Auto-association in Organotin Compounds: Butyltin Trialkoxides

By **John D. Kennedy**,*† Department of Chemistry, University of London, King's College, Strand, London WC2R 2LS
William McFarlane, Peter J. Smith, and **Raymond F. M. White,** Department of Chemistry, City of London Polytechnic, Sir John Cass School of Science and Technology, Jewry Street, London EC3N 2EY
Les Smith, Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ

The hitherto unreported series of n-butyltin trialkoxides, $Bu^nSn(OR)_3$, where R = Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, and neopentyl, has been prepared. ^{119}Sn Chemical shifts at several dilutions and temperatures have been measured by heteronuclear magnetic double resonance, and are discussed in terms of changes in co-ordination number of the tin. These depend upon the steric effect of the alkoxy-groups.

Previously we [1] and other groups [2-4] have determined ^{119}Sn chemical shift values in diverse selections of organotin compounds, often with little regard for a systematic approach except for the simplest and most readily available compounds. However, care must be exercised in the direct interpretation of measured ^{119}Sn chemical shifts: the tendency of organotin compounds which are substituted by electronegative groups to take part both in co-ordination with solvent molecules and in auto-association means that earlier values must be regarded with caution as they may relate to indefinite conditions. Any change in co-ordination about the tin results in a change of bond hybridisation and electron density at the tin atom, and this can result in a concomitant change in the nuclear shielding. Isolated values for ^{119}Sn chemical shifts determined under ambient temperature conditions and at convenient dilutions in convenient solvents may therefore often have little significance for absolute comparisons.

In the initial work on organotin compounds by Burke and Lauterbur [5] variations in chemical shift with solution conditions were noted. Subsequently these were examined in greater detail by Hunter and Reeves [2] and more recently the greater sensitivity realisable by heteronuclear double resonance techniques has permitted a more exhaustive investigation of solvent interactions using trimethyltin chloride and triethyltin chloride as model compounds.[6] It is generally accepted that solvents such as benzene, carbon tetrachloride, and dichloromethane show no tendency for co-ordination to tin, and act essentially as diluents.

The fact that tin magnetic shielding is sensitive to the co-ordination number of the tin atom permits the use of ^{119}Sn chemical shift measurements in the study of the auto-association of organotin compounds.[7] Results obtained by us have been reported for di- and tri-n-butyltin alkoxides,[8] and some monoalkyltin compounds,[9] and in this paper we describe the extension of these studies to include the n-butyltin trialkoxides.

Only eight organotin trialkoxides have been characterised to date: the trimethoxides and the triethoxides of methyl-, ethyl-, n-butyl- and phenyl-tin. All were prepared by alcoholysis of the appropriate trisdiethylamino-organostannane, and conclusions regarding the polarity of the structures were drawn from a study of the i.r. spectra.[10]

EXPERIMENTAL

Butyltin trialkoxides were all made by the same method and purified by distillation under reduced pressure. The procedure for butyltin tri-s-butoxide is described. $BuSn(NEt_2)_3$ (3·6 g, 9·2 mmol) was dissolved in benzene (Na dry; 8 ml) and Bu^sOH (3·0 ml, 2·4 g, 32·7 mmol) added slowly with stirring. Heat was evolved. The more volatile components were removed under reduced pressure and the product was distilled out, b.p. 86—88° at 0·08 mmHg, as a clear liquid, which was purified by redistillation, b.p. 78—80° at 0·005 mmHg.

