A ^{119m}Sn Mössbauer and ^{119}Sn NMR Spectroscopic Study of Some Triorganotin Alkanesulphonates

STEPHEN J. BLUNDEN and ROBIN HILL

International Tin Research Institute, Perivale, Greenford, UB6 7AQ, U.K.

Received November 7, 1983

^{119m}Sn Mössbauer data for the triorganotin alkane/arene sulphonates, R_3SnOSO_2R' (where R = Bu; R' = Me, Et, C_6H_4Me-4 and R = Ph; R' = Et, Ph) are reported, together with ^{119}Sn NMR data for Bu_3SnOSO_2R (where R = Me, Et) and are consistent with the neat compounds having an infinite chain polymeric structure in which the sulphonate groups bridge planar R_3Sn moieties. In aqueous solution, ^{119}Sn NMR spectroscopy suggests that tributyltin methane- and ethane-sulphonate form a common hydrated cationic species, $\{Bu_3Sn(H_2O)_2\}^+$. In addition, the aqueous solubilities of these two compounds, as well as Ph_3SnOSO_2R (where R = Et and Ph) are reported.

Introduction

Tri-*n*-butyl- and triphenyl-tin compounds are widely used industrially in biocidal applications [1], since, in general, they possess excellent biological activity against most types of fungi and Gram-positive bacteria [1–3]. However, the compounds in industrial use, so far, have the disadvantage of having a very low aqueous solubility [4] {*e.g.* ~20 p.p.m. for bis(tributyltin) oxide at 25 °C}, and this has precluded their use for biological applications which require an aqueous carrier, where a concentration of 0.5–1.0% of the triorganotin compound would normally be required.

One way to overcome this problem has been to emulsify the tributyltin biocide, such as bis(tributyltin) oxide, with a suitable quaternary ammonium salt, to produce a water-dispersible concentrate [5–7].

An alternative approach has been to synthesise a discrete, water-soluble, tributyltin biocide [8–13], and, to date, those compounds having the highest aqueous solubility have been found to be the tributyltin alkanesulphonates, Bu_3SnOSO_2R (R = Me, Et) [12, 13]. More recently, these two compounds have been shown to possess excellent activity against wood destroying fungi when applied to a wood substrate in aqueous solution [14, 15]. In addition, tributyltin methanesulphonate has been bioassayed against the adult snail, *Biomphalaria glabrata*, and was found to be comparable in molluscicidal activity to that of bis(tributyltin) oxide [16]. In view of their potential use as water-based biocides, we now report ^{119m}Sn Mössbauer and ^{119}Sn NMR spectroscopic data for tributyltin methane- and ethane-sulphonate and related molecules.

Experimental

The tributyl- and triphenyl-tin alkane- and arene-sulphonates were prepared according to previously published procedures [10, 13].

^{119m}Sn Mössbauer spectra were obtained using a constant acceleration microprocessor spectrometer (from Cryophysics Ltd., Oxford) with a 512-channel data store. A $Ba^{119m}SnO_3$ source was used at room temperature and samples were packed in perspex discs and cooled to 80 K using a liquid nitrogen cryostat.

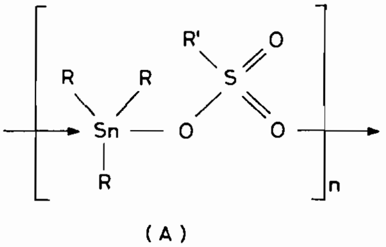
^{119}Sn NMR spectra were recorded on either JEOL FX90Q or FX60Q instruments under nuclear Overhauser suppressed conditions [17], using 10 mm tubes. Field frequency lock was to external D_2O.

U.V. Absorption spectra were recorded on a Bausch and Lomb Spectronic 505 instrument.

Aqueous solubilities were determined according to a previously published method [13].

Results and Discussion

The structure of the triorganotin alkane- and arene-sulphonates, in the pure compounds, has previously been suggested [13, 18] to be a self-associated polymer (A), with planar R_3Sn groups:



(A)

The Mössbauer parameters of some tributyl- and triphenyl-tin sulphonates are given in Table I, and are fully consistent with this structure. The large quadrupole splittings, $\Delta E_Q = 3.90-4.46$ mm s^{-1}, are indicative [1] of an infinite chain polymeric structure in the solid, in which the sulphonate groups bridge planar R_3Sn moieties. ^{119}Sn NMR chemical shifts, $\delta(^{119}Sn)$, are indicative of coordination number [19], in the liquid state, four coordinate organotin compounds {*e.g.* $(Bu_3Sn)_2O$; $\delta(^{119}Sn) = 82.8$ p.p.m. [20]} having chemical shifts to low field of five coordinate species (*e.g.* Bu_3Sn(8-hydroxyquinolinate); $\delta(^{119}Sn) = 29$ p.p.m. [19]). Therefore, the $\delta(^{119}Sn)$ values of 48.6 and 46.2 p.p.m. (Table II) recorded for Bu_3SnOSO_2Me and Bu_3SnOSO_2Et respectively are consistent with the five coordinate tin atom geometry present in (A).

