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ORGANOTIN CARBOXYLATES
I. MÖSSBAUER AND INFRARED STUDY OF TRIPHENYLTIN CARBOXYLATES AND THE NOVEL COMPOUNDS RSn(O)OCOR′

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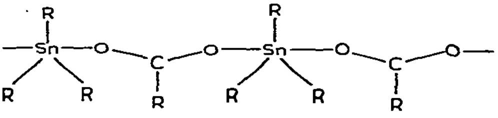
SUMMARY

Triphenyltin carboxylates are capable of existing in two forms. The straight-chain compounds are polymeric, with bridging OCO groups and pentacoordinate tin atoms. If the carboxylate chain branches at the α-position the compounds are monomeric and resemble normal esters. The different structures are readily identified from their Mössbauer and infrared spectra. It is shown that at least some of these compounds decompose to yield phenylstannoic carboxylates, which probably exist either as cyclic trimers or linear polymers, with Sn–O–Sn bridges and either chelating or ionic carboxyl groups.

INTRODUCTION

There has been considerable interest in the structures of trialkyl- and triaryltin carboxylates[1]. Solid state infrared spectra[2] for the compounds $R_3SnOCOCH_3$ ($R = CH_3$, C_2H_5, C_4H_9, C_6H_{13}) indicated a symmetrical carboxyl group, so that the compounds were either ionic or linear polymers in which the tin atom was pentacoordinate. Similar results were also obtained for trimethyltin laurate. Studies of association in CCl_4 solutions[2] eliminated the possibility of an ionic structure. The absence of a 510 cm^{-1} band for $Me_3SnOCOCH_3$ indicates a planar Me_3Sn group. In the solid state, these compounds have structure (I).



(I)

However, it has been pointed out[2] that such polymer formation in the trialkyltin carboxylates is inhibited when the alkyl groups are bulky. Thus, iso-Pr_3Sn-$OCOCH_3$ is monomeric, with tin reverting to a coordination of four.

Mössbauer spectroscopy offers an excellent tool for investigating such differences in coordination and bonding in organotin compounds. The two Mössbauer parameters of primary interest are the isomer shift, δ, and the quadrupole splitting, Δ.

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The former arises from the interaction between the nuclear charge distribution and the electron density at the nucleus, and reflects directly changes in electron density at the tin nucleus. The quadrupole splitting is due to the interaction between the nuclear quadrupole moment and the electric field gradient tensor, and is a measure of the asymmetry of the charge distribution about tin.

It is clear that both these parameters are sensitive to the bonding and stereochemistry of the tin atom. In general, the isomer shift will depend principally on relative bond ionicities[3], while changes in the quadrupole splitting will reflect primarily changes in stereochemistry.

On the basis of Mössbauer and infrared data we have suggested recently[5] that triphenyltin carboxylates could show three distinct structural types: (1) Pentacoordinate polymers of the type (I); (2) Tetracoordinate monomers resembling organic esters; (3) Essentially ionic compounds, with $Ph_3Sn^{\delta+}$ and $^{\delta-}OCOR'$ groups. These conclusions were based upon results for six compounds, two of each type, which were kindly donated by Dr. W. R. Considine of M & T Chemicals, Inc. We have now prepared in this laboratory a number of additional triphenyltin carboxylates and find that our suggestion that these compounds can exist as ionic species was incorrect. Only the first two structural types appear to be possible, and the compounds originally attributed to type (3) are not, in fact, triphenyltin carboxylates, but rather decomposition (hydrolysis) products of such compounds, having empirical formula PhSn(O)-OCOR'.

All of the straight-chain triphenyltin carboxylates which we have prepared, with chain length varying from one to eighteen carbon atoms, appear to exhibit the linear polymeric structure (I). However, if the carboxylate chain branches at the α-carbon atom, the compounds behave like normal organic esters. We shall first discuss the preparation and structures of the triphenyltin carboxylates, and then consider the interesting and unusual properties of the decomposition products of triphenyltin undecenoate and triphenyltin stearate.

EXPERIMENTAL

The Mössbauer spectrometer employed has been described[6]. The source consisted of $Ba^{119m}SnO_3$. The Doppler velocity scale was calibrated from the quadrupole splitting of an NBS standard sodium nitroprusside absorber*. All isomer shift values are reported relative to an SnO_2 absorber at 80°K.

Infrared data were recorded on a Perkin–Elmer Model 457 spectrometer. The compounds were dispersed either in Nujol or in halocarbon oil, or dissolved in CCl_4. Melting points were obtained with a Gallenkamp apparatus.