Table 1

Physical properties and analytical data [a]

Compound	B.p. (° C/mmHg)	Calc (%) C	Calc (%) H	Found (%) C	Found (%) H
$BuSn(OEt)_3$	119—121/0·005 [b]				
$BuSn(OPr^n)_3$	131—133/0·004	44·2	8·5	44·3	8·8
$BuSn(OBu^n)_3$	143—145/0·003	48·6	9·2	48·8	9·5
$BuSn(OBu^i)_3$	119—121/0·004 [c]	48·6	9·2	48·7	9·6
$BuSn(O{-}neopentyl)_3$	86—88/0·003 [d]	52·2	9·7	52·0	9·9
$BuSn(OPr^i)_3$	73—75/0·005 [e]	44·2	8·5	44·0	8·5
$BuSn(OBu^s)_3$	78—80/0·005	48·6	9·2	48·8	9·4
$BuSn(OBu^t)_3$	57—59/0·004	48·6	9·2	48·4	9·3

[a] Analytical data given only for new compounds. [b] Lit.,[10] 130° at 0·1 mmHg. [c] M.p. 58—62°. [d] M.p. 84—86°. [e] M.p. 39—41°.

Analytical data for new compounds and physical properties are presented in Table 1. Butyl trisdiethylaminostannane and butyltin trialkoxides were all prepared, manipulated, and stored under an atmosphere of dry nitrogen.

---

† *Present address*: Department of Chemistry, City of London Polytechnic, Sir John Cass School of Science and Technology, Jewry Street, London EC3N 2EY.

[1] A. G. Davies, P. G. Harrison, J. D. Kennedy, T. N. Mitchell, R. J. Puddephatt, and W. McFarlane, *J. Chem. Soc.* (*C*), 1969, 1136.

[2] B. K. Hunter and L. W. Reeves, *Canad. J. Chem.*, 1968, **46**, 1399.

[3] A. P. Tupčiauskas, N. M. Sergeyev, and Yu. A. Ustynyuk, *Org. Magnetic Resonance*, 1971, **3**, 655.

[4] P. G. Harrison, S. E. Ulrich, and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1971, **93**, 5398.

[5] J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 326.

[6] V. N. Torocheshnikov, A. P. Tupčiauskas, N. M. Sergeyev, and Yu. A. Ustynyuk, *J. Organometallic Chem.*, 1972, **35**, C25.

[7] See, for example, A. G. Davies, L. Smith, P. J. Smith, and W. McFarlane, *J. Organometallic Chem.*, 1971, **29**, 245 and references cited therein.

[8] P. J. Smith, R. F. M. White, and L. Smith, *J. Organometallic Chem.*, 1972, **40**, 341.

[9] A. G. Davies, L. Smith, and P. J. Smith, *J. Organometallic Chem.*, 1972, **39**, 279.

[10] J. Lorberth and M. R. Kula, *Chem. Ber.*, 1964, **97**, 3444.

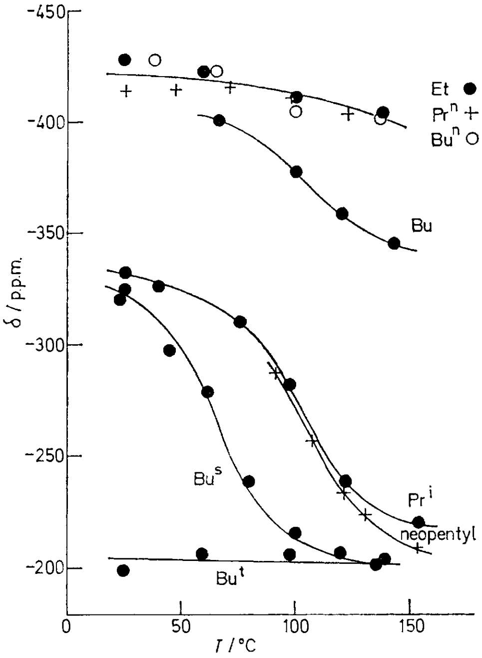
^{119}Sn Chemical shifts were obtained by ^{1}H-{^{119}Sn} double resonance using a JEOL C60-H spectrometer operating at 60 MHz and modified with an additional coil in the probe. The ^{119}Sn frequency at 22·37 MHz was supplied by a Schlumberger frequency synthesiser FS-30 and the detailed technique is described elsewhere.[1] Chemical shifts (Table 2) are expressed relative to $Me_4\,{}^{119}Sn = 0$; an algebraic increase in chemical shift δ corresponds to a decrease in shielding of the Sn nucleus.

