Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

ORGANOTIN CARBOXYLATES
II*. MÖSSBAUER AND INFRARED STUDY OF BONDING DIFFERENCES IN TRIMETHYLTIN HALOACETATES

CHRISTINE PODER AND JOHN R. SAMS
Department of Chemistry, University of British Columbia, Vancouver 8, B.C. (Canada)

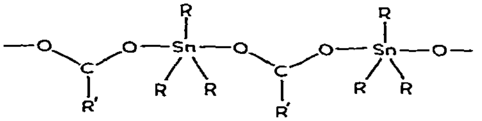
(Received April 29th, 1969)

SUMMARY

Trimethyltin haloacetates are shown to be linear polymers with pentacoordinate tin atoms and bridging OCO groups. The electron density for the Me_3Sn moiety is independent of variations in the acetato group, although the Mössbauer quadrupole splittings are linear with p*K* of the corresponding acid. These results are interpreted in terms of changes in the distribution of electron density in the two Sn–O bonds arising from similar changes in the two C–O bonds. The IR data support this suggestion.

INTRODUCTION

A number of compounds of the type $R_3SnOCOR'$ (R = alkyl, aryl; R' = alkyl) are reported to form polymers of the type (I)[1-4], with bridging OCO groups and planar R_3Sn moieties. It has been shown[2,5], however, that if the R group is bulky such polymer association does not occur. Thus, for example, trimethyl-, triphenyl- and tribenzyltin acetates have structure (I), whereas triisopropyl- and tricyclohexyltin acetates behave as normal esters, the tin atom being tetracoordinate. Furthermore, as we have recently shown[4], for triphenyltin carboxylates branching in the R′ moiety at the α-carbon (*e.g.* triphenyltin 2-ethylhexanoate) also prevents polymer formation.



(I)

Evidence to support structure (I) has come principally from IR data, which show a nearly symmetrical OCO group and only the asymmetric $Sn–C_3$ stretching band. Simons and Graham[3] have also inferred this type of association in concentrated CCl_4 solutions on the basis of $^{119}Sn–Me$ NMR coupling constants. It has been pointed out recently[4,6] that Mössbauer spectroscopy provides another convenient and

---

* For Part I see ref. 4.

fairly simple tool for the study of coordination in tin compounds, either in the solid state or as frozen solutions. Herber and co-workers[6] have suggested that organotin compounds in which the tin atom is pentacoordinate usually show a ratio of quadrupole splitting to isomer shift in excess of about 2.1, whereas in tetracoordinate tin compounds this ratio rarely exceeds 1.8.

It appears that the differences observed thus far between various triorganotin carboxylates are almost entirely due to simple steric effects, and have little to do with more subtle differences in bonding. It therefore seemed of interest to investigate via the Mössbauer effect a series of compounds having the structure (I), but differing slightly in the R′ moieties, since the usual Mössbauer parameters (isomer shift and quadrupole splitting) are quite sensitive to changes in electron density and electron distribution about the tin nucleus. Lengthening the R′ chain in triphenyltin (and presumably, trimethyltin) carboxylates has little or no effect on the Mössbauer parameters, while branching at the α-carbon prevents polymer association in the triphenyltin compounds, resulting in a dramatic change in quadrupole splitting. Thus, it seemed attractive to study a number of trimethyltin haloacetates for two reasons. First, the three trimethyltin chloroacetates have been assigned structure (I) on the basis of IR and NMR measurements[3], and it therefore seemed likely that all the haloacetates would have this structure. Second, a wide-range of acid strengths can be obtained, from a p*K* of 4.75 for acetic acid to 0.23 for trifluoroacetic acid. Since the donor properties of the anions are intimately connected with acid strength, we anticipated corresponding changes in electron density and electric field gradient at the tin nucleus, leading to differences in isomer shift and quadrupole splitting.

We discuss below Mössbauer and IR spectral data for trimethyltin acetate and seven trimethyltin haloacetates.