Triphenyltin formate and triphenyltin propionate were prepared by shaking triphenyltin chloride with a slight excess of the sodium salt of the acid in an ether/water mixture. The products were suction filtered and dried in air.

The remaining triphenyltin carboxylates were prepared by refluxing triphenyltin chloride and a slight excess of the potassium salt of the appropriate acid in methanol. Cooling the reaction mixture in an ice bath and/or evaporation of the solvent afforded white precipitates which were suction filtered, washed with water, and dried

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* The certificate for this Standard Reference Material gives the quadrupole splitting as 1.726 ± 0.002 mm/sec. This value has been confirmed by Spijkerman[17], although Herber[18] has suggested a value of 1.705 mm/sec.

in air. The products were further purified by recrystallising from CCl_4.

Microanalyses were performed by P. Borda of this Department and Drs. F. and E. Pascher, Bonn, Germany. Analytical data and melting points for our products are given in Table 1.

TABLE 1

ANALYTICAL DATA AND MELTING POINTS FOR TRIPHENYLTIN CARBOXYLATES

Compound	C(%)		H(%)		M.p. °C
	Calcd.	Found	Calcd.	Found	
$Ph_3SnOCOH$	57.72	57.86	4.05	4.01	201–202
$Ph_3SnOCOCH_2CH_3$	59.57	59.63	4.73	4.91	122–123
$Ph_3SnOCO(CH_2)_4CH_3$	61.93	63.07	5.59	6.13	110–111
$Ph_3SnOCO(CH_2)_6CH_3$	63.28	63.51	6.09	6.13	81–83
$Ph_3SnOCO(CH_2)_7CH_3$	63.90	64.23	6.31	6.29	106–108
$Ph_3SnOCO(CH_2)_8CH_3$	64.49	62.76	6.53	6.74	80–82
$Ph_3SnOCO(CH_2)_{10}CH_3$	65.57	64.35	6.92	6.82	76–78
$Ph_3SnOCO(CH_2)_{14}CH_3$	67.43	64.82	7.60	8.55	77–80
$Ph_3SnOCO(CH_2)_7CH{=}CH\text{-}(CH_2)_7CH_3$	68.46	66.97	7.61	7.97	74–79
$Ph_3SnOCO(CH_2)_{16}CH_3$	68.25	68.67	7.90	8.35	71–73
$Ph_3SnOCOC(CH_3)_3$	61.19	60.42	5.32	5.66	103–105

DISCUSSION

Triphenyltin carboxylates

Mössbauer isomer shifts δ and quadrupole splittings Δ, and infrared COO stretching frequencies are given in Table 2 for the triphenyltin carboxylates studied. For comparison we have included our results for $Me_3SnOCOCH_3$ and $Bu_3SnOCOCH_3$, together with Mössbauer parameters reported by other workers. Agreement is satisfactory, except for the quadrupole splitting of $Me_3SnOCOCH_3$, where we feel Herber's value[4] seems a bit low. It will be seen from Table 2 that on the basis of their Mössbauer parameters, the triphenyltin carboxylates fall into two different groups: (*a*) compounds 3–14, having $\delta \sim 1.3$, $\Delta \sim 3.4$; (*b*) compounds 15–17, having $\delta \sim 1.2$, $\Delta \sim 2.3$. The infrared data show the same division. It will be convenient to discuss these two groups separately.

Group (*a*). It should be kept in mind that as a tool for structural studies Mössbauer spectroscopy must rely largely on a comparison of data for unknown samples with that derived from model compounds. We have mentioned above that $Me_3SnOCOCH_3$ and $Bu_3SnOCOCH_3$ have been shown to have structure (I). Moreover, recent X-ray data[7] indicate that $(PhCH_2)_3SnOCOCH_3$ also has this structure. We can therefore say that the large quadrupole splittings observed for these compounds are due to a trigonal bipyramidal configuration about the tin atom. This leads us immediately to the conclusion that all the straight-chain triphenyltin carboxylates have structure (I), since they all have essentially the same Mössbauer parameters. Furthermore, the solid state COO absorptions for all these compounds are far removed from the usual (1740, 1240 cm^{-1}) organic ester absorptions, showing that the two oxygen atoms are nearly equivalent.

