Auto-association in Organometallic Compounds: A Nuclear Magnetic Double Resonance Study of Methyl- and n-Butyl-tin Alkoxides

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Tin-119 chemical shifts determined by $^{1}H-\{^{119}Sn\}$ double resonance have been used as a probe to investigate the auto-associative equilibria of representative simple methyl- and related n-butyl-tin alkoxides, $R^{1}_{4-n}Sn(OR^{2})_{n}$ (R^{1} = Me and Bu^{n}). It is concluded that the O $\longrightarrow$ Sn co-ordinate bond strengths. ΔH. for the dimerisation of the monomers are $\leqslant$ *ca.* 20, *ca.* 35, and *ca.* 50 kJ mol^{-1} for n = 1, 2, and 3 respectively and that for the association of the dimers they are < *ca.* 10 and $\leqslant$ *ca.* 25 kJ mol^{-1} for n = 2 and 3 respectively, consistent with the expected changes in the Lewis acidity of the tin atom. The equilibria are strongly dependent on the steric effects of the alkoxide groups. The changes in tin nuclear shielding observed are briefly discussed in terms of current theories.

METHYLTIN ALKANE-THIOLATES $Me_{4-n}Sn(SR)_{n}$ and -selenolates $Me_{4-n}Sn(SeR)_{n}$ are unassociated in the liquid phase at room temperature, and their ^{1}H, ^{13}C, ^{77}Se, and ^{119}Sn n.m.r. parameters (coupling constants and chemical shifts) have been comprehensively investigated.[1,2] Most of these show approximately linear changes with n consistent with systematic electron withdrawal from the tin atom as n increases; the exception to this is the tin chemical shift, $\delta(^{119}Sn)$, which has a U shaped dependence on n that has been described in terms of two parameters.[3] The first of these describes the extent of departure from linearity and is related to the asymmetry of electronic distribution [4] among the tin valence orbitals. The second defines the difference in chemical shift between extreme members of a series, *i.e.* $[\delta(^{119}Sn)_{n=0} - \delta(^{119}Sn)_{n=4}]$, and in $Me_{4-n}Sn(SMe)_{n}$ and $Me_{4-n}Sn(SeMe)_{n}$ for example it has values of -160 and $+80.5$ p.p.m. respectively. The origins of this effect are not understood and it is therefore important in this context to have comparative data for the oxygen congeners, the methyltin alkoxides $Me_{4-n}Sn(OR)_{n}$.

Investigations into the n.m.r. parameters of alkyltin alkoxides are however complicated by their tendency to undergo auto-association *via* intermolecular O $\longrightarrow$ Sn co-ordinate bonds.[5] The resulting oligomeric species often exist in rapid dynamic equilibrium with lower oligomers and the monomer, so that the measured n.m.r. parameters are the weighted time averages of those for the various species present. Monitoring these parameters yields information about changes in the equilibrium position and in these laboratories has been used to estimate thermochemical data for n-butyltin tri-s-butoxide and tri-isopropoxide.[6]

This communication reports the continuation of these studies to include $^{1}H-\{^{119}Sn\}$ n.m.r. experiments on a more extensive series, the methyltin alkoxides, $Me_{4-n}Sn(OR)_{n}$, together with some related compounds, in order to provide quantitative information about the changes in auto-association that occur when n is varied, and where possible to measure the tin nuclear shielding in un-

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associated monomeric species. A number of the compounds had not been synthesised previously.

EXPERIMENTAL

Organotin alkoxides were handled throughout under dry nitrogen and were prepared[7] by the alcoholysis of the appropriate diethylamino-organotin compounds using the procedure described elsewhere.[6] They were purified by repeated distillation or sublimation and physical and analytical data for new compounds are gathered in Table 1.

TABLE 1

Physical properties and analytical data[a]

Compound	B.p. (°C) [p/mmHg]	Calc. (%) C	Calc. (%) H	Found (%) C	Found (%) H
MeSn(OBu^t)$_3$	48—50 [0.15]	44.2	8.6	44.0	8.8
MeSn(OBu^s)$_3$	77—79 [0.004]	44.2	8.6	44.3	8.8
MeSn(OPr^i)$_3$	69—70 [0.09]	38.6	7.8	38.3	8.0
MeSn(OEt)$_3$	128—130 [0.004][b,c]	31.2	6.7	31.0[d]	6.6[d]
MeSn(OBu^i)$_3$	*ca.* 135 [0.003][e]	44.2	8.6	42.5[f]	8.2[f]
Me$_2$Sn(OBu^t)$_2$	43—45 [1.2]	40.7	8.2	40.9	8.4
Me$_2$Sn(OBu^s)$_2$	66—68 [1.3]	40.7	8.2	40.3	8.0
Me$_2$Sn(OBu^i)$_2$	67—68 [0.004]	40.7	8.2	40.8	8.5
Me$_2$Sn(OBu^n)$_2$	81—83 [0.003][g]			*a*	*a*
Me$_2$Sn(OPr^i)$_2$	Sublimed [1.3][h]	36.0	7.5	36.1	7.6
Me$_2$Sn(OPr^n)$_2$	70—72 [0.006][i]			*a*	*a*
Me$_2$Sn(OEt)$_2$	56—58 [0.003][j]			*a*	*a*
Me$_2$Sn(O-neo-C$_5$H$_{11}$)$_2$	Sublimed [0.1][k]	44.5	8.8	44.4	8.9

