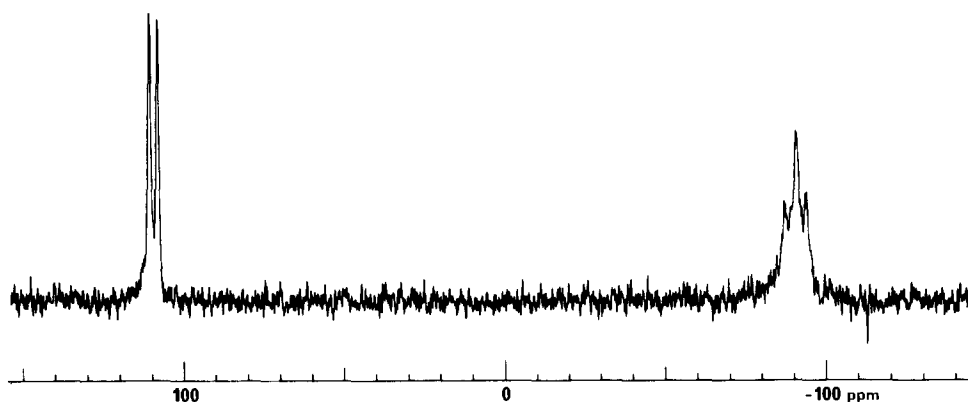
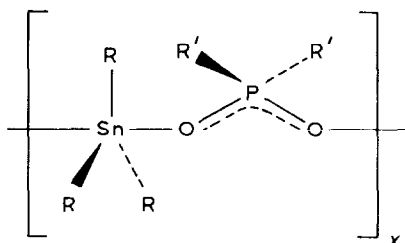


Fig. 1. ^{119}Sn NMR spectrum of $(\text{Bu}_3\text{SnO})_2\text{P(O)Ph}$, at -50°C .

resolvable (Table 2) at -50°C . For compound III, two sets of reasonably well resolved $^{117,119}\text{Sn}$ satellites (termed inner and outer) were observed. These are later ascribed to a doublet arising from coupling to one tin atom and the outer lines of a triplet arising from coupling to two tin atoms respectively. For II, two sets of partially resolved (inner and outer) satellites were observed and these are also discussed later. For I, however, no fine structure was resolvable, but the presence of satellites could be inferred from the line shape at the base of the resonance.

The ^{119}Sn and ^{31}P NMR spectra described above may be interpreted in terms of compounds I-III possessing the following auto-associated structure A, where $\text{R} = \text{Bu}$ and $\text{R}' = \text{Ph}$ or OSnBu_3 .



(A)

The splitting of the high frequency (4 coordinate) tin resonances (compounds I and II) into doublets arises from coupling to just one phosphorus atom, whereas the 5 coordinate signals (compounds I-III) are split into triplets, which implies equal coupling to two phosphorus atoms. The ^{31}P NMR spectra are also in accord with Structure A, as confirmed by the presence of inner and outer satellites, corresponding to the presence of phosphorus sites with one or two neighbouring magnetic tin nuclei. The component intensities in the reasonably well resolved multiplet, in the ^{31}P spectrum of III, at -50°C , were found to be in the ratio 0.01/0.24/1.00/0.24/0.01, which is consistent with the values 0.01/0.19/1.00/0.19/0.01, predicted from the isotopic abundances when some allowance for overlap is made.

