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

MÖSSBAUER SPECTRA OF ORGANOTIN COMPOUNDS
III*. COMPOUNDS SHOWING MÖSSBAUER EFFECTS AT ROOM TEMPERATURE

R. C. POLLER, J. N. R. RUDDICK AND B. TAYLOR
Chemistry Department, Queen Elizabeth College, Campden Hill Road, London W. 8 (Great Britain)
D. L. B. TOLEY
The Tin Research Institute, Fraser Road, Greenford, Middlesex (Great Britain)

(Received April 6th, 1970)

SUMMARY

The validity of the generalization that, if a compound shows a Mössbauer effect at room temperature then its structure is polymeric, has been tested for a number of organotin compounds. Those compounds which, from other evidence, are considered to be polymeric showed significant Mössbauer absorption at room temperature.

INTRODUCTION

Measurements of Mössbauer spectra of tin compounds are usually made with the sample at 78°K so as to increase the probability of recoilless absorption of γ-rays. Certain compounds, however, show a marked effect at room temperature and the empirical observation was made that this phenomenon could be correlated with the presence of polymeric structures[1]. There has subsequently been some theoretical justification for these observations when it was shown that both the Debye temperatures and characteristic temperatures for crystals of polymeric tin compounds were significantly higher than those of crystals of monomeric species[2]. If this method of detecting polymeric structures is generally applicable it represents a valuable aid to structure assignment. In the present paper the Mössbauer spectra of a number of organotin compounds, many of which are thought to have polymeric structures, are reported and discussed.

EXPERIMENTAL

Details of the Mössbauer spectrometer have been described elsewhere[3]. Measurements were made with the samples at 78°K and 300°K, the spectra, were calibrated with β-tin and tin(IV) oxide the separation being 2.56 mm/sec. The error associated with the isomer shift and quadrupole splitting measurements is estimated

---

* The papers under refs. 3 and 7 are considered as Parts I and II of this series.

as ±0.05 mm/sec. The Mössbauer results were computed on the University of London Atlas computer using a programme kindly supplied by Dr. T. C. Gibb[4] which was modified to suit our requirements.

Derivatives of bis(8-hydroxy-5-quinolyl)methane[5], 8-hydroxyquinoline[3], 4,4′-bipyridine[6], 4-phenylpyridine[6], 2,2′-bipyridine[7,8], *trans*-1,4-dithiane 1,4-dioxide[9], *cis*-1,4-dithiane 1,4-dioxide[9], 1,4-dithiane 1-oxide[9] and dimethyl sulphoxide[10] were made by published procedures and had melting points in agreement with literature values. Triphenyltin acetate, propionate, chloroacetate and isobutyrate were made by dissolving equimolar proportions of triphenyltin hydroxide and the carboxylic acid in anhydrous benzene, the solutions were boiled under reflux for 1 h and the solvent evaporated under reduced pressure to give near quantitative yields. Recrystallisation from benzene (acetate and propionate) or a mixture of chloroform and diethyl ether (chloroacetate) gave pure products having literature[11] melting points. The isobutyrate was crystallised from a mixture of chloroform and diethyl ether when it had m.p. 116–118°, lit.[15] m.p. 123–125°. Attempts to make the corresponding trifluoroacetate, trichloroacetate and pivalate by this procedure gave the insoluble phenylstannoxane carboxylates $PhSn(OCOR)O(R=CF_3, CCl_3, CMe_3)$ which all had m.p. >360°. Triphenyltin pivalate was prepared by heating an equimolar mixture of triphenyltin chloride and sodium pivalate in ethanol under reflux for 30 min. The suspension was then stirred at room temperature for 48 h, the sodium chloride filtered off and the solvent removed by evaporation under reduced pressure. The crude product was recrystallised from a mixture of benzene and light petroleum giving pure triphenyltin pivalate, m.p. 112°, lit.[12] m.p. 112–115°. Analytical values for new compounds and for triphenyltin isobutyrate are given in Table 1.

TABLE 1

ANALYTICAL VALUES

Compound	Found (%)			Calcd. (%)		
	C	H	Sn	C	H	Sn
$Ph_3SnOCOCH(CH_3)_2$	60.4	5.5	21.7	60.4	5.1	21.6
$PhSn[OCOC(CH_3)_3]O$	42.5	4.7	37.8	42.2	4.5	37.9
$PhSn[OCOCCl_3]O$	25.3	1.5	31.9	25.7	1.3	31.7
$PhSn[OCOCF_3]O$	30.0	1.6	36.8	29.6	1.55	36.55

RESULTS

Mössbauer parameters obtained are given in Table 2. Computation was used to fit Lorentzian curves to the experimental points and to calculate the values of the isomer shift (δ), quadrupole splitting (Δ) and the half widths (Γ). The room temperature effect (R) is the ratio of the magnitude of the Mössbauer effect at room temperature to that at 78°K and it can be shown[1a] that, providing each experimental point represents at least 1×10^5 counts, values of R of 0.031 and above are significant.