EXPERIMENTAL

All the trimethyltin haloacetates were prepared in a very straightforward way by mixing stoichiometric quantities of trimethyltin hydroxide and the appropriate haloacetic acid in water. Evaporation to dryness yielded white crystalline products which were purified by recrystallisation from carbon tetrachloride. Microanalyses were performed by P. Borda of this Department, and the analytical results are given in Table 1.

TABLE 1

ANALYTICAL DATA FOR TRIMETHYLTIN HALOACETATES

Compound	C (%)		H (%)		X (%)	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
$Me_3SnOCOCH_2I$	17.2	17.2	3.2	3.1	36.4	36.6
$Me_3SnOCOCH_2Br$	19.9	20.9	3.7	3.8	26.5	26.4
$Me_3SnOCOCH_2Cl$	23.3	23.6	4.3	4.2	13.8	13.2
$Me_3SnOCOCHCl_2$	20.6	20.8	3.5	3.4	24.3	24.0
$Me_3SnOCOCBr_3$	13.1	13.8	2.0	2.2	52.2	52.5
$Me_3SnOCOCCl_3$	18.4	18.4	2.8	2.7	32.6	32.3
$Me_3SnOCOCF_3$	21.7	21.6	3.3	3.2	20.6	20.4

Solid state IR spectra were recorded on a Perkin–Elmer Model 457, the solids being dispersed in Nujol or halocarbon oil between KBr plates. Solution spectra in CCl_4 were determined in the sodium chloride region on a Perkin–Elmer Model 21 using compensated cells. The Mössbauer spectrometer was of the constant acceleration type, the electromechanical velocity transducer being phase-locked to a 400-channel analyser operating in time mode. The detector was a Reuter–Stokes RSG-60 proportional counter with 2 atm Xe/CH_4 fill gas. A narrow-line 5 mc $Ba^{119m}SnO_3$ source was employed, and the velocity scale was calibrated against an NBS standard sodium nitroprusside absorber. All Mössbauer measurements were made with the powdered absorbers at 80° ± 1°K, and isomer shifts are reported relative to SnO_2 at this temperature.

RESULTS AND DISCUSSION

Mössbauer isomer shifts and quadrupole splittings for trimethyltin acetate and seven trimethyltin haloacetates are given in Table 2. All the spectra consisted of simple quadrupole-split doublets as shown in Fig. 1. IR data in the carbonyl/carboxyl

TABLE 2

MÖSSBAUER PARAMETERS FOR THE COMPOUNDS $(CH_3)_3SnOCOR$ AT 80°K

R	$\delta^{a,b}$ (mm·sec^{-1})	Δ^a (mm·sec^{-1})	ρ (Δ/δ)
CH_3	1.35	3.68	2.72
CH_2I	1.37	3.83	2.80
CH_2Br	1.34	3.90	2.91
CH_2Cl	1.41	3.89	2.76
$CHCl_2$	1.37	4.08	2.98
CBr_3	1.43	4.13	2.89
CCl_3	1.44	4.15	2.88
CF_3	1.38	4.22	3.05

[a] ±0.03 mm·sec^{-1}. [b] Relative to SnO_2 at 80°K.

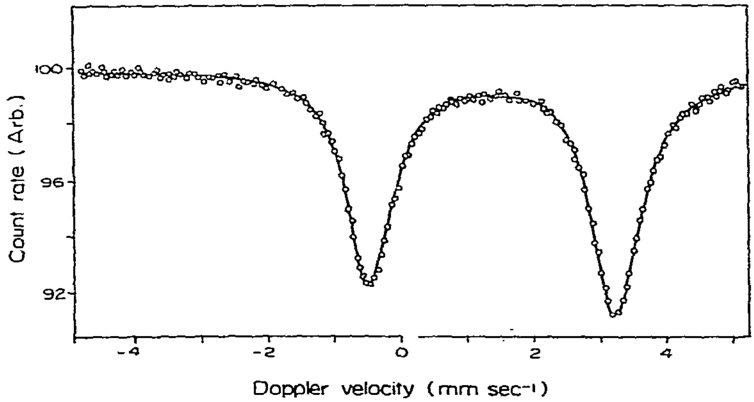


Fig. 1. Mössbauer spectrum of $(CH_3)_3SnOCOCH_3$ at 80°K. Velocity scale is relative to SnO_2 at 80°K.

region from both solid state and solution spectra, and in the Sn–C_3 stretching region for the solids are listed in Table 3.