TABLE 2

MÖSSBAUER PARAMETERS AND OCO STRETCHING FREQUENCIES

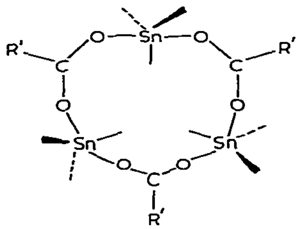
Compound	δ[a,b] (mm·sec^{-1})	Δ[a] (mm·sec^{-1})	ρ ($=\Delta/\delta$)	OCO frequencies (cm^{-1}) Mull	Solution
1 $Me_3SnOCOMe$	1.35	3.68	2.72	1558, 1418	
	1.34[c]	3.47[c]			
2 $Bu_3SnOCOMe$	1.46	3.64	2.49	1560, 1416	
	1.38[d]	3.67[d]			
3 $Ph_3SnOCOH$	1.37	3.58	2.61	1559, 1390	1644, 1358
4 $Ph_3SnOCOMe$	1.27	3.40	2.68	1548, 1420	1640, 1370
5 $Ph_3SnOCOEt$	1.33	3.42	2.57	1535, 1412	1632, 1381
6 $Ph_3SnOCO(CH_2)_2COMe$	1.29	3.43	2.66	1538, 1405	1642, 1366
7 $Ph_3SnOCO(CH_2)_4Me$	1.32	3.43	2.60	1534, 1407	1634, 1381
8 $Ph_3SnOCO(CH_2)_6Me$	1.29	3.35	2.60	1525, 1415	1631, 1382
9 $Ph_3SnOCO(CH_2)_7Me$	1.28	3.36	2.62	1525, 1409	1628, 1368
10 $Ph_3SnOCO(CH_2)_8Me$	1.27	3.46	2.72	1532, 1404	1630, 1382
11 $Ph_3SnOCO(CH_2)_{10}Me$	1.24	3.41	2.75	1531, 1406	1628, 1380
12 $Ph_3SnOCO(CH_2)_{14}Me$	1.25	3.44	2.75	1530, 1408	1630, 1381
13 $Ph_3SnOCO(CH_2)_7$-$CH{=}CH(CH_2)_7Me$	1.27	3.38	2.66	1523, 1412	1631, 1383
14 $Ph_3SnOCO(CH_2)_{16}Me$	1.26	3.33	2.64	1532, 1410	1629, 1380
15 $Ph_3SnOCOCMe{=}CH_2$	1.21	2.26	1.87	1593, 1346	1610, 1360
	1.15[e]	2.10[e]			
16 $Ph_3SnOCOCH(Et)Bu$	1.21	2.26	1.87	1630, 1336	1625, 1340
17 $Ph_3SnOCOCMe_3$	1.21	2.40	1.98	1622, 1330	1624, 1332

[a] ±0.03 mm·sec^{-1}. [b] Relative to SnO_2 at 80°K. [c] Ref. 4. [d] Ref. 19. [e] Ref. 20.

Although we have not made a quantitative study of solubilities, all the triphenyltin carboxylates were found to be sufficiently soluble in CCl_4 to allow their infrared spectra to be determined. In every case the COO bands for the straight-chain compounds in solution (where they are presumably monomeric) are shifted strongly towards the normal ester frequencies (Table 2). It therefore appears that these compounds are monomeric with tetracoordinate tin atoms in dilute solution, but pentacoordinate polymers in the solid state.

Herber *et al.*[4] have argued that so long as the range of bond ionicities in a series of compounds is not too large, the ratio of quadrupole splitting to isomer shift ($\rho \equiv \Delta/\delta$) can be used to distinguish between compounds in which the tin atom is pentacoordinate and those in which it is tetracoordinate. They suggest that (with δ relative to SnO_2), a value of $\rho > 2.1$ was evidence of pentacoordination about the tin atom, whereas if $\rho < 1.8$ the tin atom was tetracoordinate. All the compounds in this group have ρ values of about 2.6, (see Table 2), and would therefore satisfy Herber's criterion for pentacoordinate tin.

The trimethyltin acetate used in this work was the "normal" insoluble form. The soluble form reported by Simons and Graham[8] was prepared following the method of these authors. The Mössbauer parameters of the soluble form ($\delta = 1.33$ mm sec^{-1}; $\Delta = 3.66$ mm sec^{-1}) are the same within experiment error as those of the insoluble form. This is to be expected if the structural differences are those suggested by Graham[8], *i.e.* that the soluble form is a cyclic polymer such as (II) in the solid state, while the insoluble form is a linear polymer of the type (I). In both cases, the tin atom is in a trigonal bipyramidal configuration, so that the microsymmetry about the tin atom is essentially the same. It is clear that the Mössbauer effect is relatively insensitive to long-range structural differences. Consequently, it is not inconceivable that the straight-chain triphenyltin carboxylates have structure II rather than I.