[a] Analytical data given only for new compounds. [b] Lit.,[7] 110° at 0.1 mmHg. [c] Rapid distillation; slow fractionation yielded Me$_2$Sn(OEt)$_2$, b.p. 56—58° at 0.003 mmHg, plus a solid, sublimed at *ca.* 160° (bath) and 0.003 mmHg. [d] Integrated ^{1}H n.m.r. showed that the product contained 50 ± 5 mole % of the dialkoxide. Me$_2$Sn(OEt)$_2$ requires C 30.2, H 6.7%. [e] Rapid distillation; slow fractionation yielded Me$_2$Sn(OBu^i)$_2$, b.p. 67—68° at 0.004 mmHg plus a solid, sublimed/decomposed at *ca.* 160° (bath) and 0.005 mmHg to give liquid, b.p. *ca.* 160° at 0.005 mmHg. [f] See note *d*; Me$_2$Sn(OBu^i)$_2$ requires C 40.7, H 8.2%. [g] Lit., 100° at 0.1 mmHg (W. Gerrard, E. F. Mooney, and R. G. Rees, *J. Chem. Soc.*, 1964, 740). [h] M.p. 66—68°. [i] Lit., 130° at 0.5 mmHg (W. Gerrard *et al.*, *op. cit.*). [j] Lit., 82° at 0.1 mmHg (ref. 7 and W. Gerrard *et al.*, *op. cit.*). [k] M.p. 98—101°.

Preparations were straightforward with the following exceptions. Rapid distillation of the reaction mixtures for methyltin triethoxide and tri-isobutoxide MeSn(OR)$_3$ (R = Et and Bu^i) using a pre-heated stillhead yielded products which had elemental analytical data and integrated ^{1}H n.m.r. spectra consistent with their being approximately equimolar mixtures of the trialkoxide and the corresponding dialkoxide Me$_2$Sn(OR)$_2$. Slow fractionation of these mixtures however resulted in complete disproportionation to form pure dialkoxide and (presumably) the tetra-alkoxide Sn(OR)$_4$. The tri-n-propoxide and tri-n-butoxide behaved similarly but these were not quantitatively investigated. [This disproportionation occurs in the opposite sense to that reported for a number of dialkyltin dialkoxides,[8,9] which give trialkyltin alkoxides and (presumably) alkyltin trialkoxides.]

N.m.r. experiments were performed using a JEOL spectrometer equipped with variable temperature facilities and with a nominal proton measuring frequency of 60 MHz; ^{1}H-{^{119}Sn} double resonance experiments were carried out as described elsewhere.[1,10] Samples were examined as neat liquids or as solutions in mesitylene or benzene as indicated. Tin chemical shifts (Tables 2 and 3) are expressed in p.p.m. to low field of Me$_4$Sn, for which $\Xi_{100}(^{119}\mathrm{Sn})$ is taken to be 37 290 665 Hz. It should be noted that the sign convention used has the disadvantage that a negative chemical shift corresponds to a positive shielding.

Density and volume expansion measurements were carried out using a mercury-calibrated 5 mm o.d. precision-bore glass tube in conjunction with a variable temperature bath. All the dialkoxides and trialkoxides measured had densities d_{18} within the range 1.18 ± 0.12 and first expansion coefficients α_T within the range $1.3 \pm 0.2 \times 10^{-3}$ K^{-1} for $20 < T < 150$ °C.

RESULTS

In the ^{1}H n.m.r. spectra of the methyltin alkoxides [compounds (1)—(12) and (16)—(19) in Table 2] at least one of the ^{119}Sn satellites of the *Sn*-methyl proton resonance [$^2J(^{119}\mathrm{Sn}-^1\mathrm{H})$ = 57—104 Hz; natural abundance of ^{119}Sn = 8.68%] was generally sharp and clear of the other resonances so that ^{1}H-{^{119}Sn} double resonance experiments to obtain the ^{119}Sn resonance frequency were straightforward.[1] The ^{119}Sn spectrum was sufficiently sharp in most cases (see for example ref. 11) for the frequency to be determined to within ±5 Hz. For the butyltin compounds [compounds (13)—(15) in Table 2] the more complex satellite system[10] and broadened tin spectrum resulting from the larger number of couplings $^nJ(^{119}\mathrm{Sn}-^1\mathrm{H})$ reduced the accuracy to *ca.* ±100 Hz. Tin chemical shifts recorded under convenient conditions are presented in Table 2, together with an indication as to the co-ordination state of the tin atom.