TABLE 3

INFRARED CARBONYL/CARBOXYL AND ASYMMETRIC Sn–C_3 STRETCHING FREQUENCIES FOR $(CH_3)_3SnOCOR$ COMPOUNDS (CM^{-1})

R	CCl_4 solution		Solid state		
	ν(C=O)	ν(C–O)	ν(C=O)	ν(C–O)	ν_{as}(Sn–C_3)
CH_3	1650	1320	1558	1418	553
CH_2I	1659	1320	1581	1383	551
CH_2Br	1660	1330	1590	1381	551
CH_2Cl	1687	1339	1618	1382	555
$CHCl_2$	1696	1330	1626	1380	554
CBr_3	1688	1294	1633	1339	554
CCl_3	1701	1295	1647	1348	557
CF_3	1720	1290	1652	1340	555

Both the Mössbauer and IR results show conclusively that in the solid state all the compounds are pentacoordinate polymers of the type (I), as anticipated. A comparison of solution and solid state carbonyl/carboxyl frequencies shows the expected shift from the monomeric ester form in solution to the associated polymeric form with bridging OCO groups in the solids. The absence of ν_s(Sn–C_3) in all the compounds implies planar Me_3Sn moieties. All the compounds have quadrupole splittings greater than 3.6 mm·sec^{-1}, whereas tetracoordinate $R_3SnOCOR'$ compounds show splittings[4] of ~ 2.3 mm·sec^{-1}.

A closer examination of the Mössbauer results in Table 2 reveals some very interesting features. First, all the isomer shifts fall into the very narrow range $\delta = 1.39 \pm 0.05$ mm·sec^{-1}. This means that the total *s*-electron density at the tin nucleus is essentially the same for all the compounds. One might have expected that increasing the electronegativity of the substituents on the α-carbon atom of the acetate group would serve to withdraw electron density from the tin atom. This constancy of *s*-electron density about the tin atom suggests either that there is no significant difference in electron withdrawal from tin with changes in electronegativity of the α-carbon substituents, *or* that the tin atom is able to compensate for such differences by in turn withdrawing electron density from the methyl groups bonded to it. We can eliminate the latter possibility as follows.

The NMR measurements of Simons and Graham[3] on the trimethyltin chloroacetates show two important features that have apparently not been remarked upon before. In the first place, the Me_3Sn chemical shifts are nearly constant (τ 9.33 ± 0.06 in $CDCl_3$ solution) and show very little deshielding of the methyl protons with decreasing p*K* of the chloroacetic acid. Secondly, $J(^{119}Sn\text{–}Me)$ and $J(^{117}Sn\text{–}Me)$ are both constant within experimental error for these compounds. Since the coupling constants are proportional to the product of electron densities $|\psi_{Sn}(O)^2| \cdot |\psi_{Me}(O)^2|$, this product is therefore constant. Furthermore, the differential Mössbauer isomer shift depends only upon $|\psi_{Sn}(O)^2|$, and since this is constant, so also is $|\psi_{Me}(O)^2|$.

It is clear then that any rehybridization of the tin bonding orbitals caused by differences in the haloacetates does not appreciably alter the electron density about the Me_3Sn group. These results show that not only is there no significant difference in electron withdrawal from tin amongst the various haloacetate compounds, but there is no significant difference in electron withdrawal from the Me_3Sn group *as a whole*.

It should be pointed out that this situation is quite different from that recently observed[7] in compounds of the type Me_3SnR, where R is an aryl group with halogen substituents. In the latter compounds changes in electronegativity of R, while leaving the isomer shift essentially constant, caused considerable differences in the methyl–tin coupling constants. Thus, although the tin atoms maintained a fixed electron density, changes in the R group caused a redistribution of this electron density amongst the four tin–carbon bonds. Of course in the Me_3SnR compounds one is changing a group bonded directly to tin, while in the trimethyltin haloacetates changes are being made in a group three bonds removed from the tin atom.