DISCUSSION

(*a*). *Derivatives of bis(8-hydroxy-5-quinolyl)methane* (LH_2)

Compounds derived from this tetradentate ligand have been reported and,

TABLE 2

MÖSSBAUER DATA

No.	Compound	δ[a,b]	Δ[a]	Γ_1[a]	Γ_2[a]	R[c]
(I)	$Me_2SnL\cdot H_2O$[d]	0.87	2.00	0.80	0.80	0.035
(II)	$Bu_2SnL\cdot H_2O$	1.00	2.05	0.83	0.90	0.044
(III)	$Ph_2SnL\cdot H_2O$	0.78	1.65	0.90	0.85	0.045
(IV)	$(C_8H_{17})_2SnL$	1.00	2.05	0.85	0.85	0
(V)	Me_2SnOx_2[e]	0.88[f]	1.98[f]	0.72	0.80	0
(VI)	Bu_2SnOx_2	1.02[f]	2.04[f]	0.70	0.75	0
(VII)	Ph_2SnOx_2	0.78[f]	1.64[f]	0.80	0.75	0
(VIII)	$(C_8H_{17})_2SnOx_2$	1.13	1.86	0.75	0.79	0
(IX)	$Bu_2SnCl_2\cdot$4,4'-Bipy[g]	1.58	4.00	0.84	0.82	0.057
(X)	$Ph_2SnCl_2\cdot$4,4'-Bipy	1.30	3.59	0.74	0.75	0.040
(XI)	$Bu_2SnCl_2\cdot$4-Phepy[h]	1.51	3.98	0.70	0.80	0
(XII)	$Bu_2SnCl_2\cdot$2,2'-Bipy[i]	1.56[j]	3.83[j]			
(XIII)	$Ph_2SnCl_2\cdot$2,2'-Bipy	1.26[k]	3.51[k]	0.80	0.75	0
(XIV)	$Ph_2SnCl_2\cdot$Pyrazine	1.32	3.00	0.85	0.81	0.035
(XV)	$Ph_2SnCl_2\cdot$*t*-DTDO[l]	1.26	3.78	0.79	0.82	0.159
(XVI)	$Ph_2SnCl_2\cdot$*c*-DTDO[m]	1.24	3.72	0.73	0.78	0.091
(XVII)	$Ph_2SnCl_2\cdot$2DTO[n]	1.24	3.72	0.75	0.75	0
(XVIII)	$Ph_2SnCl_2\cdot 2\ Me_2SO$	1.23	3.54	0.82	0.75	0
(XIX)	$Me_2SnCl_2\cdot 2\ Me_2SO$	1.39	4.10	0.81	0.80	0
(XX)	$Ph_3SnOCOCH_3$	1.26	3.34	0.75	0.80	0.078
(XXI)	$Ph_3SnOCOCH_2CH_3$	1.28	3.31	0.78	0.81	0.110
(XXII)	$Ph_3SnOCOCH(CH_3)_2$	1.26	3.21	0.84	0.80	0.080
(XXIII)	$Ph_3SnOCOCH_2Cl$	1.30	3.46	0.75	0.80	0.183
(XXIV)	$Ph_3SnOCOC(CH_3)_3$	1.22	2.30	0.75	0.79	0
(XXV)	$Ph_3SnOCOC(CH_3)=CH_2$	1.21[p]	2.26[p]			
(XXVI)	$PhSn[OCOC(CH_3)_3]O$	0.59	2.00	0.84	0.080	0.385
(XXVII)	$PhSn[OCOCCl_3]O$	0.72	2.33	0.79	0.77	0.057
(XXVIII)	$PhSn[OCOCF_3]O$	0.66	2.64	0.78	0.80	0
(XXIX)	$PhSn[OCO(CH_2)_8CH=CH_2]O$	0.57[p]	2.31[p]			
(XXX)	$PhSn[OCO(CH_2)_{16}CH_3]O$	0.56[p]	2.32[p]			

[a] mm/sec. [b] Isomer shift measurements refer to tin(IV) oxide. [c] R = room temperature effect = the ratio of the Mössbauer effect at room temperature to that at 78°K. [d] LH_2 = bis(8-hydroxy-5-quinolyl)methane. [e] OxH = 8-hydroxyquinoline. [f] Ref. 3. [g] 4,4'-Bipy = 4,4'-bipyridine. [h] 4-Phepy-4-phenylpyridine. [i] 2,2'-Bipy = 2,2'-bipyridine. [j] Ref. 18. [k] Ref. 7. [l] *t*-DTDO = *trans*-1,4-dithiane 1,4-dioxide. [m] *c*-DTDO = *cis*-1,4-dithiane 1,4-dioxide. [n] DTO = 1,4-dithiane 1-oxide. [p] Ref. 15.

from the high melting points and insolubility of the derivates $R_2SnL\cdot H_2O$ (R = Me, Bu, Ph), it was concluded that these compounds have polymeric structures[5]. This conclusion is supported by the small but significant room temperature Mössbauer effect shown by these compounds. Molecular weight measurements have shown that the corresponding dioctyltin compound, $(C_8H_{17})_2SnL$, is trimeric[5] and this compound does not have a significant R value.