Many of the compounds exhibited significant reversible changes in tin shielding with temperature and/or dilution in non-co-ordinating solvents. For the trimethyltin alkoxides Me$_3$SnOR (R = Me, Et, Pr^i, or Bu^t) (1)—(4) these were small. The limiting changes observed were all to low field and were *ca.* 7, 6, 0, and 1.5 p.p.m. respectively; Me$_2$Sn(O-neo-C$_5$H$_{11}$)$_2$ (12) behaved similarly. The t-butoxides Me$_2$Sn(OBu^t)$_2$ (8) and MeSn(OBu^t)$_3$ (17) showed accurately linear increases in tin shielding with temperature of +0.06 and +0.11 p.p.m. K^{-1} (Figure 1). This behaviour seems to be general for compounds with highly shielded tin nuclei and for example has a value of +0.26 p.p.m. K^{-1} in MeSnI$_3$ [$\delta(^{119}\mathrm{Sn}) = -700$ p.p.m. at 25 °C].

The dialkyltin dialkoxides R$^1_2$Sn(OR^2)$_2$, with the exception of compounds (8) and (12) discussed above, showed large non-linear decreases in shielding with temperature, and the results for compounds (6), (9), (10), (13)—(15) are presented graphically in Figure 1. The behaviour of compounds (5),

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TABLE 2

Tin-119 chemical shifts of methyltin alkoxides and some related compounds

Compound	t/°C	Solution conditions	$\delta(^{119}Sn)$ [a]	Co-ordination no. of tin atom [b]
Me_3SnOMe (1)	24	Saturated in C_6H_6	+129 ± 2	4
Me_3SnOEt (2)	24	50% v/v in C_6H_6	+119 ± 2	4
Me_3SnOPr^i (3)	24	50% v/v in C_6H_6	+109 ± 2	4
Me_3SnOBu^t (4)	24	50% v/v in C_6H_6	+91 ± 2	4
$Me_2Sn(OEt)_2$ (5)	24	50% v/v in mesitylene [b]	−126 ± 2	5
$Me_2Sn(OPr^i)_2$ (6)	74	Neat liquid	−73 ± 2	4—5
$Me_2Sn(OPr^n)_2$ (7)	24	Neat liquid	−129 ± 1	5
$Me_2Sn(OBu^t)_2$ (8)	24	Neat liquid	−1.8 ± 0.1	4
$Me_2Sn(OBu^s)_2$ (9)	28	Neat liquid	−93 ± 1	4—5
$Me_2Sn(OBu^i)_2$ (10)	24	Neat liquid	−121 ± 1	5
$Me_2Sn(OBu^n)_2$ (11)	24	Neat liquid	−133 ± 1	5
$Me_2Sn(O\text{-neo-}C_5H_{11})_2$ (12)	110	Neat liquid	+12 ± 1 [c]	4
$Bu^n{}_2Sn(OPr^i)_2$ (13)	22	Neat liquid	−100 ± 2 [d]	4—5
$Bu^n{}_2Sn(OBu^i)_2$ (14)	22	Neat liquid	−154 ± 4 [e]	5
$Bu^n{}_2Sn(OPh)_2$ (15)	23	Neat liquid (super-cooled)	−142 ± 4 [f]	5
$MeSn(OEt)_3$ (16)	24	50% v/v in mesitylene [b]	−434 ± 10 [g]	6
$MeSn(OBu^t)_3$ (17)	24	Neat liquid	−177.2 ± 0.2	4
$MeSn(OBu^s)_3$ (18)	24	Neat liquid	−302 ± 1	5
$MeSn(OBu^i)_3$ (19)	24	50% v/v in mesitylene [b]	−452 ± 5 [h]	6

[a] P.p.m. to low field of Me_4Sn. [b] See text. [c] +15 at 131 °C. [d] Lit.,[9] −90 ± 5. [e] Lit.,[9] −150 ± 2. Lit.,[9] −138 ± 2, saturated solution in C_6H_6; −120 ± 2, neat liquid at 70 °C. [g] −407 ± 5 at 72 °C. [h] −406 ± 10 at 65 °C.

(7), and (11) was similar to that of compound (10). Figure 1 shows that the chemical shifts of compounds (9) and (13)—(15) asymptotically approached limiting low-field values in the range +10 to −50 p.p.m. at high temperatures, and high-field values in the range −110 to −160 p.p.m. at low temperatures. Similar behaviour was observed for compounds (6) and (10) when they were examined in solutions in mesitylene (Figure 2); their thermal instability precluded examination of the neat liquids at sustained temperatures above *ca.* 150 °C.