TABLE I. ^{119m}Sn Mössbauer Data for R_3SnOSO_2R' Compounds.

Compound	δ (mm s^{-1})	ΔE_Q (mm s^{-1})
Bu_3SnOSO_2Me	1.51^a	4.14^a
Bu_3SnOSO_2Et	1.48^a	4.26^a
$Bu_3SnOSO_2C_6H_4Me$-4	1.56^b	4.46^b
Ph_3SnOSO_2Et	1.36^b	3.98^b
Ph_3SnOSO_2Ph	1.38^c	3.90^c

^{a}Error = ±0.02 mm s^{-1}. ^{b}Error = ±0.05 mm s^{-1}. ^{c}Reference 18.

TABLE II. ^{119}Sn NMR Chemical Shifts.

Compound	Solvent	Concentration	$\delta(^{119}Sn)^a$ (p.p.m.)
Bu_3SnOSO_2Me	Neat	–	48.6^b
Bu_3SnOSO_2Me	H_2O	1% w/v	21.8^b
Bu_3SnOSO_2Et	Neat	–	46.2^b
Bu_3SnOSO_2Et	H_2O	1% w/v	21.5^b
Me_3SnCl	H_2O	1% w/v	40.1^b
Me_3SnCl	CCl_4	5 M	164^c
$Me_2BuSnCl$	Neat	–	157.1^c
Bu_3SnCl	CCl_4	^{d}	141^c

^{a}Relative to Me_4Sn. ^{b}Error = ±0.5 p.p.m. ^{c}Reference 19. ^{d}Not reported.

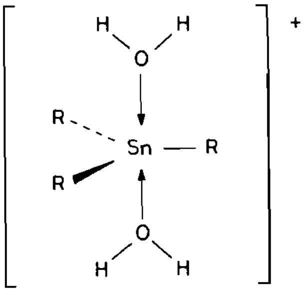
The aqueous solubilities, at 25 °C, of Bu_3SnOSO_2R (R = Me and Et) have been reported [13] to be in the range 1–2% w/v. However, present evaluations of the solubility of these compounds, together with data for the triphenyltin derivatives, Ph_3SnOSO_2R (R = Et and Ph), are given in Table III.

TABLE III. Aqueous Solubilities.

Compound	% w/v Solubility of compounds at 25 °C		
	After 1 day	After 7 days	After 28 days
Bu_3SnOSO_2Me	2.8	3.1	3.2
Bu_3SnOSO_2Et	2.4	2.9	3.1
Ph_3SnOSO_2Et	0.1	^{a}	^{a}
Ph_3SnOSO_2Ph	0.1	^{a}	^{a}

^{a}Not measured.

^{119}Sn NMR spectra were recorded for aqueous solutions of Bu_3SnOSO_2Me and Bu_3SnOSO_2Et, and, additionally, for Me_3SnCl in water (Table II). It can be seen that the chemical shift values of the two tributyltin alkanesulphonates are approximately 20 p.p.m. to high field of that of Me_3SnCl in water. A shift of 20–30 p.p.m. to high field is often found to occur upon substitution of the methyl groups in a trimethyltin species by n-butyl radicals ($\delta(^{119}Sn)$ values of $Me_2BuSnCl$ le$_3$BuSnCl and Bu_3SnCl are included in Table II for comparison). Therefore, since it is known [21, 22] that Me_3SnCl, in water, forms a hydrated trimethyltin cation, $\{Me_3Sn(H_2O)_2\}^+$, it is proposed that the organotin species present in aqueous solutions of tributyltin alkanesulphonates is the hydrated tributyltin cation $\{Bu_3Sn(H_2O)_2\}^+$, and this has recently been demonstrated [23] crystallographically, in the salt of $\{Bu_3Sn(H_2O)_2\}^+\{C_5(CO_2Me)_5\}^-$, to have structure (B; R = Bu).