(II)

Group (*b*). When the carboxylate chain branches at the α-carbon atom position, as in compounds (15)–(17) in Table 2, it is evident that a different type of structure from that discussed above is obtained.

The ρ value of ~ 1.9 for these compounds suggests that here the tin atom is tetrahedrally coordinated. Note that the decrease in ρ is caused entirely by the large diminution in quadrupole splitting. A change from sp^3d to sp^3 hybridization about the tin atom should have little effect upon the *s*-electron density at the tin nucleus, and this is reflected in the very similar isomer shifts for these three compounds and for the polymeric triphenyltin carboxylates.

It will be seen from Table 2 that the COO stretching bands for the branched-chain compounds are also very different from those of the polymeric carboxylates. These bands are essentially the same as those for the solutions of the polymeric compounds, showing that these branched-chain carboxylates do not have the symmetrical carboxyl group. These data are consistent with the suggestion that the α-branched-chain carboxylates resemble structurally the organic esters. The fact that the COO bands still differ appreciably from the normal ester positions is probably due to the influence of the heavy metal atom[2].

It is perhaps not surprising that branching in the R′ moieties of structure (I) should prevent association of molecules into polymers, since such association is also prevented in trialkyltin acetates when the alkyl group is bulky. There remains the possibility that branched-chain triphenyltin carboxylates could still form polymeric structures provided the branching occurs sufficiently far from the carboxyl group that steric hindrance with the Ph_3Sn moiety were avoided.

Decomposition products of triphenyltin stearate and undecenoate

These two compounds are interesting from several points of view. Firstly, the fact that these triphenyltin compounds are unstable on prolonged standing (approximately three years) in sample phials is itself interesting. The only reaction likely to occur under these conditions is hydrolysis, and although we are not able to determine the mechanism for the hydrolysis reaction we are forced to conclude on the basis of the analytical data that at least one of the products formed is volatile (*vide infra*). The reaction is slow kinetically, but for the undecenoate sample at least, *does occur* under normal storage conditions, as we shall show below. However, a sample of triphenyltin stearate prepared by us and allowed to stand under apparently similar conditions has shown no sign of decomposition after several months, and another sample from the same preparation stirred in warm water for 24 h showed no change.

The solid state infrared spectra of the decomposition products are very similar to those of the straight-chain triphenyltin carboxylates in the sodium chloride region, but there are interesting differences below 600 cm^{-1} and the solution spectra are different. The Mössbauer isomer shifts lie at much lower positive velocity than for the triphenyltin carboxylates, and are in fact the smallest shifts yet reported for any organotin compounds. The melting points for both products are very much higher than for the triphenyltin carboxylates. At this point it will be helpful to present the various experimental evidence pertaining to these compounds and discuss its probable interpretation.

TABLE 3

ANALYTICAL DATA AND MELTING POINTS FOR DECOMPOSITION PRODUCTS OF TRIPHENYLTIN UNDECENOATE AND TRIPHENYLTIN STEARATE

Element	Calcd.		Found	Atom ratio
Triphenyltin undecenoate, $C_{29}H_{34}O_2Sn$, m.p. 292–296°, dec.				
C	65.31		54.72	19.47
H	6.43		6.18	26.19
O	6.00		11.24	3.00
Sn	22.26		27.78	1.00
Triphenyltin stearate, $C_{36}H_{50}O_2Sn$, m.p. 266–270°, dec.				
C	68.26	58.20[a]	58.43	24.17
H	7.96	8.14[a]	8.07	39.78
O	5.05	9.69[a]	9.80	3.04
Sn	18.74	23.96[a]	23.89	1.00

[a] Calcd. for $C_{24}H_{40}O_3Sn$.

(*i*). *Analytical results.* Analytical results and melting points for the two compounds are given in Table 3. We shall consider first the product obtained from triphenyltin stearate, since here the situation is more clear-cut.

The stearate sample has the empirical formula $C_{24}H_{40}O_3Sn$, rather than the formula $C_{36}H_{50}O_2Sn$ required for triphenyltin stearate. This could be accounted for by the addition of one water molecule and the subsequent loss of two benzene molecules from the parent compound. There seems to be no way of accounting for the low C and H percentages and the high Sn percentage found other than via a volatile hydrocarbon decomposition product. On this basis, then, the tin-containing residue would have the formula $[PhSn(O)OCOR']_n$. It seems extremely unlikely that the carboxylate group would be subject to hydrolytic attack, and as we shall see below, the infrared spectrum shows the presence of a symmetrical carboxyl group, rather than a free acid function.