In comparing tin-phosphorus couplings derived from ^{119}Sn and ^{31}P spectra, it should be noted that those from the latter are averaged between ^{117}Sn and ^{119}Sn nuclei and hence are expected to be ca. 2% smaller in magnitude. The tin-phosphorus splittings derived from ^{119}Sn and ^{31}P spectra (Tables 1 and 2) in some cases exhibited significant differences, even after allowing for the averaging effect described above. However, in III, where there is only 5 coordinate tin, consistent couplings of 116 and 114 Hz are observed in the ^{119}Sn and ^{31}P spectra respectively. In the ^{119}Sn spectrum of II, values of 85 Hz and 114 Hz are observed for $^2J(^{119}\text{Sn}-\text{O}-^{31}\text{P})$ for 4 coordinate and 5 coordinate tin respectively. The inner satellites in the ^{31}P spectrum of II have a splitting of 101 Hz. This is interpreted in terms of averaging of couplings due to exchange of tin atoms between 4- and 5-coordinate sites on a time scale which is comparable to or faster than the difference in J values displayed in the ^{119}Sn spectrum (29 Hz), but is less than 4436 Hz (199.5 ppm), corresponding to the shift difference in the ^{119}Sn spectrum. The above interpretation is preferred to that of having unresolved couplings of 114 and 85 Hz, since, despite the intrinsic linewidth of ca. 25 Hz, the lineshape of the satellites does not correspond to the asymmetric one expected from simple overlap

of unresolved satellites, which would be weighted (2/1) in favour of 5-coordinate splitting. For ^{119}Sn nuclei, exchange averaging of the couplings would give a value of $(85 + 114 + 114)/3 = 104$ Hz, which reduces to approximately 102 Hz when allowance for ^{117}Sn is made, and is in very good agreement with the observed value of 101 Hz.

From the ^{119}Sn NMR spectra of II and III, it is apparent that the Sn–O–P couplings are identical, within experimental error, for five coordinate tin. The outer satellites in the ^{31}P spectrum of III, at -50°C , are well resolved, with splitting consistent with coupling to two tin nuclei with the same J value, as found for the inner satellites. In II, the outer satellites are only just discernible and the J value deduced (ca. 100–105 Hz) corresponds to that for the inner satellites (101 Hz) within experimental error, and results from the averaging process described previously.

$^{119\text{m}}\text{Sn}$ Mössbauer data for the compounds studied are presented in Table 3, and are consistent with Structure A existing in the solid state.

The spectra recorded for compounds I and II consist of two overlapping doublets, one in the range expected for *trans*-trigonal bipyramidal R_3SnX_2 and the other for distorted tetrahedral R_3SnX configurations [10]. Compound III showed just one doublet, characteristic of the former stereochemistry.

It is possible that autoassociation, as illustrated in Structure A, could result in oligomers or polymers in either a linear or cyclic conformation. However, autoassociation of triorganotin oxygen derivatives has been found, in the solid state, to generally lead to linear structures [10]. No molecular weight data were obtained in the present study and so a precise value of the chain length could not be derived. However, in the ^{31}P spectrum of III, at -50°C , a second small peak was observed 5.25 ppm downfield from the main resonance, and this may be ascribed to the terminal phosphorus atoms in the linear structure, as suggested by Ridenour and Flagg [6] for $\text{Me}_3\text{SnOP(O)Me}_2$. The ratio of the intensity of this signal to the main ^{31}P resonance was ca. 1/20 and this would imply an average value of x , in Structure A, to be approximately 40.

The autoassociation involving $-\text{Sn}-\text{O}-\text{M}-\text{O}-\text{Sn}-$ ($\text{M} = \text{P}$) links, is a further example of that recently proposed for the bis(trialkyltin) carbonates ($\text{M} = \text{C}$) [11]. The equivalence of the chain M–O bonds, in solution, is confirmed by observation of equal phosphorus–tin coupling constants, a feature not available in the previous case [11]. It therefore seems that the structural features ascribed to compounds I–III, in solution, may be applicable to a wide variety of trialkyltin derivatives of other oxy-acids, which have the O–M–O structural sub-unit where $\text{M} = \text{C}, \text{N}, \text{S}, \text{P}$.

TABLE 3
 $^{119\text{m}}\text{Sn}$ MÖSSBAUER DATA FOR COMPOUNDS I–III

Compound	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ_1 (mm s^{-1})	Γ_2 (mm s^{-1})
I	1.36	2.57	1.10	1.10
	1.37	3.74	0.88	0.92
II	1.37	2.76	1.09	1.06
	1.40	3.82	0.98	1.06
III	1.43	3.83	0.99	0.99

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