(B)

The U.V. absorption spectrum of an aqueous solution of Bu_3SnOSO_2Et ($\lambda_{max} \approx 210$ nm) was similar to that of Me_3SnCl in water ($\lambda_{max} \approx 208$ nm), providing further evidence for the existence of the hydrated tributyltin cationic species (B; R = Bu).

The biological activities of tributyltin methane- and ethane-sulphonate, when impregnated in aqueous solution into Scots pine sapwood, towards two wood destroying fungi, *Coniophora puteana* and *Coriolus versicolor*, have been shown to be similar [15]. This indicates that the anionic sulphonate moiety has little effect on their fungitoxicity, and this may now be rationalised by the formation of a common cationic species in solution, *i.e.* $\{Bu_3Sn(H_2O)_2\}^+$.

Acknowledgements

We wish to thank the International Tin Research Council, London, for permission to publish this paper and Dr. P. J. Smith of the International Tin Research Institute for helpful comments on the manuscript.

References

1 A. G. Davies and P. J. Smith, in 'Comprehensive Organometallic Chemistry', eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press, Oxford (1982), Ch. 11, p. 519.

2 A. K. Sijpesteijn, J. G. A. Luijten and G. J. M. van der Kerk, in 'Fungicides: An Advanced Treatise', ed. D. C. Torgeson, Academic Press, New York (1969), Vol. 2, p. 331.

3 B. A. Richardson, *Rec. Brit. Wood Preserv. Assn. Ann. Conv.*, Cambridge, p. 37 (1970).

4 S. J. Blunden, L. A. Hobbs and P. J. Smith, in 'Environmental Chemistry: Vol. III', ed. H. J. M. Bowen, Royal Society of Chemistry Specialist Periodical Report (1984) in press.

5 B. A. Richardson, *Stone Ind.*, *8*, 2 (1973).

6 B. A. Richardson and T. R. G. Cox, *Tin and Its Uses, 102*, 6 (1974).

7 E. W. B. Da Costa and O. Collett, *Mat. und Org., 14*, 131 (1979).

8 A. J. Crowe and P. J. Smith, *Inorg. Chim. Acta, 19*, L7 (1976).

9 A. J. Crowe, P. J. Smith and P. G. Harrison, *J. Organomet. Chem., 204*, 327 (1981).

10 A. J. Crowe, *Ph.D. Thesis*, University of London (1980).

11 H. O. Wirth, H. J. Lorenz and H. H. Friedrich, *U.S. Patent*, 3,933,877 (1976).

12 H. Shioyama, Y. Kuriyama and R. Suzuki, *Jap. Patent*, 18,449 (1976).

13 S. J. Blunden, A. H. Chapman, A. J. Crowe and P. J. Smith, *Internat. Pest Control, 20*, 5, July/Aug. (1978).

14 R. Hill, P. J. Smith, J. N. R. Ruddick and K. W. Sweatman, *14th Int. Res. Group Wood Pres. Meet.*, Austral., Doc. No. IRG/WP/3229, {*I.T.R.I. Public No. 629*} (1983).

15 R. Hill, P. J. Smith and J. N. R. Ruddick, *Int. J. Wood Pres.*, in press (1983).

16 P. J. Smith, A. J. Crowe, V. G. K. Das and J. Duncan, *Pestic. Sci., 10*, 419 (1979).

17 S. J. Blunden, A. Frangou and D. G. Gillies, *Org. Mag. Res., 20*, 170 (1982).

18 P. G. Harrison, R. C. Phillips and J. A. Richards, *J. Organomet. Chem., 114*, 47 (1976).

19 P. J. Smith and A. P. Tupčiauskas, in 'Annual Reports on NMR Spectroscopy', ed. G. A. Webb, Academic Press, London (1978), Vol. 8, p. 291.

20 S. J. Blunden, P. J. Smith, P. J. Beynon and D. G. Gillies, *Carbohydr. Res., 88*, 9 (1981).

21 R. S. Tobias, in 'Organometals and Organometalloids: Occurrence and Fate in the Environment', eds. F. E. Brinckman and J. M. Bellama, *Am. Chem. Soc. Symp. Ser., 82*, 130 (1978).

22 F. E. Brinckman, G. E. Parris, W. R. Blair, K. L. Jewett, W. P. Iverson and J. M. Bellama, *Environ. Health Perspect., 19*, 11 (1977).

23 A. G. Davies, J. P. Goddard, M. B. Hursthouse and N. P. C. Walker, *J. Chem. Soc. Chem. Commun.*, 597 (1983).