

Preliminary communication

The structure of polymeric dialkyltin oxides [R₂SnO] (R = Me, ⁿBu) as probed by high-resolution solid-state ¹¹⁹Sn NMR

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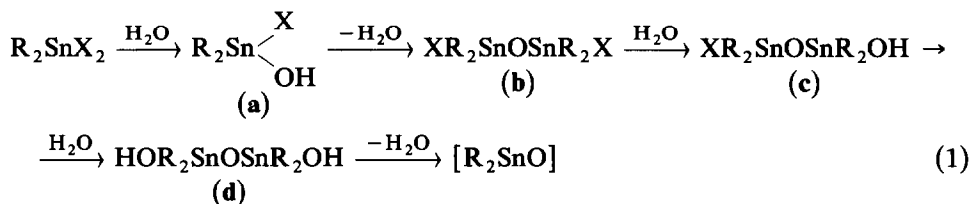
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Abstract

Tin-119 CP/MAS high-resolution NMR spectra have been obtained for two solid polymeric dialkyltin oxides. Values for isotropic chemical shifts and shielding tensor components are reported. The data are discussed in terms of postulated chemical structures.

Dialkyltin oxides [R₂SnO] are the ultimate hydrolysis products of dialkyltin halogenides R₂SnX₂ [1] (eq. 1). The resulting dialkyltin oxides are amorphous



solids of unknown exact structure. Because of their chemical properties [2] (high temperatures of decomposition and general insolubility in all solvents but those with which they react), and on the basis of IR- [3] and Mössbauer spectroscopy [4]. It has been concluded that dialkyltin oxides are polymers. Bulky alkyl ligands R can prevent the polymerisation: di-*t*-butyltin oxide for instance exists as a trimer [^tBu₂SnO]₃ both in solution (δ(¹¹⁹Sn) – 84.3 ppm, ²J (¹¹⁹Sn¹¹⁷Sn) 369 Hz) [5,6] and in the solid state [5].

The ¹¹⁹Sn cross polarisation/magic angle spinning (CP MAS) spectra of [Me₂SnO] and [ⁿBu₂SnO] (see Fig. 1) provide some structural information for this class of compound. The isotropic chemical shifts δ(¹¹⁹Sn) (–152 ppm for R = Me; –177 ppm for R = ⁿBu) clearly show the tin to be five-coordinate. The effect on the chemical shift of changing the alkyl group from Me to Buⁿ is as expected. Very similar ¹¹⁹Sn chemical shifts are found for solutions of cyclic dibutyltin alkoxides, as well as for acyclic dialkyltin dialkoxides [7]. On the basis of solution state NMR

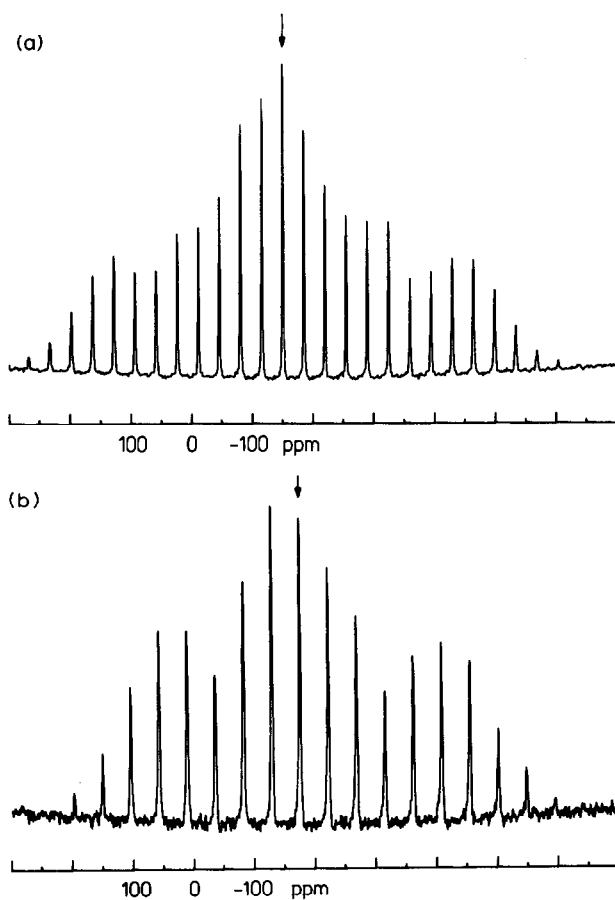
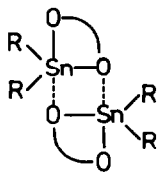