RESULTS AND DISCUSSION

The butyltin trialkoxides were made by the alcoholysis of butyltrisdiethylaminostannane according to the method used by Lorberth and Kula [10] for the preparation of mono-organotin ethoxides and methoxides. Yields were essentially quantitative. The butyltin trialkoxides,

$$\mathrm{Bu^nSn(NEt_2)_3 + 3ROH \xrightarrow{-\Delta} Bu^nSn(OR)_3 + 3Et_2NH} \qquad (1)$$

apart from the trimethoxide,[10] are colourless, low-melting solids or liquids, and there is significant variation in viscosity among individual members of the series. All are very susceptible to atmospheric hydrolysis, the apparent order of susceptibility for the undiluted compounds being tertiary alkoxy > secondary alkoxy > primary alkoxy, but they are thermally stable and underwent no significant decomposition over 2 h at 150°.



Variation with temperature of the ^{119}Sn chemical shifts of the n-butyltin trialkoxides, $Bu^nSn(OR)_3$, where R = Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, and neopentyl, in p.p.m. relative to $Me_4\,{}^{119}Sn = 0$

The ^{119}Sn n.m.r. chemical shifts for butyltin triethoxide, tri-n-propoxide, tri-isopropoxide, tri-n-butoxide, tri-isobutoxide, tri-s-butoxide, tri-t-butoxide, and tri-neopentoxide, determined at various temperatures for the neat liquid, and at 25° for various dilutions, are given in Table 2. The temperature variations are presented graphically in the Figure.

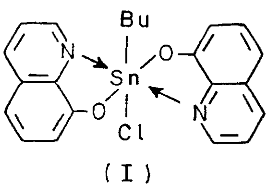
TABLE 2

^{119}Sn Chemical shifts of n-butyltin trialkoxides (p.p.m. relative to Me_4Sn)

Compound	Neat liquid T/° C	$-\delta$	Solution in C_6H_6 at 25° Concn. (mol %)	$-\delta$
$BuSn(OEt)_3$	25	428 ± 14		
	60	423 ± 5	48	432 ± 9
	100	412 ± 5	33	432 ± 9
	138	405 ± 5	16	432 ± 9
$BuSn(OPr^n)_3$	25	414 ± 10		
	47	415 ± 9	32	396 ± 9
	71	417 ± 5	23	387 ± 5
	99	412 ± 5	18	387 ± 9
	122	405 ± 5		
$BuSn(OBu^n)_3$ [a]	38	428 ± 14		
	65	423 ± 9	38	418 ± 9
	100	406 ± 9	22	405 ± 9
	138	405 ± 5	12	387 ± 9
$BuSn(OBu^i)_3$	66	401 ± 5		
	100	378 ± 5	44	397 ± 10
	120	360 ± 5	27	397 ± 10
	143	347 ± 5	16	392 ± 14
$BuSn(OPr^i)_3$	25	333 [b]		
	40	327 ± 2	76	330 ± 5
	76	311 ± 5	46	327 ± 5
	97	284 ± 2	20	323 ± 5
	122	240 ± 5	10	307 ± 10
	154	222 ± 9		
$BuSn(OBu^s)_3$	23	321 ± 2	Neat	325 ± 5
	45	298 ± 5	41	312 ± 5
	62	280 ± 2	32	298 ± 5
	80	240 ± 14	25	284 ± 5
	100	217 ± 2	19	275 ± 5
	120	209 ± 5		
	140	206 ± 5		
$BuSn(OBu^t)_3$	25	200 ± 5		
	60	208 ± 5	33	199 ± 5
	98	208 ± 5	18	199 ± 5
	136	204 ± 5	12	199 ± 5
$BuSn(O{-}neopentyl)_3$	92	289 ± 2		
	108	259 ± 2		
	122	236 ± 5		
	131	227 ± 2	Dilution studies not performed	
	153	212 ± 2		

[a] M.p. 58—62°. [b] Extrapolated from dilution curve (m.p. 39—41°).