Although the isomer shifts are virtually unaffected by halogenation of the acetate group, the same cannot be said of the quadrupole splittings, which show quite marked differences. We can eliminate the possibility that the observed changes in Δ could arise here from intramolecular steric interactions between the halogens and the methyl groups bonded to tin, since of the three trihaloacetate compounds the trifluoroacetate would be least likely to show such an effect. We notice, however, a definite trend of increasing quadrupole splitting with increasing strength of the acid from which the compound is derived. In fact, a plot of quadrupole splitting against pK for the acid is

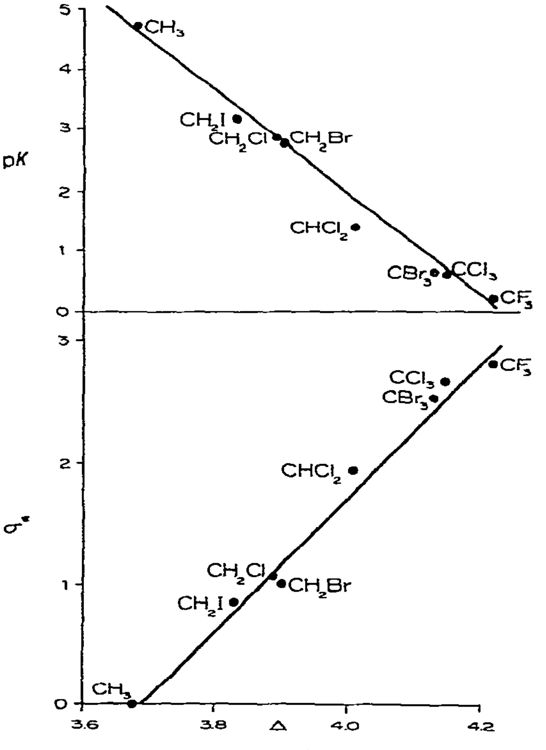


Fig. 2. Plot of quadrupole splitting against pK of the acid (upper) and Taft inductive factor σ^* (lower), for trimethyltin acetate and several trimethyltin haloacetates.

linear, as shown in Fig. 2.

Since the lowering of the pK value is caused by an increase in the sum of electronegativities of the α-carbon substituents, the explanation which first comes to mind for the observed trend in Δ is the usual inductive effect. We have also plotted in Fig. 2 the quadrupole splittings against the Taft inductive factors[8] σ^*, and again an essentially linear correlation is found. Since σ^* is in one sense a measure of the ease of ester solvolysis, one would expect that the trifluoroacetate group for example is less tightly held to the Me_3Sn moiety than is the acetate. Thus, the tighter the polymeric structure, the smaller the quadrupole splitting.

An alternative but basically equivalent argument can be couched in terms of Lewis acid–base behaviour. We have noted[9] that in adducts of $SnCl_4$ with O-donor substances there is a tendency for the quadrupole splitting to increase with decreasing Lewis basicity of the donor molecule(s). Clearly, the anion of a strong protonic acid will be a rather weak Lewis base, and it appears that a similar trend is being observed here as in the $SnCl_4$ adducts.

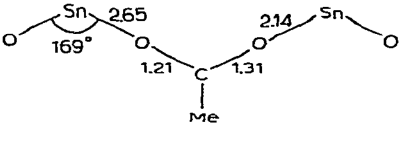
However, the constancy of the isomer shifts and methyl–tin coupling constants suggests that we be careful in our interpretation of "inductive effects" and "donor–acceptor interactions", since here these effects clearly do not influence the electron *density* about the Me_3Sn moiety, but only the *distribution* of a *fixed* electron density. It seems wise to treat this problem in some detail.