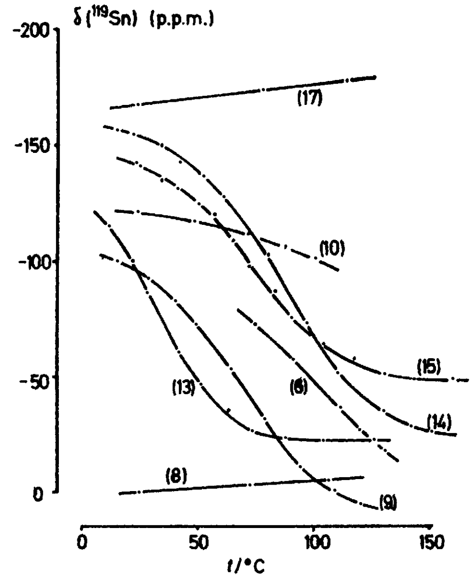


FIGURE 1 Variation with temperature of the ^{119}Sn chemical shifts $\delta(^{119}Sn)$ of the neat alkyltin alkoxides (6), (8)—(10), (13)—(15), and (17)

Large decreases in tin shielding with temperature were also observed for the methyltin trialkoxides $MeSn(OR)_3$ (16), (18), and (19). The tri-s-butoxide (18) had a limiting low temperature chemical shift of −302 p.p.m., but no indication of an approach to a high-temperature shielding minimum was observed up to the limits of dilution and temperature at which reliable $^1H-\{^{119}Sn\}$ experiments were possible (Figure 2). However, calculations based on the dissociative process occurring suggested a limiting low-field value of *ca.* −180 p.p.m. Methyltin triethoxide and tri-iso-butoxide (16) and (19) could not be examined as pure

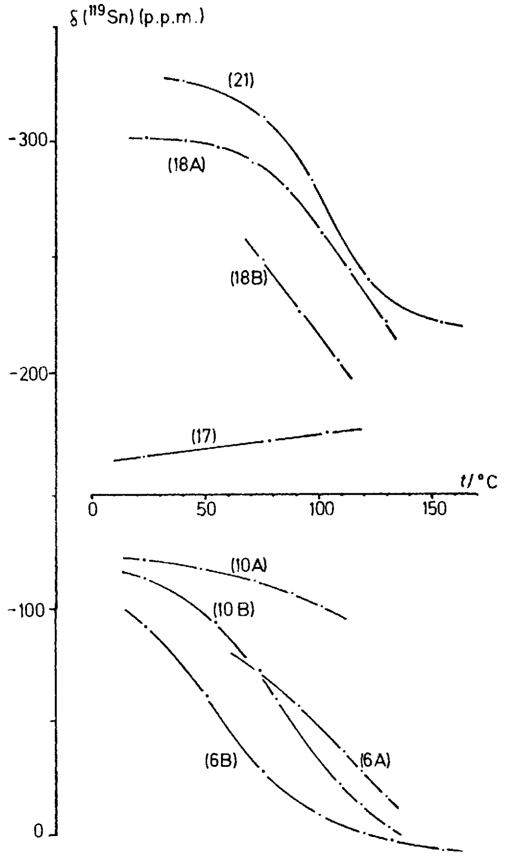
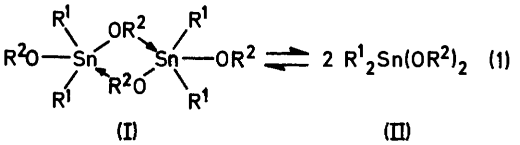


FIGURE 2 Effect of dilution on the temperature variation of the ^{119}Sn chemical shifts $\delta(^{119}Sn)$ of the alkyltin alkoxides (6) (A, neat; B, 14 mole % in mesitylene), (10) (A, neat; B, 3 mole % in mesitylene), (17) (neat), (18) (A, neat; B, 12 mole % in mesitylene), (21) (neat; data from ref. 6)

compounds due to the disproportionations inherent in the isolation procedure. Nevertheless, $^1H-\{^{119}Sn\}$ experiments carried out in mesitylene solution in the presence of the corresponding dialkoxides showed that they had very high field shieldings [$\delta(^{119}Sn)$ *ca.* −450 p.p.m.] which decreased somewhat with increase in temperature (Table 2).