The n-butyltin trialkoxides exhibit a substantial range of ^{119}Sn chemical shift values, from *ca.* −205 for the tri-t-butoxide to *ca.* −425 p.p.m. for the linear chain alkoxides. It has generally been found that co-ordinative association results in a shift of the ^{119}Sn resonance to higher field, and it is probable that the high field shift of δ *ca.* −425 p.p.m. is indicative of six-co-ordination in the butyltin trialkoxides. This is confirmed by the fact that the monoalkyltin compound butylchlorotin dioxinate (I), in which six-co-ordination



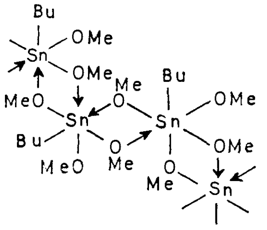
(I)

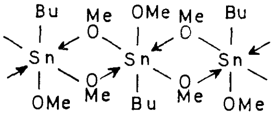
is expected, exhibits a similarly high-field ^{119}Sn chemical shift value (δ -395 ± 5 p.p.m. for a saturated solution in CH_2Cl_2). The higher viscosity of those butyltin trialkoxides which have high field chemical shifts suggests that six-co-ordination may involve an oligomeric or polymeric degree of interaction. The low-field value of -205 p.p.m. for the tri-t-butoxide, which is a very mobile oil, can be ascribed to essentially monomeric four-co-ordination. This is confirmed by the failure of the chemical shift to change on heating or dilution. This implies that the steric effect of the t-butoxy-groups is so large that any possible co-ordinative association is totally inhibited at room temperature and above. This parallels the behaviour of the similarly monomeric di-n-butyltin di-t-butoxide,[8] and similar behaviour is also observed in the tetra-t-alkoxides of Group IVB and of Group IVA metals.[11-13]

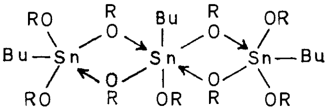
Trialkoxide chemical shifts between these two extremes therefore indicate associative equilibria, which are rapid on the n.m.r. time scale, with a mean degree of co-ordination between four and six. The extent of association of the trialkoxides, which involves an increase of co-ordination number, would be expected to decrease with increasing dilution and/or temperature, as is observed. As can be seen from the curves in the Figure, the compounds exhibit four types of behaviour.

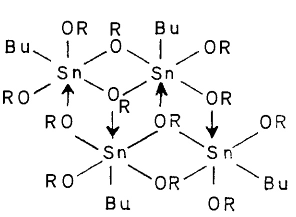
(1) The butyltin trialkoxides with an unbranched alkoxy-group, [*i.e.* BuSn(OR)$_3$ where R = Et, Pr^n, Bu^n] are essentially six-co-ordinate at room temperature, the association presumably involving octahedral structures with both bridging and non-bridging alkoxy-oxygen atoms. In the butyltin trimethoxide,[10] a solid of high m.p., and only sparingly soluble in polar solvents, the degree of association is at a maximum and probably involves a polymeric structure, *cis* (IIA) or *trans* (IIB). Mono-organotin trifluorides have such a structure,[14] with both bridging and non-bridging fluorine atoms. In the triethoxide, tri-n-propoxide and tri-n-butoxide, however, the increased bulk of the alkoxy-group inhibits such complete association, and the degree of dissociation increases with increasing temperature. These three compounds are liquids, so it appears that the degree of association does not approach too closely to a polymeric one, except perhaps at very low temperatures, and may involve discreet trimeric or tetrameric species such as (IIIA) and (IIIB). These, which may be in equilibrium with longer chain aggregates based on structure (II), are analogous to structures which are believed to occur for Group IVA tetra-alkoxides in the liquid phase.[12,13,15-19] Structure (IIIA) is unlikely as this would be expected to give a mean ^{119}Sn chemical shift closer to a five-co-ordinate value, which would be at much lower field than that observed. The tetrameric species (IIB), in which all the tin atoms are six-co-ordinate, is a particularly attractive possibility, as it would result from the association of two dimeric units (see below). Simple tetra-n-alkoxides of tin are known to be tetrameric in benzene solution.[11]

(2) In the case of n-butyltin tri-isobutoxide the extra 2-methyl substituent increases further the steric hindrance to association. This compound therefore, although essentially six-co-ordinate at room temperature, shows an increased tendency towards dissociation as the temperature is increased. At higher temperatures the chemical shift appears to tend towards a limiting value of *ca.* -340 p.p.m., which we believe to represent an essentially five-co-ordinate situation.