Saponification of the stearate sample yielded a tin-containing residue which was insoluble in all the usual organic solvents. We can conclude from this that the tin residue does not contain a Ph_3Sn moiety, and that there are two or fewer phenyl groups in the molecule. This is not inconsistent with the empirical formula above.

With the undecenoate product, the situation is complicated by the fact that the sample is a mixture of triphenyltin undecenoate and its hydrolysis product. That there are two species present can be seen clearly in the Mössbauer spectrum, shown in Fig. 1. Peaks 1 and 2 (reading from lower to higher velocity) constitute the quadrupole doublet attributable to the decomposition product, and peaks 1 and 3 another doublet superimposed upon the first, and having the same parameters as the other straight-chain triphenyltin carboxylates listed in Table 2. From relative intensities and line areas one can estimate the fraction of each species present. The ratio of intensities of peak 3 to peak 2 showed a steady decline during nine months of observation from 0.196 to 0.100 indicating that the decomposition was still progressing. We estimate that at the time the microanalysis was performed some 15% of the triphenyltin undecenoate had not undergone hydrolysis.

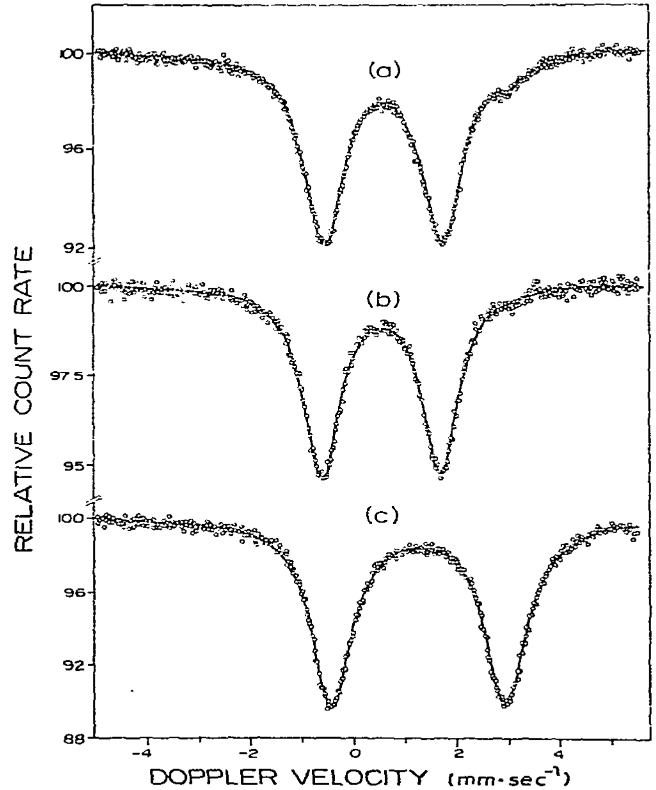


Fig. 1. Mössbauer spectra recorded at 80°K, with velocity scale relative to SnO_2 at the same temperature. (a) $PhSn(O)OCO(CH_2)_8CH{=}CH_2$; (b) $PhSn(O)OCO(CH_2)_{16}Me$; (c) $Ph_3SnOCO(CH_2)_{16}Me$.

If we assume that the analytical sample consisted of 15% triphenyltin undecenoate and 85% phenylstannoic undecenoate (in order to be consistent with the product postulated for the stearate), the following calculated percentages are obtained: C, 54.31; H, 6.18; O, 10.97; Sn, 28.54%. These are in very good agreement with those found in the microanalysis (Table 3), and lend further support to the formation of a product having formula $[PhSn(O)OCOR']_n$.

(*ii*). *Thermal gravimetric analysis.* A TGA curve determined for the stearate sample showed almost no weight loss below ~300°, when the compound then decomposed and lost approximately 69.8% of its weight. The calculated weight loss for phenylstannoic stearate ⟶ SnO_2 is 69.6%. Thus, these results are not inconsistent with the proposed formula.

(*iii*). *Infrared data.* The solid state infrared absorptions between 2000–250 cm^{-1} are given in Table 4 for triphenyltin stearate (our preparation) and the decomposition products of triphenyltin stearate and undecenoate. Many of the bands, especially the benzene ring absorptions, were assigned following Poller[9]. We have attempted to indicate in the footnotes to Table 4 the corresponding absorptions found in the other straight-chain triphenyltin carboxylates, in Ph_3SnCl and in $(Ph_3Sn)_2$, although of course the exact position of a given band varies from compound to compound.