The molecular weight and i.r. characteristics of the dialkyltin dialkoxides [12,13] are usually interpreted in terms of an auto-associative equilibrium [equation (1)] in the liquid phase between dimeric and monomeric forms (I) and (II). Increases in the co-ordination number of tin atoms generally result in substantial increases in the tin nuclear shielding,[14] and the extreme high and low field shifts of Figure 1 can therefore be ascribed to the five-co-ordinate dimer (I) and four-co-ordinate monomer (II) respectively. Intermediate chemical shifts are the result of the equilibration represented by equation (1). This also provides a mechanism for the exchange of the alkoxide groups which accounts for the lack of observed coupling $^3J(^{119}Sn-O-C-^1H)$. The observation of only one ^{119}Sn resonance position shows that the equilibration is rapid and that the rate of exchange of (I) and (II) is > *ca.* 2.5 × 10⁴ Hz.



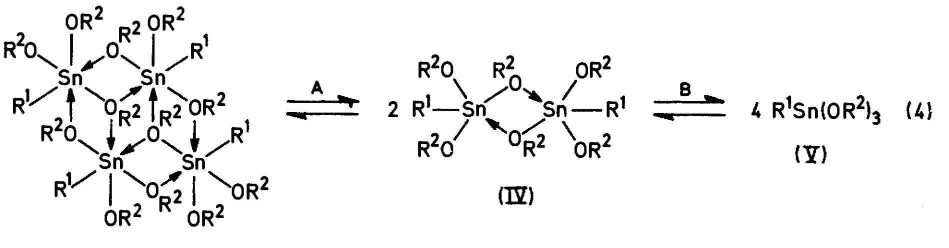
(I) (II)

TABLE 3

Thermochemical data and limiting tin chemical shifts for the dissociation of alkyltin alkoxide dimers [a]

Compound	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}	δ_{dimer} (p.p.m.) [b]	δ_{monomer} (p.p.m.) [b]
(6) [c]	+60 ± 10 [d]	+190 ± 40	−113	+7 [e]
(9)	+75 ± 2	+228 ± 10	−107 [f]	+10 [f]
(10) [c]	+66 ± 4	+190 ± 12	−118 [f]	+10
(13)	+80 ± 6 [g]	+255 ± 17	*ca.* −140 [f]	−22.5
(14)	+74 ± 2	+226 ± 17	−160	−24
(15)	+78 ± 2	+238 ± 7	−148	−48 [f]
(18)	+115 ± 11	+280 ± 20	−302	*ca.* −180 [f]
$Bu^nSn(OBu^s)_3$ (20) [h]	+88 ± 7	+280 ± 20	−333 [f]	−206
$Bu^nSn(OPr^i)_3$ (21) [h]	+95 ± 7	+206 ± 20	−333 [f]	−213
$Bu^nSn(O\text{-neo-}C_5H_{11})_3$ (22) [h]	*ca.* +90	*ca.* +250	−333 [f]	−203
$Bu^n_2Sn(OBu^n)_2$ (23) [i]	+59 ± 13		−161	
$[Me_2(Me_3SiO)_2Sn]_2O$ (24) [j]	+38 ± 4	+121		
$Me_3SnCl \longleftarrow$ dioxan (25) [k]	+21.5 ± 6.5			

[a] Neat liquids unless otherwise stated. [b] To low field of Me_4Sn. [c] Dilute solution in mesitylene. [d] +70 ± 5 in neat liquid. [e] +3 in neat liquid. [f] Estimated by extrapolation and refinement (see text). [g] Lit.,[9] +100 ± 17. [h] Recalculated from data in ref. 6. [i] From ref. 9. [j] From ref. 16. [k] From ref. 17; solution of Me_3SnCl in dioxan.



(III)

The observed tin chemical shift δ_{obs} is therefore a weighted mean of the limiting values for (I) and (II) and can be used to measure the degree of dissociation α of the dimer (I), the relationship being given by equation (2) in which δ_{dimer} and δ_{monomer} are the tin chemical shifts for dimer (I) and monomer (II) respectively. The equilibrium constant K_T at temperature T is then given by equation (3) in which (n/V_T) is the number of moles of dimer per unit volume calculated on the basis of no dissociation.

$$\alpha = 1 - (\delta_{\text{obs}} - \delta_{\text{monomer}})/(\delta_{\text{dimer}} - \delta_{\text{monomer}}) \qquad (2)$$

$$K_T = \frac{4\alpha^2}{(1-\alpha)} \cdot \frac{n}{V_T} \qquad (3)$$

Using these equations data from the curves of Figures 1 and 2 were processed to estimate the changes in enthalpy ΔH and entropy ΔS for the dissociation described by equation (1). The limiting chemical shifts δ_{dimer} and δ_{monomer} were obtained from the plot directly or estimated by extrapolation followed by refinement to produce linear plots of ΔG *versus* T and $R\ln K_T$ *versus* T^{-1}. Any linear changes with temperature of δ_{dimer} and/or δ_{monomer} of <0.1 p.p.m. K^{-1} will have negligible effects on the derived parameters. The results are in Table 3.

