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Solid State Monomeric and Polymeric Forms of Triphenyltin Trichloroacetate

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Several years ago we reported the preparation, infrared and Mössbauer spectra of a series of triphenyltin halogenoacetates, $Ph_3SnOCOR$ (R = CH_3, CH_2I, CH_2Br, CH_2Cl, $CHCl_2$, CCl_3 and CF_3) [1]. The spectral data indicated $Ph_3SnOCOCl_3$ to be a tetracoordinate monomer in the solid state, whereas the other members of the series are pentacoordinate polymers showing trends consonant with those observed in the homologous trimethyltin compounds [2]. The exceptional behaviour of triphenyltin trichloroacetate was attributed to a steric interaction between the Ph_3Sn moiety and the bulky CCl_3 group, similar to that previously observed [3] for $Ph_3SnOCOCMe_3$ and $Ph_3SnOCOCMe{=}CH_2$.

In connexion with a continuing study of the kinetics of the slow solid-state hydrolysis of triorganotin carboxylates by atmospheric moisture, to produce organostannoxane derivatives, we recently had occasion to measure the Mössbauer spectrum of a sample of $Ph_3SnOCOCCl_3$ which had been stored in an evacuated sealed phial for about five years. This spectrum showed the sample to contain a mixture of two species, but neither set of parameters corresponded to that anticipated for a phenylstannoxane carboxylate [4] and chemical analysis of the sample gave no evidence of decomposition. The Mössbauer parameters of one of these species corresponded to those of the original monomeric complex [1], whereas the second species showed a much larger quadrupole splitting ($\Delta E_Q \cong 3.8$ mm/s). Since this splitting is approximately the magnitude expected [1] for a pentacoordinate polymeric form of $Ph_3SnOCOCCl_3$, we suspected that an incomplete solid-state monomer → polymer phase transition had occurred with ageing of the sample. We have subsequently isolated what appears to be polymeric triphenyltin trichloroacetate in pure form. To our knowledge this is the first example of such polymorphism in solid organotin carboxylates.

The product obtained from the reaction of triphenyltin hydroxide with trichloroacetic acid and other strong carboxylic acids is dependent on both the solvent and the reaction temperature. Procedures carried out in non-polar solvents such as carbon tetrachloride or benzene, and those that involve heating of the reaction mixture, tend to cause phenyl–tin bond rupture. For example, the reaction of Cl_3CCOOH with Ph_3SnOH in refluxing benzene produces the phenylstannoxane derivative $PhSn(O)OCOCCl_3$ [4]. Such bond cleavage is inhibited by using a polar solvent and carrying out the reaction at room temperature. Thus, our original route [1] to the monomeric form **1** of $Ph_3SnOCOCCl_3$ proceeded at 25 °C in anhydrous methanol, leading to formation of the adduct $Ph_3SnOCOCCl_3 \cdot MeOH$, from which the pure compound was obtained on recrystallization from carbon tetrachloride. When the reaction subsequently was carried out at room temperature using absolute ethanol as solvent, a product was obtained which could be dried only with difficulty. After holding the sample under vacuum ($\sim 10^{-2}$ torr) for four days, a white powdery solid **2** was obtained which analyzed correctly for triphenyltin trichloroacetate. *Anal.* Found: C, 46.72; H, 2.88; Cl, 20,93. Required for $C_{20}H_{15}O_2SnCl_3$: C, 46.88; H. 2.95; Cl, 20.76%.

Mössbauer parameters and OCO stretching frequencies for the presumed polymeric solid compound **2** are distinctly different from those for either the monomer **1** or the methanol adduct (see Table). On dissolution in carbon tetrachloride the OCO bands of **2** show the type of shift typically associated with a polymer–monomer transition [1–3, 5–7], and it is clear that neither **1** nor **2** is associated in dilute CCl_4 solution.

The Mössbauer quadrupole splitting observed for **2** (3.90 mm/s) is in excellent agreement with values

TABLE. ^{119}Sn Mössbauer Parameters^a and C–O Stretching Frequencies.

Compound	$\delta^{b,c}$ (mm/s)	ΔE_Q^b (mm/s)	Solid State (cm^{-1})		CCl_4 Solution (cm^{-1})	
			ν_a(OCO)	ν_s(OCO)	ν(C=O)	ν(C–O)
$Ph_3SnOCOCCl_3$ (polymer)	1.37	3.90	1618	1421	1702	1290
$Ph_3SnOCOCCl_3$ (monomer)^d	1.30	2.97	1700	1305	1700	1292
$Ph_3SnOCOCCl_3 \cdot MeOH^d$	1.33	3.50	1665	1334	1702	1294

^{a}Recorded at *ca.* 80 °K. ^{b}±0.03 mm/s. ^{c}Relative to $BaSnO_3$. ^{d}Data from [1].

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predicted [1] for a pentacoordinate polymeric compound of this formula, either from a partial quadrupole splitting treatment (3.84 mm/s)† or from a correlation of ΔE_Q with the Taft inductive factor σ^* (3.94 mm/s). Moreover, this value is substantially larger than any reasonable upper estimate for a tetracoordinate species involving these ligands [9]. We also note that the isomer shift of **2** agrees with that predicted for pentacoordinate $Ph_3SnOCOCCl_3$ from data for other polymeric triphenyltin halogenoacetates [1]. Although these spectroscopic data provide only indirect evidence for the structure of **2**, we feel there is little doubt that this compound is indeed a pentacoordinate polymeric form of $Ph_3SnOCOCCl_3$.

Attempts to recrystallize **2** from carbon tetrachloride yielded mixtures of polymer and monomer (as shown by IR and Mössbauer spectra of the products), with a preponderance of the latter. Although these observations might be thought to suggest that **1** is the more stable modification, the fact that **1** converts at least partially to **2** with ageing would imply the contrary. Obviously, the possible influences of such factors as solvent, temperature, and rate of crystal growth on the nature of the product obtained, require further detailed studies which we plan to undertake.

The existence of both monomeric and polymeric solid state species for $Ph_3SnOCOCCl_3$ is extremely interesting, since the available evidence on triorganotin carboxylates [1–7, and references therein] clearly indicates that steric interactions between the R_3Sn fragment and the tail of the carboxylate function *alone* prevent the tin atom from adopting a pentacoordinate structure. That is, in the absence of steric effects, the exothermicity due to formation of a fifth bond more than compensates for the unfavourable entropy decrease caused by association, to produce a lower free energy for the polymeric structure. It appears that $Ph_3SnOCOCCl_3$ represents a truly borderline case in which the steric interactions are very nearly balanced by the tendency of the tin atom to increase its coordination number to five.

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† A more recent regression analysis by Clark and coworkers [8] gives 3.70 mm/s, but erroneously quotes the quadrupole splitting of **1** given in ref. 1 as 3.97 rather than 2.97 mm/s.