Mössbauer and Infrared Evidence for the Structures of Triphenyltin Carboxylates

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THERE has been considerable interest in the structures of trialkyl- and triaryl-tin carboxylates.[1-3] Solid-state i.r. spectra[3] for the compounds R_3SnOAc ($R = Me, Et, Bu, C_6H_{13}$) showed they were either ionic or linear polymers in which the tin atom was five-co-ordinate. Association studies for CCl_4 solutions eliminated the former possibility. Similar conclusions have been drawn[3] concerning the structure of trimethyltin laurate.

We report Mössbauer and i.r. data for six triphenyltin carboxylates, which indicate that at least three different structural types are possible in these compounds, depending upon length and branching of the carboxylate chain.

The Mössbauer spectrometer has been described.[4] For all measurements the absorbers were maintained at 80° K. Isomer shift values are reported relative to an SnO_2 absorber at 80° K. I.r. data were recorded on a Perkin–Elmer Model 457 spectrophotometer, with the compounds dispersed in Nujol or halogenocarbon oil. Mössbauer isomer shifts (δ) and quadrupole splittings (Δ) and CO·O stretching frequencies are given in the Table; also included are results for Me_3SnOAc.

Mossbauer parameter and i.r. frequencies of triphenyltin carboxylates

	Compound	δ (mm. sec.$^{-1}$)	Δ (mm. sec.$^{-1}$)	CO·O frequencies (cm.$^{-1}$)
(I)	$\mathrm{Me_3SnOAc}$	1·35	3·68	1560, 1420
(II)	$\mathrm{Ph_3SnOAc}$	1·27	3·40	1545, 1420
(III)	$\mathrm{Ph_3SnO_2C{\cdot}[CH_2]_2Ac}$	1·28	3·43	1538, 1420
(IV)	$\mathrm{Ph_3SnO_2C{\cdot}[CH_2]_8{\cdot}CH:CH_2}$ ..	0·57	2·31	1533, 1415
(V)	$\mathrm{Ph_3SnO_2C{\cdot}[CH_2]_{16}Me}$	0·56	2·32	1537, 1412
(VI)	$\mathrm{Ph_3SnO_2C{\cdot}CMe:CH_2}$	1·21	2·26	1642, 1345
(VII)	$\mathrm{Ph_3SnO_2C{\cdot}CHEtBu^n}$	1·21	2·26	1625, 1305

The large quadrupole splittings for the acetates [(I) and (II)] and for triphenyltin levulinate (III) are consistent with a trigonal bipyramidal configuration for the tin atom in these compounds. The CO·O absorptions are far removed from the usual (1740 and 1240 cm.$^{-1}$) organic-ester frequencies, and show that the two oxygens are nearly equivalent. We conclude that compounds (II) and (III) have the polymeric structure previously deduced[3] for (I).

The undecenoate (IV) and stearate (V) show large diminutions in both isomer shifts and quadrupole splittings, but no significant change in the CO·O stretching bands. The CO·O frequencies again point to a symmetrical carboxylate group, which could be explained either by an ionic or polymeric structure. However, the Mössbauer spectra for these compounds indicate that they are very different from compounds (II) and (III). The fairly small quadrupole splittings suggest a tetrahedral configuration for the tin atom,[5] and the isomer shifts are the smallest yet reported for any organotin compounds. For $\mathrm{Sn^{IV}}$ compounds, a decrease in δ corresponds to an increase in ionic character.[6] Indeed, the δ values for these three compounds are smaller even than for $\mathrm{SnCl_4}$ (~0·8 mm. sec.$^{-1}$). We therefore conclude that compounds (IV) and (V) are largely ionic. To test this hypothesis, we have also recorded the i.r. spectra of triphenyltin acetate (II) and stearate (V) in $\mathrm{CCl_4}$ solution. The CO·O bands for the stearate are unchanged in solution (1535 and 1411 cm.$^{-1}$), whereas those for the acetate (monomeric in solution) have moved to 1640 and 1314 cm.$^{-1}$, indicating an asymmetrical carboxy-group in this compound. These results eliminate the possibility of a polymeric structure for the stearate.

When the carboxylate chain branches at the 2-position, as in triphenyltin methacrylate (VI) and 2-ethylhexanoate (VII), a third type of structure obtains. The quadrupole splitting again indicates a tetrahedrally co-ordinated tin atom, while the isomer shift is essentially the same as for the polymeric triphenyltin carboxylates. Moreover, the CO·O bands have moved more than halfway towards the normal positions for organic esters, showing that these compounds do not have the symmetrical carboxylate group. The change from *sp*^{3}*d* to *sp*^{3} bonding for the tin atom should have very little effect on the *s*-electron density at the nucleus because 5*d* orbitals provide virtually no shielding of 5*s* electrons. This is reflected in the very similar δ values for these two compounds and for the polymeric triphenyltin carboxylates. The infrared data are consistent with the suggestion that the branched-chain compounds resemble structurally the organic esters. The fact that the CO·O bands still differ appreciably from the normal ester positions is probably due to the influence of the heavy metal atom.[3]

Therefore, the acetate (II) and levulinate (III) are linear polymers of the type postulated[3] for trialkyltin acetates, in which the tin atom is pentaco-ordinate and the carboxyl group is symmetrical. If the (straight) carboxylate chain is sufficiently long, as in compounds (IV) and (V), an ionic rather than polymeric structure is found. The carboxylate group is still symmetrical, but the tin atom is now tetraco-ordinate. A branching of the carboxylate chain at the number two carbon, as in (VI) and (VII), appears to provide sufficient steric hindrance to prevent formation of a polymer and these compounds resemble normal organic esters.

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