The ^{119}Sn n.m.r. and molecular weight characteristics of the butyl- and ethyl-tin trialkoxides [6,15] are also consistent with the existence of a dynamic equilibrium (4), but now involving six-co-ordinate tetramers (III) as well as dimeric (IV) and monomeric (V) aggregates.[6] Here tin chemical shifts of *ca.* −440 p.p.m. can be associated with the six-co-ordinate species (III) [compounds (16) and (19), Table 2],

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of *ca.* −300 p.p.m. with five-co-ordinate species (IV) [compound (18)] and of *ca.* −180 p.p.m. with the four-co-ordinate monomer (V) [compound (17)]. The existence of the two equilibria (4A and B) inhibits accurate evaluation of the dissociation of compounds (16) and (19), but that of compound (18) can be described in terms of equation (4B) only, and thermodynamic parameters were calculated as described above. These are also incorporated in Table 3 together with comparison data from the literature.[6,9,16,17]

It should be pointed out that the disadvantage of the approach adopted here for the estimation of ΔH and ΔS is that the measurements were carried out on the neat liquids, and that any interactions other than the particular $O \longrightarrow Sn$ co-ordinate links under consideration were ignored. The variations in mobility among the di- and tri-alkoxides suggest that these other interactions may in some cases be significant, and therefore cause the values of ΔH and ΔS obtained from neat liquids to be too high. However, a comparison with the results obtained on dilute solutions [compounds (6) and (10), Table 3] shows that for the dimerisation of the dialkoxides [equation (1)] for example, the maximum changes due to these effects are only of the order of 10 kJ mol^{-1} and 35 J mol^{-1} K^{-1} respectively per mole of dimer.

All the above major variations in tin chemical shift were parallelled by changes in $^2J(^{119}Sn-C-^1H)$ which had the following limiting magnitudes in Hz: for $MeSn(OR)_3$ 105 ± 2 [low temperature limit for compounds (16) and (19)], 95 ± 2 [low temperature limit for compound (18)], and 89.5 ± 0.5 (high temperature limit); for $Me_2Sn(OR)_2$, 75 ± 2 (low temperature limit) and 65 ± 2 (high temperature limit); and for Me_3SnOR 57.1 ± 0.9. The variations in these limiting values as R was altered were within the ranges quoted. Only in the case of Me_3SnOR (1)—(4) was any significant trend noted: for $R = Me$, 57.8 ± 0.2; for $R = Et$, 57.6 ± 0.2; for $R = Pr^i$, 57.0 ± 0.2; and for $R = Bu^t$, 56.4 ± 0.2 Hz. The relationship between $\delta(^{119}Sn)$ and $^2J(^{119}Sn-^1H)$ as the temperature was varied was investigated in detail for compound (9) and was found to be linear between 24 and 120 °C. It is noted that the equilibria of equations (1) and (4) can also be monitored by observation of suitable tin–proton coupling constants $^nJ(^{119}Sn-^1H)$. For the compounds studied here it was more convenient and accurate to use $\delta(^{119}Sn)$ since the change in the coupling constants was generally small and their measurement was often hindered by the presence of other lines in the proton spectrum.

DISCUSSION

In the alkyltin alkoxides $R^1_{4-n}Sn(OR^2)_n$ the effective bulk of the groups bonded to tin and to oxygen controls the degree of auto-association of the Sn–O units. All the compounds studied here have a methyl or primary alkyl group on the tin atom. These have similar local steric effects which are minimal, and therefore the variations in behaviour for a given value of n can be ascribed principally to the differences between the alkoxy groups. The steric inhibition in the n-alkoxides is small, and for the alkyltin tri-n-alkoxides and tri-isobutoxides the ^{119}Sn chemical shifts (Table 2 and ref. 6) are consistent with the formation of tetrameric aggregates (III) [equation (4)] which dissociate somewhat on increase in temperature [equation (4A)]. This conclusion is in accord with the molecular weight behaviour[15] of ethyl- and n-butyl-tin triethoxides which have degrees of aggregation of 3.30 and 3.38 respectively in boiling benzene solution.

Examination of models suggests that formation of six-co-ordinate tetramers from the tri-s-alkoxides (18) and (20)—(22) cannot take place due to gross non-bonded interactions between the β-hydrogen atoms of the alkoxide groups, and the n.m.r. data (Table 2 and Figure 2) confirm that liquid-phase auto-association does in fact stop when five-co-ordination is reached. For these compounds therefore the dissociation observed is from dimer (IV) to monomer (V) [equation (4B)]. This conclusion is also supported by molecular weight measurements[15] on ethyl- and n-butyl-tin tri-isopropoxides which have degrees of aggregation of 1.53 and 1.49 respectively in boiling benzene solution. The entropy changes ΔS of *ca.* −280 J mol^{-1} K^{-1} associated with the dimerisation are high (Table 3) and presumably contain significant contributions arising from the loss of internal rotational freedom of the alkoxy-groups that is dictated by the very specific intramolecular orientation required for $O \longrightarrow Sn$ co-ordination. As expected there is no significant difference in the values for ΔS between the *Sn*-methyl and *Sn*-n-butyl compounds. The enthalpy changes ΔH imply values of *ca.* 50 kJ mol^{-1} per $O \longrightarrow Sn$ co-ordinate link; the slightly higher value for the *Sn*-methyl compound (18) may reflect the relative inductive effects of the methyl and butyl groups.