In the 2000–600 cm^{-1} region the spectra of all three compounds are essentially identical, except that a few weak to very weak absorptions are not resolved in one

TABLE 4

SOLID STATE INFRARED ABSORPTIONS IN THE 2000-250 CM^{-1} REGION

PhSn(O)-undecenoate	PhSn(O)-stearate	Ph_3Sn-stearate	Assignment	Notes
	1710 w			
1635 w				
1569 m, sh	1565 s, sh	1572 m, sh		[b]
1536 m, b	1537 m, b	1532 s, b	$\nu_{as}(OCO)$	[b]
1481 m	1483 m	1481 m	$\nu(C–C)$	[a]
1432 s	1432 s	1430 s	$\nu(C–C)$	[a]
1415 m	1412 m	1410 m	$\nu_s(OCO)$	[b]
1332 w	1330 w	1320 w		[a]
1304 vw	1305 w	1305 w		[a]
1270 vw	1265 vw	1270 vw		[a]
1170 w	1180 vw	1160 w	C–H in-plane	[a]
	1120 vw	1120 vw	deformation	[c]
1078 m, sh	1080 m, sh	1081 m, sh	C–H in-plane	[a]
1025 m	1027 m	1026 m	deformation	[a]
	1000 w	1000 m	Ring vibration	[a]
912 w		912 vw	C–H out-of-plane	[c]
894 vw		896 w		[c]
		852 vw		[c]
729 s	728 s	731 s, sh	C–H out-of-plane	[a]
697 s	697 s	699 s	deformation	[a]
	669 w	663 w		[c]
	587 sh			
560–550 s, b	570–550 s, b		$\nu_{as}(Sn–O–Sn)$	[d]
503 m, b	501 m, b			[d]
448 m, sh	446 m	453 s, sh	$\nu(B_1)$	[a]
346 s	346 s			[d]
		276–268 s, b	$\nu_{as}(Sn–Ph)$	[a]

[a] Corresponding bands observed in all straight-chain triphenyltin carboxylates studied, in Ph_3SnCl and in $(Ph_3Sn)_2$. [b] Corresponding bands observed in all straight-chain triphenyltin carboxylates studied, but missing in Ph_3SnCl and $(Ph_3Sn)_2$. [c] Present in some, but not all, compounds studied. [d] Absent in all triphenyltin compounds studied.

or both decomposition products. Both decomposition products have carboxyl bands in the same regions as those for the straight-chain triphenyltin carboxylates, from which we can conclude that the carboxyl group is either bridging, chelating or ionic. All three compounds show the usual benzene ring absorptions, and in particular, all have a band at 1080 cm^{-1}. This band, assigned to a C–H in-plane deformation vibration, has been shown[10] to be characteristic of the phenyltin group.

Below 600 cm^{-1} the decomposition products show very different spectra from those of the triphenyltin carboxylates. The only band in common is at ~450 cm^{-1}, and this is considerably more intense in the triphenyltin compounds. Poller[11] assigns this band to the substituent-sensitive $16b(B_1)$ mode of a mono-substituted benzene. The fact that this band is but slightly shifted in the decomposition products can be taken as further evidence of a phenyltin group in these compounds.

The strong absorptions at ~270 cm^{-1} in the triphenyltin derivatives can be assigned to ν_{as}(Sn–Ph)[11]. Note that these bands are absent in the decomposition products. It is likely that ν(Sn–Ph) in these latter compounds should occur below 250 cm^{-1}, as should ν_s(Sn–Ph) in the branched-chain triphenyltin carboxylates.

The broad strong bands around 560–550 cm^{-1} in the decomposition products are helpful in trying to assign a structure to these compounds. Several workers[9,12,13] have noted that whereas the Sn–O–Sn asymmetric stretch occurs at about 775 cm^{-1} in hexaphenyldistannoxane, the corresponding vibration in mono- and dialkyl- and aryltin oxides is found in the range 580–545 cm^{-1}. No other absorptions are expected in this region for phenyltin compounds, and we can therefore assign these bands with confidence to ν_{as}(Sn–O–Sn). Although both symmetric and asymmetric stretching modes are possible for the Sn–O–Sn group, we are not aware of any assignments for the symmetric mode. It does not seem unreasonable to tentatively assign the bands at ~502 cm^{-1} in the PhSn(O)OCOR′ compounds to ν_s(Sn–O–Sn). It should be noted that these assignments imply that the decomposition products are polymeric, with tin–oxygen linkages. It seems difficult, however, to visualise the required stoichiometry without invoking a polymeric structure. Note also that the presence of Sn–O–Sn groups in these compounds effectively eliminates the possibility of bridging carboxyl groups.