It is of interest to compare the Mössbauer parameters of these compounds with those of the closely related 8-hydroxyquinoline (OxH) derivatives. Apart from the expected absence of a room temperature effect in the monomeric 8-hydroxyquinolinates there is excellent agreement between the two sets of parameters. From the magnitude of the quadrupole splittings[13] and the known structure of the dioxinates[3] essentially octahedral structures with an all-*cis* ligand arrangement are likely for the R_2SnL compounds.

(*b*). *Bipyridine adducts*

From the 1/1 stoichiometry shown by the adducts of 4,4′-bipyridine, $R_2SnCl_2 \cdot$ 4,4′-Bipy, it was concluded that the ligand was functioning in a bidentate manner and that the adducts were polymeric (the corresponding monodentate ligand, 4-phenylpyridine, gives 1/2 adducts $R_2SnCl_2 \cdot 2$Phepy)[6]. Inspection of Table 2 shows that the Mössbauer spectra support these observations with a measurable room temperature effect being recorded for the 4,4′-bipyridine adducts. The value of quadrupole splittings indicates that the organic groups are *trans*[13] and the close similarity between the parameters for analogous 2,2′-bipyridine and 4,4′-bipyridine compounds suggests that, in the latter, the nitrogen atoms are *cis*. The room temperature effect observed for the related pyrazine complex is consistent with the polymeric structure postulated for this compound[6].

(*c*). *Sulphoxide complexes*

From the positions of the ν(SO) bands in the infrared spectra of complexes of *trans*-1,4-dithiane 1,4-dioxide (*t*-DTDO) such as $R_2SnCl_2 \cdot$*t*-DTDO it was concluded that the ligand is bidentate and the structures are polymeric[9]. This is confirmed by the large *R* value shown by compound (XV) (Table 2). The infrared spectra of complexes of *cis*-1,4-dithiane 1,4-dioxide (*c*-DTDO) showed ν(SO) bands characteristic of free SO groups and it was concluded that compounds such as $Ph_2SnCl_2 \cdot$*c*-DTDO are monomeric with a 5-coordinate tin atom and a monodentate *c*-DTDO group[9]. Here the Mössbauer results are in direct conflict with the infrared evidence since $Ph_2SnCl_2 \cdot$*c*-DTDO shows an effect at room temperature. While an X-ray crystal structure determination would be needed to resolve this conflict it is possible that the structure assignments made earlier[9] for the adducts of *cis*-1,4-dithane 1,4-dioxide may need revision.

Also included in Table 2 are Mössbauer parameters for related adducts of dithiane 1-oxide (DTO) and dimethyl sulphoxide. The results for the three diphenyltin dichloride adducts, (XV)–(XVIII) are very similar and the slightly higher δ and Δ values for $Me_2SnCl_2 \cdot 2\ Me_2SO$ are consistent with replacing phenyl by alkyl groups in isostructural compounds [*cf.* compounds (IX) and (X)]. Compound (XIX) is known[14] to have *trans*-methyl groups and *cis*-chlorine atoms and it seems probably that compounds (XV)–(XIX) all have the same stereochemistry.

(*d*). *Phenyltin carboxylates*

Mössbauer parameters for triphenyltin carboxylates have been reported recently[15] but no measurements at room temperature were recorded. Our values of the isomer shifts and quadrupole splittings for triphenyltin acetate and propionate are in good agreement with those previously reported[1a,15] and the values for the isobutyrate and chloroacetate are similar. These four compounds show room temperature effects in agreement with the assigned polymeric structure involving bridging carboxylate groups. The Mössbauer parameters of triphenyltin pivalate, (XXIV), are almost identical with those reported for triphenyltin methacrylate, (XXV), and the absence of a room temperature effect in compound (XXIV) supports the conclusion[15] that steric hindrance in the acid residue results in a monomeric structure.