These parameters are more difficult to estimate for the dimer–tetramer equilibrium (4A) due to the dissociation of the dimer itself [equation (4B)]. Nevertheless the behaviour of compounds (16) and (19) (Table 2) and of the analogous n-butyltin trialkoxides[6] suggests that the values of ΔH and ΔS per mole of tetramer are similar to those discussed above for process (4B) per mole of dimer which implies a mean $O \longrightarrow Sn$ co-ordinate bond strength of $\leqslant$ *ca.* 25 kJ mol^{-1}, consistent with the reduction in the Lewis acidity of the tin atom expected on increase in co-ordination number. By contrast, Figures 1 and 2 show that the association of the dialkyltin di-n-alkoxides (5), (7), and (11) and isobutoxides (10) and (14) does not proceed beyond the five-co-ordinate dimer (I) [equation (1)]. It is unlikely that this is due to steric inhibition, and an *X*-ray diffraction study on the related cyclic diorganotin alkoxide 1,1-dibutyl-1-stanna-2,6-dioxacyclohexane shows that six-co-ordination in fact occurs in the solid phase, although the compound remains dimeric in solution.[18] Interdimer interaction must therefore be weak, and, for the compounds examined here, the absence of significant six-co-ordination above the minimum temperatures of *ca.* 20 °C used, together with an assumed entropy change ΔS of 200 J mol^{-1} K^{-1}, would predict an upper limit for ΔH of *ca.* 30 kJ mol^{-1} for any dimer–tetramer equilibrium, *i.e.* a mean $O \longrightarrow Sn$

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co-ordinate bond strength of <10 kJ mol^{-1}. Similar arguments apply to the possible dimerisation of the monomeric trimethyltin alkoxides Me_3SnOR (1) and (2) which become five-co-ordinate in the solid phase.[19] For these the tin chemical shift behaviour indicates only vestigial amounts of auto-association in solution at 25 °C; in this case an upper limit of *ca.* 20 kJ mol^{-1} per $O \longrightarrow Sn$ link is obtained, which is of the same order as that found[17] for $O \longrightarrow Sn$ co-ordination between Me_3SnCl and dioxan [entry (25), Table 3].

For the dimerisation of the neat liquid dialkyltin dialkoxides (6), (9), and (13)—(15) the enthalpy change is lower than that for the trialkoxides discussed above, and corresponds to a bond strength of *ca.* 35 kJ mol^{-1} per $O \longrightarrow Sn$ co-ordinate link; it is of interest that the value for di-n-butyltin diphenoxide (15) is not significantly different from that for the corresponding dialkoxides (13) and (14). The entropy changes ΔS of *ca.* 230 J mol^{-1} K^{-1} are also lower than for the corresponding trialkoxides. This is presumably due to the less stringent steric requirements for the accommodation of four rather than six bulky alkoxide groups around the Sn_2O_2 unit. It is likely that the differences in ΔS among the three compounds (13)—(15) reflect the differences in steric effects of the OR groups.

In the alkyltin t-butoxides $R_{4-n}Sn(OBu^t)_n$ (4), (8), and (17) the bulk of the alkoxide group is such as to inhibit auto-association completely. These compounds therefore show no increased shielding with decrease in temperature, and their i.r.[13] and molecular weight[15] characteristics are also in accord with their being monomeric.

Subject to the limitations outlined in the Results section, the approach used here therefore offers a comparison of the $O \longrightarrow Sn$ co-ordinate bond strengths for the auto-association of the alkyltin alkoxides, $R^1_{4-n}Sn(OR^2)_n$, and shows that for the dimerisation of the monomeric species [*e.g.* equations (1) and (4B)] they have values of $\leqslant$ *ca.* 20, *ca.* 35, and *ca.* 50 kJ mol^{-1} for $n = 1$, 2, and 3 respectively, consistent with the increase in Lewis acidity of the tin atoms expected on increased electronegative substitution. The electron-acceptor properties of the tin atoms are considerably mitigated by the increase in co-ordination number from four to five, and the results for the dimerisation of the dimers [*e.g.* equation (4A)] show that for both $n = 2$ and 3 this corresponds to a reduction in co-ordinate bond strength of *ca.* 25 kJ mol^{-1} for the formation of each second $O \longrightarrow Sn$ link. The electronic requirements of the tin atoms in the trialkyltin alkoxides ($n = 1$) are completely satisfied by the unit increase in co-ordination number from four to five.