There remain the intense absorptions at 346 cm^{-1} in the PhSn(O)OCOR′ products, which seem difficult to assign with any certainty. The Sn–Cl stretch in Ph_3SnCl occurs at this position, but no chloride was detectable in these products. We feel it unlikely that this band is attributable either to ν(Sn–Ph) or ν_s(Sn–O–Sn).

Solution spectra (CCl_4) of the decomposition products were recorded in the sodium chloride region, using compensated cells. The COO frequencies for both compounds were the same in solution as in the solid state (± 5 cm^{-1}), and the band positions did not move for an eight-fold change in concentration. These results can be interpreted in terms either of chelating or ionic carboxylate functions, but along with our assignment of the 560 cm^{-1} band in the solids, appear inconsistent with the assumption of bridging OCO groups.

(*iv*). *Mössbauer spectra.* We have seen above that the Mössbauer isomer shifts for both straight-chain and α-branched triphenyltin carboxylates are substantially the same. They are, however, very different from those of the PhSn(O)OCOR′ compounds (Table 5 and Fig. 1) and the latter require careful consideration because of their small magnitude.

TABLE 5

MÖSSBAUER PARAMETERS FOR RSn(O)OX COMPOUNDS AT 80°K

Compound	$\delta^{a,b}$ (mm·sec^{-1})	Δ^{a} (mm·sec^{-1})	ρ (=Δ/δ)
$PhSn(O)OCO(CH_2)_8CH=CH_2$	0.57	2.31	4.05
$PhSn(O)OCO(CH_2)_{16}Me$	0.56	2.32	4.14
BuSn(O)OCOMe	0.70[c]	2.26[c]	3.24
BuSn(O)OH	0.65	1.71	2.63

[a] ±0.03 mm sec^{-1}. [b] Relative to SnO_2 at 80°K. [c] A.G. Davies, private communication.

For tin compounds, there is a fairly regular trend in isomer shifts with electronic structure. Ionic stannic compounds ($4d^{10}5s^0$) exhibit nearly zero (or negative) isomer shifts relative to SnO_2. In tin(IV) compounds there is a basic $5s^1 5p^3$ configuration, almost always accompanied by some electron withdrawal from tin, so that shifts for these species (~1.3 mm sec^{-1}) are generally smaller than that for grey tin (~2.0 mm sec^{-1}), in which each tin atom is tetrahedrally surrounded by four other tin atoms, so that each has exactly one 5s electron.

Lees and Flinn[14] have derived a general equation for the isomer shift in tin compounds as a function of the numbers of tin 5s and 5p electrons. With respect to SnO_2, this equation is:

$$\delta = -0.43 + 3.01 n_s - 0.20 n_s^2 - 0.17 n_s n_p$$

where n_s is the number of 5s electrons and n_p the number of 5p electrons. Since this equation contains two unknowns, there is no unique solution in our case. However, if we impose the very reasonable constraint that n_p should lie within the limits $0 \leqslant n_p \leqslant 3$, then it is possible to calculate a range of permissable values of n_s on the basis of a given experimental value of δ. Taking the average of the isomer shifts for the triphenyltin carboxylates and for the decomposition products, and with the above restriction on n_p, we find:

$Ph_3SnOCOR'$: $0.59 \leqslant n_s \leqslant 0.72$;

PhSn(O)OCOR': $0.34 \leqslant n_s \leqslant 0.41$.

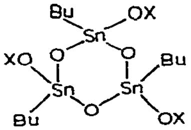
These results imply that there is a reduction of 30–50% in s-electron density at the tin nucleus for the decomposition products.

This decrease in s-electron density about tin could be equally well explained in two different ways. First, that the phenylstannoic carboxylates have appreciable ionic character. This would not be unreasonable in view of the trend discussed above, and would also be consistent with the infrared data. On the other hand, in the structure we postulate below the tin atom is bonded to four oxygen atoms, and the shift in δ towards the value for SnO_2 (in which tin is hexacoordinate) could be due solely to electronegativity effects. This view requires the existence of chelating carboxyl groups, which also is not inconsistent with the infrared results.

As will be noted from Table 5 the quadrupole splittings for the decomposition products are essentially the same as those for the branched-chain triphenyltin carboxylates. On this basis it is tempting to conclude that in all these compounds the tin atom is tetracoordinate. On the other hand it could be argued that the much lower

s-electron density at the tin nucleus in the decomposition products might cause a concomitant shift in the asymmetry of the $5p$-electron distribution about tin, thereby leading to an ambiguity in the interpretation of the quadrupole splittings for these compounds. In the absence of further information it would appear that the quadrupole splittings do not rule out either four- or five-fold coordination about the tin atom in the decomposition products.