Of more interest are the mode of formation and structure of compounds of the type PhSn(OCOR)O which, in our work, arose inadvertently during routine synthesis of $Ph_3SnOCOR$ compounds by the reaction:

$$Ph_3SnOH + RCOOH \rightarrow Ph_3SnOCOR + H_2O$$

the water being removed azeotropically with benzene. This reaction proceeded satisfactorily with acetic, propionic, isobutyric and chloroacetic acids but trichloroacetic, trifluoroacetic and pivalic acids gave high melting insoluble products with analyses corresponding to the formulation PhSn(OCOR)O [$R = CCl_3$, CF_3, $C(CH_3)_3$]. Since phenyl–tin bonds can be cleaved by carboxylic acids[16] it seems likely that these compounds arise via the phenyltin tricarboxylates which are subsequently hydrolysed according to the following scheme:

$$Ph_3SnOCOR + 2\,RCOOH \rightarrow PhSn(OCOR)_3 + 2\,C_6H_6$$
$$PhSn(OCOR)_3 + H_2O \rightarrow PhSn(OCOR)O + 2\,RCOOH$$

The second step is reasonable since it is known[16] that tin polycarboxylates are readily hydrolysed. Acid cleavage of aryl–tin bonds is an electrophilic substitution reaction at carbon[17] and it is reasonable that the strongest acids Cl_3CCOOH and CF_3COOH should react in this manner; the difficulty is why the weak pivalic acid (pK_a 5.03) should also effect cleavage. It is possible that the tetrahedral environment of the tin atom in triphenyltin pivalate is sterically favourable for the cleavage reaction. (Authentic triphenyltin pivalate was made from triphenyltin chloride and sodium pivalate). It has been shown[15] that triphenyltin undecenoate and stearate, on long storage, were converted to compounds of the type PhSn(OCOR)O. This conversion is reasonable if it is assumed that water was present together with a catalytic amount of the acid RCOOH.

Compounds (XXVI)–(XXVIII) all have melting points >360° and are very insoluble indicating that their structures are polymeric. Compound (XXVI) shows a very marked Mössbauer absorption at room temperature the effect is reduced in compound (XXVII) and absent in compound (XXVIII) suggesting a dependence of molecular weight on X in $Ph(OCOCX_3)O$ in the sense $X = Me > Cl > F$. The isomer shifts and quadrupole splittings are in good agreement with those reported for the corresponding undecenoate and stearate indicating that compounds (XXVI)–(XXX) all have the same structure. It has been suggested[15] that these compounds are cyclic trimers, however their general physical properties plus the room temperature Mössbauer effects lead us to prefer polymeric structures containing bridging oxygen atoms.

ACKNOWLEDGEMENTS

We thank the Science Research Council for a grant for the Mössbauer spectrometer, the International Tin Research Council for support and Messrs. Albright and Wilson Ltd. for generous gifts of chemicals.

REFERENCES

1 (a). R. H. Herber and H. A. Stöckler, *Tech. Rept. Ser. No. 50, IAEA*, (1966) 110;
(b). H. A. Stöckler, H. Sano and R. H. Herber, *J. Chem. Phys.*, 47 (1967) 1567.
2 H. A. Stöckler and H. Sano, *Chem. Commun.*, (1969) 954.

3 R. C. Poller and J. N. R. Ruddick, *J. Chem. Soc. A*, (1969) 2273.
4 B. J. Duke and T. C. Gibb, *J. Chem. Soc. A*, (1967) 1478.
5 R. C. Poller and D. L. B. Toley, *J. Inorg. Nucl. Chem.*, 31 (1969) 2973.
6 R. C. Poller and D. L. B. Toley, *J. Chem. Soc. A*, (1967) 1578.
7 W. R. McWhinnie, R. C. Poller, J. N. R. Ruddick and M. Thevarasa, *J. Chem. Soc. A*, (1969) 2327.
8 D. L. Alleston and A. G. Davies, *J. Chem. Soc.*, (1962) 2050.
9 R. C. Poller and D. L. B. Toley, *J. Chem. Soc. A*, (1967) 2035.
10 H. G. Langer and A. H. Blut, *J. Organometal. Chem.*, 5 (1966) 288.
11 R. W. Weiss, *Organometallic Compounds*, Vol. 2, Springer-Verlag, New York, Second Ed., 1967.
12 G. J. D. Peddle, *J. Organometal. Chem.*, 14 (1968) 139.
13 B. W. Fitzsimmons, N. J. Seeley and A. W. Smith, *J. Chem. Soc. A*, (1969) 143.
14 N. W. Isaacs, C. H. L. Kennard and W. Kitching, *Chem. Commun.*, (1968) 820.
15 B. F. Ford, B. V. Liengme and J. R. Sams, *J. Organometal. Chem.*, 19 (1969) 53, 67; 21 (1970) 345.
16 A. Henderson and A. K. Holliday, *J. Organometal. Chem.*, 4 (1965) 377.
17 O. Buchman, M. Grosjean and J. Nasielski, *Helv. Chim. Acta*, 47 (1964) 1695.
18 M. A. Mullins and C. Curran, *Inorg. Chem.*, 6 (1967) 2017.