(IIA)


(IIB)


(IIIA)


(IIIB)

(3) The effect of a third 2-alkyl substituent, as in the tri-neopentoxide, or of a second 1-alkyl substituent, as in the tri-isopropoxide and tri-s-butoxide, is even more pronounced. At the lower temperatures the chemical shifts converge to a value of *ca.* -330 rather than *ca.* -400 p.p.m. expected for a six-co-ordinate species. This suggests that, for steric reasons, six-co-ordination is completely inhibited, and that at the lower temperatures the isopropoxy- and s-butoxy-compounds are essentially five-co-ordinate species in the neat liquid state. Increase in temperature results in a dramatic decrease in auto-association, the high temperature values tending to a limiting chemical shift value of *ca.* -210 p.p.m., this corresponding to a four-co-ordinate monomeric species.

(4) Three 1-alkyl substituents on the methoxide group increase the steric effect to such an extent that the tri-t-butoxide exhibits only four-co-ordinate behaviour.

As expected, the temperature variations of associative behaviour were parallelled by the behaviour on dilution (Table 2) down to the limit of dilutions (*ca.* 10 mol %) in which sufficiently accurate measurements could be made. It is of interest that the b.p.s of the trialkoxides (Table 1)

---

[11] J. C. Maire, *Ann. Chim. France*, 1961, **6**, 969.

[12] R. C. Mehrotra, *Inorg. Chim. Acta Rev.*, 1967, **1**, 99,

[13] D. C. Bradley and C. E. Holloway, *J. Chem. Soc.* (*A*), 1968, 1316.

[14] L. E. Levchuk, J. R. Sams, and F. Aubke, *Inorg. Chem.*, 1972, **11**, 43.

[15] R. L. Martin and G. Winter, *J. Chem. Soc.*, 1961, 2947.

[16] J. A. Ibers, *Nature*, 1963, **197**, 686

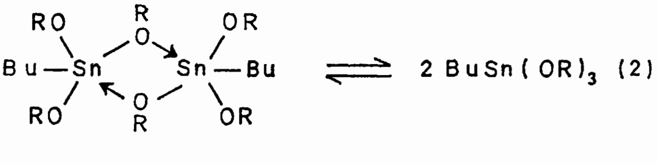
[17] R. L. Martin and G. Winter, *Nature*, 1963, **197**, 687.

[18] H. Weingarten and J. R. Van Wazer, *J. Amer. Chem. Soc.*, 1965, **87**, 724.

[19] W. R. Russo and W. H. Nelson, *J. Amer. Chem. Soc.*, 1970, **92**, 1521.

reflect the degree of association, which again has parallels in the behaviour of tetra-alkoxides of Group IVA metals.[20]

The detection of only one ^{119}Sn resonance signal at any particular temperature and dilution for each of the compounds indicates that equilibration under our conditions was rapid on an n.m.r. time scale. Four- and five-co-ordinate ^{119}Sn resonance frequencies for the tri-s-butoxy-compound, for example, differ by *ca.* 2850 Hz at our magnetic field strength which indicates a mean lifetime of < *ca.* $1{\cdot}5 \times 10^{-4}$ s for a tin atom in either of the two particular co-ordination modes involved in the association–dissociation process. If five-co-ordinate tin is taken to be the result of essentially dimeric aggregation (IV) as is believed to occur for many alkoxyorganotin species,[8,21–24] then the ^{119}Sn chemical shifts observed for our secondary alkoxides between room temperature and 150° are primarily a time-averaged result of a rapid dimer–monomer equilibration [equation (2)].