Fig. 1. ^{119}Sn CP MAS spectra of (a) dimethyltin oxide (spinning speed 2.7 kHz, 3870 transients [13]), and (b) di-n-butyltin oxide (spinning speed 3.5 kHz, 920 transients). Arrows indicate centre bands, determined by variation of the spinning speed. Conditions: 100 kHz spectral width, 10 s recycle delay, 1 ms contact time.

data a dimeric oxygen-bridged structure with trigonal bipyramidal *cis*- R_2SnX_3 geometry (I) has been suggested [8] for both the cyclic and acyclic systems, while



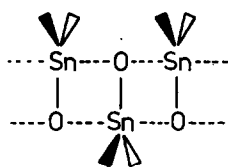
(I)

^{119}Sn resonances to even lower frequencies (i.e. in the range -210 to -220 ppm) have been explained by the formation of oligomeric species with essentially 6-coordinate tin [7].

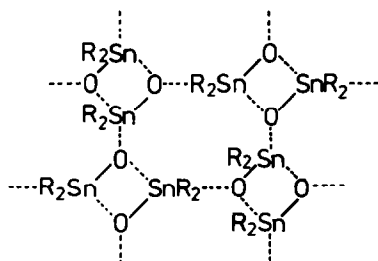
The tensor components of the ^{119}Sn shielding for $[\text{Me}_2\text{SnO}]$ ($\eta = 0.89$ $\Delta\sigma = 392$ ppm) and $[\text{nBu}_2\text{SnO}]$ [9] ($\eta = 0.83$ $\Delta\sigma = 371$ ppm) can also be satisfactorily rationa-

lised, assuming a trigonal bipyramidal $cis\text{-R}_2\text{SnX}_3$ geometry. The fairly large asymmetry parameters clearly contradict a $trans\text{-R}_2\text{SnX}_3$ geometry: in this case one would expect an axially symmetric or, at least, a nearly axially symmetric spinning sideband pattern.

There are two possible ways to construct a polymeric lattice from R_2SnO units involving $cis\text{-R}_2\text{SnX}_3$ geometry; either a linear ladder-type structure (II) or a cross-linked network (III):

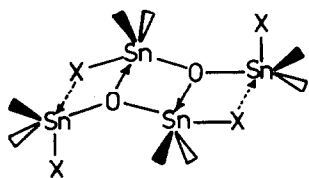


(II)

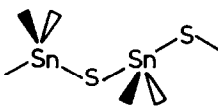


(III)

Evidence for both structural types has been claimed from Mössbauer- and from IR-spectroscopic studies [10]. Recently, several X-ray crystal structures of precursor-compounds *b*, *c*, and *d* in the stepwise hydrolysis of R_2SnX_2 have been reported [11]. In all cases dimeric units of the ladder-type are found (IV).



(IV)



(V)

Diisopropyltin sulfide [${}^i\text{Pr}_2\text{SnS}$] $_n$ has been shown to be a tetracoordinated open-chain polymer (V) [12]. In both structures II and III, the four-membered Sn_2O_2 unit of the related dimeric compounds *b*, *c*, and *d* is preserved.

Certainly, ${}^{119}\text{Sn}$ NMR spectroscopy is far more sensitive to the local environment of the ${}^{119}\text{Sn}$ nucleus under consideration than to long-range effects. Cross polarisation is very efficient for both compounds [Me_2SnO] and [${}^n\text{Bu}_2\text{SnO}$], and only one fairly sharp ${}^{119}\text{Sn}$ resonance ($\nu_{1/2}$ 160 and 240 Hz, respectively) is observed in the solid state ${}^{119}\text{Sn}$ CP MAS spectra. These findings are an indication of long-range order in both compounds, and they require a fairly rigid lattice. It is expected that a reticulated network III will display a higher degree of rigidity than a chain polymer II. The solid state NMR data obtained, therefore, favour a cross-linked structural model for dialkyltin oxides. However, it should be pointed out that with the limited NMR data available so far, this qualitative conclusion has to be understood as a suggestion rather than as proof.

Experimental

[Me_2SnO] and [${}^n\text{Bu}_2\text{SnO}$] were purchased from Alfa Chemicals. The ${}^{119}\text{Sn}$ CP MAS spectra were obtained using a Bruker CXP 200 spectrometer, operating at

74.63 MHz, at ambient probe temperature (approx. 30 °C). $\delta(^{119}\text{Sn})$ is given with reference to external SnMe_4 . The tensor components were calculated from the spinning sideband pattern using the method of Maricq and Waugh [9]. The data were refined by simulation of the spinning sideband pattern using a program written by J. Ascenso. We believe the values of η and $\Delta\sigma$ are likely to be accurate to ± 0.1 and ± 10 ppm, respectively.

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