The electric field gradient (efg) can be completely specified in terms of the z-component of the efg tensor $V_{zz} = \partial^2 V/\partial z^2$, and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. In terms of these parameters, the quadrupole splitting for ^{119}Sn is given by

$$\Delta = \tfrac{1}{2} e \cdot Q \cdot V_{zz} \cdot (1 + \eta^2/3)^{\frac{1}{2}}$$

where Q is the nuclear quadrupole moment.

Although the formal point-group symmetry about the tin atom in these compounds is D_{3h}, it seems likely that there may be some slight distortion from axial symmetry in these compounds, and hence a non-vanishing η. We can take as a guide the X-ray structure of tribenzyltin acetate, recently reported by Alcock and Timms[5], the salient features of which are shown in (II).



(II)

Distances are given in Å. The benzyl groups have been omitted from (II) for the sake of clarity, but it should be pointed out that the tin atom lies only 0.02 Å out of the plane of the three benzyl methylene carbons. Alcock and Timms[5] suggest that the distortion of the O–Sn–O bond angle from 180° is probably steric in origin, and arises from the fairly bulky benzyl groups. It therefore seems likely that the O–Sn–O angle is much closer to 180° in the trimethyltin compounds, but η may nevertheless be nonzero. However, if the O–Sn–O distortion is mainly steric in origin, then η will not be linear in pK but will depend strongly on the size of the halogen substituents. Since Δ *is* linear in pK, we can safely assume that if η is nonzero in this series of compounds it is (a) small, and/or (b) nearly constant. In either case the preponderant effect on Δ will come from V_{zz}, and to a good first approximation we can assume $\eta = 0$. Because the Me_3Sn moiety is substantially unaffected by differences in the haloacetate groups, the increasing magnitude of V_{zz} as one passes from the acetate to the trifluoroacetate can only arise from differences in the two tin–oxygen linkages. Thus, although the local symmetry about tin is formally D_{3h} in all the compounds reported here, it is probably more accurate to describe the symmetry of the *charge distribution* about tin as C_{3v}. This suggestion is supported by the structure shown in (II), in which the two Sn–O bond distances are very different. Furthermore, we predict that with increasing electronegativity of the α-carbon substituents the difference in the two Sn–O bond lengths will increase.

Our reasons for supposing this are as follows. First, note that in structure (II) the two C–O bond lengths are slightly different. In the polymeric trimethyl-, tributyl- and triphenyltin acetates, the carbonyl/carboxyl IR bands lie in the regions 1548–1560 cm^{-1} and 1416–1420 cm^{-1}, respectively[4], and it is likely that the corresponding bands for tribenzyltin acetate are in the same regions. As shown in Table 3, these bands shift in a fairly regular fashion with increasing acid strength as one progresses from trimethyltin acetate to trimethyltin trifluoroacetate, the carbonyl band increasing in frequency, the carboxyl band decreasing. For example, the solid state carbonyl–carboxyl band separation is only 140 cm^{-1} in trimethyltin acetate, and increases to 312 cm^{-1} in the trifluoroacetate compound. From simple Hooke's law considerations it is expected that these changes in bond stretching frequencies reflect corresponding changes in bond length. There is ample evidence to support this point of view. Thus, Walsh[10] has found that the bond length of a carbonyl group increases with polarity, Rundle and co-workers[11] have shown that the carbonyl stretching frequency is a monotonic (although not quite linear) function of the bond length, and Kagarise[12] has pointed out that in molecules of the type XYC=O there is a linear relation between the sum of electronegativities of X and Y and the carbonyl stretching frequency.

The usual[13] discussion of carbonyl/carboxyl frequency shifts in acetato–metal complexes has centred round the effect of coordination strength of the metal. The effect here is obviously different in origin and pertains only to variations in the acetato functions. Although trends similar to those observed here have been noted in tributyltin chloroacetates[14,15] and fluoroacetates[15], in sodium chloroacetates[14], and in trimethyltin chloroacetates[3], none of these authors has considered what these frequency shifts imply regarding changes in the two carbon–oxygen bond distances, and concomitant changes in the oxygen–metal bonding.