We mentioned above the necessity of relying on results for model compounds when interpreting Mössbauer data for unknown samples. During the preparation of this manuscipt two newly prepared compounds have been brought to our attention, which are invaluable in postulating a structure for the phenylstannoic carboxylates. These are $[BuSn(O)OH]_3$ and $[BuSn(O)OAc]_3$, which are reported[15] to be cyclic trimers of the type (III), having Sn–O–Sn linkages. Some similar compounds have also been mentioned by Neumann[16]. The Mössbauer parameters for these compounds are included in Table 5. The isomer shifts are very nearly the same as those for the phenylstannoic carboxylates, and the difference is probably attributable to a difference in electronegativity between butyl and phenyl groups (compare the results for Bu_3SnOAc and Ph_3SnOAc in Table 2).



(III)
X=H, Ac

The quadrupole splitting for BuSn(O)OAc is essentially the same as those for phenylstannoic stearate and undecenoate, but that for BuSn(O)OH is appreciably lower. Since the latter compound clearly contains tetracoordinate tin, we suggest that the increased splittings in the three carboxylates are indicative of pentacoordination about the tin atom in these compounds, with both carboxyl oxygens bonded to tin. (Note that "Herber's rule" regarding ρ vlues is not applicable here.) This suggestion seems reasonable on two counts. First, replacement of H by Ac in structure (III) without any change in the direct bonding to the tin atom should have very little effect on the Mössbauer spectrum. Indeed, it would be difficult to rationalise the 30% increase in quadrupole splitting on this basis. Second, the infrared data show conclusively that the OCO groups in the phenylstannoic carboxylates are symmetrical. The fact that these quadrupole splittings are well below those for the pentacoordinate Ph_3Sn carboxylates is undoubtedly due to the large difference in s-electron density about tin in the two types of compounds.

The Mössbauer parameters for these four compounds are so unusual and distinctive as to make virtually positive the assignment of a structure such as (III) to the PhSn(O)OCOR′ compounds. Of course one could equally well assume a linear polymeric structure with bridging oxygens, and it would be very difficult to distinguish the two possibilities.

(*v*). *Thin-layer chromatography*. Both products were chromatographed on alumina and on silica, and both exhibited the same behaviour. On alumina, neither material moved. On silica with benzene as elutant, one fraction of each sample moved rapidly, whilst the other fraction remained stationary. This second fraction could be moved using a more polar elutant, such as methanol.

This behaviour can be explained in terms of an ionic structure in solution, with the carboxylate moiety being less tightly held by the silica and capable of being eluted by benzene, whereas the phenyltin residue would require a more polar solvent. We feel that the clean separation observed is more indicative of an ionic species than of a mixture of compounds.

(*vi*). *Summary of the evidence.* Microanalytical data for the decomposition products of triphenyltin stearate and undecenoate indicate that they have the empirical formula $PhSn(O)OCOR'$. The loss of one or more phenyl groups from the parent compounds is supported by the fact that on saponification the tin-containing residue is insoluble in all the usual organic solvents. Furthermore, thermal gravimetric analysis shows the correct weight loss for $PhSn(O)OCOR' \rightarrow SnO_2$.

The infrared spectra show absorptions which are attributable to a phenyltin group, and to ν(Sn–O–Sn) in a monophenyltin compound. The COO bands are indicative of symmetrical carboxyl groups in both the solid state and in solution, so that these groups must be either chelating or ionic.

Results of thin-layer chromatography lend support to the suggestion of ionic carboxyl groups, at least *in solution*. The Mössbauer isomer shifts appear to be consistent with the presence of either chelating or ionic carboxyl groups *in the solid state*. Comparison of the Mössbauer parameters with those for the known compounds BuSn(O)OH and BuSn(O)OAc allows us to assign a structure such as (III) (or alternatively, a linear oxygen-bridged polymeric structure) with pentacoordinate tin atoms to these compounds.

There remains the question of mechanism for the decomposition reaction leading from triphenyltin carboxylates to the products obtained. One would naturally suppose that such a reaction would require quite severe conditions. The fact remains, however, that the undecenoate sample has continued to undergo change whilst in a closed phial at room temperature under normal storage conditions. As we have been unable to induce any decomposition in the sample of triphenyltin stearate we prepared, the most likely suggestion appears to be the presence of some small amount of impurity in the M & T samples which has acted as a catalyst for the reaction. It seems unlikely that a definite answer can be found.

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