The reasons for the observed increases in tin nuclear shielding of >100 p.p.m. per unit increase in co-ordination number (Table 3) are not understood, and are difficult to rationalize merely in terms of increased electron density on the tin atom. Approximate values[20] of the diamagnetic shielding σ^d for isolated In, Sn, Sb, and Te atoms show increases of *ca.* 130 p.p.m. per unit increase in atomic number, but it is likely that the increases are much less for the isoelectronic series Sn^+, Sn, Sn^-, Sn^{2-} because of the decrease in effective nuclear charge. In fact extrapolation from values obtained *via* Hartree–Fock self-consistent function calculations of the electrostatic potential at the nucleus[20] for series of ions M^+, M, M^- would imply a change of only *ca.* 15 p.p.m. for the addition of one electron to the tin valence shell to give Sn^-, which is clearly much less than the changes observed. The increases in shielding may therefore be due to a reduction in σ^p, the 'paramagnetic' component of the shielding expression.[4,21,22] This will be affected both by the changes in bond order and symmetry of the electron distribution among the tin 5*p* and 5*d* orbitals that occur on increased co-ordination, and by the reduction in effective nuclear charge which will lead to a radial expansion of the tin valence orbitals thus decreasing σ^p *via* $\langle r^{-3} \rangle$ terms.

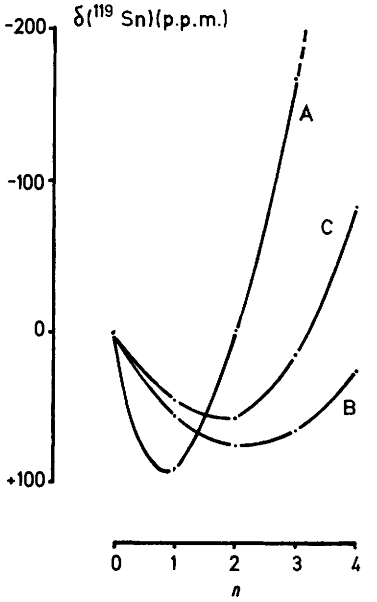

FIGURE 3 Variation with n of ^{119}Sn chemical shifts $\delta(^{119}Sn)$ for the unassociated compounds: A, $Me_{4-n}Sn(OBu^t)_n$; B, $Me_{4-n}Sn(SBu^t)_n$ (data from ref. 2); C, $Me_{4-n}Sn(SeMe)_n$ (data from ref. 1). Complete data for $Me_{4-n}Sn(SeBu^t)_n$ are not available, but $Sn(SeBu^t)_4$ has $\delta(^{119}Sn)$ -262 p.p.m.[3]

The changes of $\delta(^{119}Sn)$ with n for the monomeric methyltin t-butoxides $Me_{4-n}Sn(OBu^t)_n$ (4), (8), and (17) are reproduced in Figure 3, together with data for analogous sulphur and selenium compounds. The markedly sharper curvature of the plot for the t-butoxides may be ascribed to the greater changes in electronic asymmetry about tin due to the larger electronegativity difference between the methyl and alkoxy groups, but the high field shielding at high n is not easily rationalised. The higher field shifts of the selenolates compared to the thiolates are examples of the known

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shielding effect due to heavy atoms which have non-bonding electrons in their valence shells,[3,23-25] and on this basis the shifts for the oxygen compounds are expected to be at still lower field. The behaviour of $\delta(^{29}Si)$ in the analogous silicon compounds $Me_{4-n}Si(ER)_n$ where E = O, S, or Se, is qualitatively similar,[26,27] but ^{13}C shielding in the alkoxycarbon compounds $H_{4-n}C(OR)_n$ decreases rapidly and monotonically with *n*.[28] It is therefore tempting to ascribe the higher field shifts of the tin and silicon alkoxides to the incidence of $p\pi \longrightarrow d\pi$ bonding, but the mechanism by which this may affect the shielding is far from clear, and it should also be noted that some success has been achieved in explaining the difference in ^{13}C and ^{29}Si shielding behaviour in alkoxides on the basis of calculations which completely neglect silicon 3*d*-orbital participation.[29]

The changes in chemical shift $\delta(^{119}Sn)$ for monomeric species as the alkoxide group is varied are similar to those observed for the alkanethiolate analogue which have been discussed elsewhere.[2,3] The changes in coupling $^2J(^{119}Sn-C-^1H)$ are also in accord with general trends noted for methyltin compounds on increase in co-ordination number or on changing substitution. These are usually rationalised in terms of isovalent redistribution of *s* character among the tin hybrid orbitals and of variation in effective nuclear charge of the tin atom,[2,30-32] although other factors are also important.[33,34]

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