From the foregoing discussion it should be apparent that with decreasing p*K* of the acid from which the trimethyltin (halo)acetate is formed, there is a change from essentially equivalent OCO groups to quite pronounced carbonyl and carboxyl character of the two C–O bonds. That is, the so-called inductive effect in these cases is merely one of localisation of electron density in the carbonyl bond, and stabilisation of the localised structure. This increasing inequivalence of the two C–O bonds we feel is then manifested as an increasing inequivalence of the two Sn–O bonds, and finally appears as a change in quadrupole splitting in the Mössbauer spectrum.

The analysis we have presented above leads quite naturally to the conclusion that the isomer shifts and methyl–tin coupling constants *should* be effectively constant in these compounds, since all one is really doing via the "inductive effect" is altering the distribution of electron density between the two C–O bonds, and *not* withdrawing any electron density from the OCO groups. No other analysis seems to explain all the facts.

It is instructive to make a more complete comparison between the present results for $Me_3SnOCOR'$ compounds and our observations[8] on polyhalogenoaryltin derivatives of the type Me_3SnR (*vide supra*). In both series of compounds δ is effectively constant while Δ shows marked variations. In the former compounds however, $J(^{119}\text{Sn–Me})$ is nearly constant, but in the latter there is a linear relation between $J(^{119}\text{Sn–Me})$ and Δ. These results can be readily understood when one notes that in the haloacetates, changes in electronegativity of R′ can be accommodated quite easily merely by altering the electron distribution in the two Sn–O bonds, without involving the methyl groups directly. On the other hand, any redistribution of electron density in the Me_3SnR compounds with changes in electronegativity of R (keeping $|\psi_{Sn}(O)^2|$ constant) necessarily affects the methyl groups. Finally, it should be pointed out that in both series of compounds, the tin atom adopts an essentially fixed electron density, changes in R (or R′) serving merely to redistribute this constant density amongst the various bonds.

It would seem that Mössbauer spectroscopy, coupled with the more usual IR and NMR techniques, provides a powerful and elegant tool for structural analysis in organotin chemistry, and should be more widely applied. Of course, the final word on the structure and bonding in these compounds must come from X-ray data, and we hope that detailed structures for the trimethyltin acetate and trifluoroacetate compounds will soon be available.

ACKNOWLEDGEMENTS

We thank the National Research Council of Canada for support of this project.

REFERENCES

1 M. J. Janssen, J. G. A. Luijten and G. J. M. van der Kerk, *Recl. Trav. Chim. Pays-Bas*, 82 (1963) 90.
2 R. C. Poller, *J. Organometal. Chem.*, 3 (1965) 321.
3 P. B. Simons and W. A. G. Graham, *J. Organometal. Chem.*, 10 (1967) 457.
4 B. F. E. Ford, B. V. Liengme and J. R. Sams, *J. Organometal. Chem.*, 19 (1969) 53.
5 N. W. Alcock and R. E. Timms, *J. Chem. Soc.*, *A*, (1968) 1873, 1876.
6 R. H. Herber, H. A. Stöckler and W. T. Reichle, *J. Chem. Phys.*, 42 (1965) 2447.
7 T. Chivers and J. R. Sams, *Chem. Commun.*, (1969) 249.
8 R. W. Taft, in M. S. Newman (Ed.), *Steric Effects in Organic Chemistry*, Wiley, New York, 1956, p. 619.
9 F. Aubke, P. Yeats and J. R. Sams, to be published.
10 A. D. Walsh, *Trans. Faraday Soc.*, 42 (1946) 561.
11 M. Margoshes, F. Fillwalk, V. A. Fassel and R. E. Rundle, *J. Chem. Phys.*, 22 (1954) 381.
12 R. E. Kagarise, *J. Amer. Chem. Soc.*, 77 (1955) 1377.
13 K. Nakamoto, J. Fujita, S. Tanaka and M. Kobayashi, *J. Amer. Chem. Soc.*, 79 (1957) 4904.
14 R. A. Cummins and P. Dunn, *Aust. J. Chem.*, 17 (1964) 185.
15 M. Vilarem and J.-C. Maire, *C.R. Acad. Sci., Paris*, 262 (1966) 480.