(IV)

The degree of dissociation, α, may be written in terms of the observed chemical shift δ_{obs}, that of the dimer δ_D, and that of the monomer δ_M [equation (3)]. The

$$\alpha = 1 - (\delta_{obs} - \delta_M)/(\delta_D - \delta_M) \qquad (3)$$

equilibrium constant K for equation (2) is given by equation (4) where n is the number of moles of dimer

$$K = 4\alpha^2 n/(1 - \alpha)v \qquad (4)$$

before dissociation. If it is assumed that the change in (n/v) with temperature is negligible, then the application of these expressions to values taken from the curves of the Figure results in linear plots for ln$K$ *versus* $1/T$ and ΔG *versus* T for the secondary alkoxides. Taking ^{119}Sn chemical shift values of δ −333 for the five-co-ordinate dimeric species (IV) and −213 p.p.m. for the four-co-ordinate monomer results in values of ΔH +24·5 ± 2 kcal mol^{-1} for dimer and ΔS +54 ± 7 cal mol^{-1} K^{-1} for the monomerisation of the tri-isopropoxide. Similar calculations for the tri-s-butoxide, taking five- and four-co-ordinate values of −333 and −206 p.p.m. respectively give values for ΔH of +23·5 ± 2·5 kcal mol^{-1} for dimer and ΔS +68·5 ± 4 cal mol^{-1} K^{-1}.

The ΔH values of *ca.* +12 kcal mol^{-1} per Sn ← O associative bond are greater than that obtained by Considine *et al.* (ΔH +4·5 ± 1 kcal mol^{-1}) from a study of the associative behaviour of 1,1,3,3-tetramethyl-1,3-bistrimethylsiloxydistannoxane.[25] This is to be expected: increased electronegative substitution on the tin atom increases the electron affinity of the vacant 5*d* orbitals on Sn, which in turn increases the strength of any co-ordinative bond. The entropy values (ΔS *ca.* 65 cal mol^{-1} K^{-1}) are large, much greater than that obtained for the disiloxydistannoxane (ΔS 29 cal mol^{-1} K^{-1}) and probably reflect the very stringent orientation requirements for the trialkoxide association that are dictated by the larger steric effect of the secondary alkoxy-groups. This is to some extent confirmed by the slightly larger values for the s-butoxide, corresponding to the extra steric effect expected from the extra 2-methyl group. It must be pointed out, however, that contributions to the entropy term may arise from the possibility that the state of molecular aggregation involving five-co-ordinate tin may be greater than two in these systems.

Owing to the higher m.p. (86—88°) of the tri-neopentoxide, complete data at lower temperatures were not obtained. This precludes a more accurate calculation of ΔH and ΔS values for this compound. From the shape of the curve in the Figure, however, it appears that ΔH is very similar to that for the two tri-s-alkoxides (*ca.* 22·5 kcal mol^{-1}) and that ΔS is of the same order, though somewhat smaller (*ca.* 59 cal mol^{-1} K^{-1}).

We thank the S.R.C. for support.

[3/720 *Received, 5th April*, 1973]

---

[20] D. C. Bradley, R. C. Mehrotra, W. Wardlaw, and J. D. Swanwick, *J. Chem. Soc.*, 1953, 2025 and references cited therein.

[21] J-C. Pommier and J. Valade, *J. Organometallic Chem.*, 1968, **12**, 433.

[22] J. Mendelsohn, J-C. Pommier and J. Valade, *Compt. rend.*, 1966, *C*263, 921.

[23] J-C. Pommier and J. Valade, *Compt. rend.*, 1968, *C*268, 633.

[24] A. C. Chapman, A. G. Davies, P. G. Harrison, and W. McFarlane, *J. Chem. Soc.* (*C*), 1970, 821.

[25] W. J. Considine, G. A. Baum, and R. C. Jones, *J. Organometallic Chem.*, 1965, **3**, 308.