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Corresponding Member of the Academy of Sciences of the USSR V. I. GOLDANSKII, E. F. MAKAROV,

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Abstract

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STUDY OF THE STRUCTURE OF POLYMERIC ORGANOTIN OXIDES R_2SnO BY MEANS OF THE MÖSSBAUER EFFECT

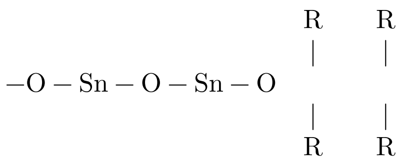
The application of the Mössbauer effect in chemistry opens up great possibilities for studying the structure and properties of molecules of organoelement compounds (^{1}).

In the present communication, new assumptions are put forward concerning the structure of molecules of organotin oxides of tetravalent tin, R_2SnO, based on a comparison of the results, presented here, of our studies of the Mössbauer effect in these oxides and in related compounds—organotin carboxylates, bisalkyl-substituted tin oxides, and distannane derivatives.

Experiments on the study of the Mössbauer effect in all the organotin compounds named were carried out on an installation of the Institute of Chemical Physics of the Academy of Sciences of the USSR, providing uniformly accelerated motion of the absorber relative to the source. The source of 23.8-keV γ-quanta (Sn^{119*}) was tin dioxide, SnO_2, kept at room temperature. The spectra of resonance absorption of γ-quanta were recorded with an AI-100 100-channel amplitude analyzer.

The spectra of resonance absorption of γ-quanta of the organotin compounds studied were investigated at the temperature of liquid nitrogen; at room temperature the Mössbauer effect was not observed. The Mössbauer spectra for all the compounds studied consist of two lines. Examples of such spectra are given in Fig. 1, the value of each channel being 0.108 mm/sec; zero velocity corresponds to the 49th channel.

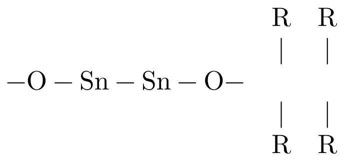
The organotin oxides of tetravalent tin R_2SnO studied in the present work (where $R = CH_3$, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, C_6H_5, n-Cl–C_6H_4, n-Br–C_6H_4, n-I–C_6H_4) are solid, infusible substances that decompose at elevated temperature. Although the formulas of these oxides are usually written in the form R_2SnO, their structure is more accurately expressed by the formula $(R_2SnO)_n$. It had long ago been suggested (^{2}) that the structure of such compounds corresponds to that of a linear polymer. Adjacent units of the chain of such a polymer can evidently be represented in the form of "head-to-tail" formulas:



$$-O-Sn-O-Sn-O\quad\begin{matrix}R & R\\ | & |\\ & \\ | & |\\ R & R\end{matrix}$$

(1)

or "head-to-head" :



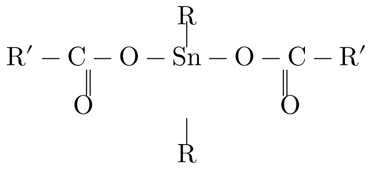
$$-O-Sn-Sn-O-\quad\begin{matrix}R & R\\ | & |\\ & \\ | & |\\ R & R\end{matrix}$$

(2)

As was shown in our works (^{1,3,4}) on examples of several dozen organotin compounds, the decisive influence on the form of Mössbauer spectra—at least for molecular crystals—is exerted by the chemical bonds nearest to the emitter and absorber. Thus, Mössbauer spectroscopy of molecules, quite analogous to other spectroscopic methods, proves to be possible.

Fig. 1. Spectrum of resonance absorption at $T = 78°K$ for the compound (n-Br $- C_6H_4)_2$SnO (**A**), the same for (n-$C_4H_9)_2Sn(OCOC_{11}H_{23})_2$ (**B**)

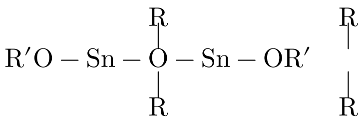
On the basis of what has been said, one could expect that the positions of the lines in the Mössbauer spectra of the organotin oxides R_2SnO, if structures (1) and (2) are assumed for them, should be similar to those observed in the spectra of the organotin carboxylates studied by us, which have the structure:



$$R'-\underset{\overset{\|}{O}}{C}-O-\underset{\overset{|}{R}}{\overset{R}{\underset{|}{Sn}}}-O-\underset{\overset{\|}{O}}{C}-R'$$

(3)

where R = n-C_4H_9; R′ = CH_3, C_7H_{15}, $C_{11}H_{23}$, $C_{17}H_{35}$; and of bis-alkyl-substituted tin oxides having the structure:



$$R'O-Sn-\underset{R}{\overset{R}{O}}-Sn-OR'\quad\begin{matrix}R\\ |\\ \\ |\\ R\end{matrix}$$

(4)

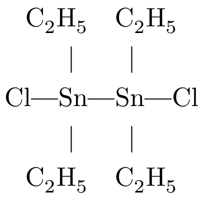
Table 1

Values of chemical shifts* ($-\delta$) and quadrupole splitting (Δ)

Compound	Δ, mm/sec	$-\delta$, mm/sec	Compound	Δ, mm/sec	$-\delta$, mm/sec
$(CH_3)_2SnO$	1.82	1.78	$(n\text{-}C_4H_9)_2Sn(OCOCH_3)_2$	3.50	1.36
$(n\text{-}C_3H_7)_2SnO$	2.10	1.60	$(n\text{-}C_4H_9)_2Sn(OCOC_7H_{15})_2$	3.45	1.35
$(n\text{-}C_4H_9)_2SnO$	2.06	1.72	$(n\text{-}C_4H_9)_2Sn(OCOC_{11}H_{23})_2$	3.35	1.36
$(n\text{-}C_5H_{11})_2SnO$	2.11	1.62	$(n\text{-}C_4H_9)_2Sn(OCOC_{17}H_{35})_2$	3.56	1.34
$(C_6H_5)_2SnO$	1.73	1.82	$(n\text{-}C_4H_9)_2Sn-O-Sn(n\text{-}C_4H_9)_2$ $\vert \qquad \vert$ $CH_3OCO \qquad OCOCH_3$	3.24	1.40
$(n\text{-}Cl-C_6H_4)_2SnO$	1.73	1.82	$(C_2H_5)_2Sn-Sn(C_2H_5)_2$ $\vert \qquad \vert$ $Cl \qquad Cl$	3.34	1.36
$(n\text{-}Br-C_6H_4)_2SnO$	1.83	1.78	$(C_6H_5)_3SnOH$	2.7	1.35
$(n\text{-}J-C_6H_4)_2SnO$	1.73	1.86	$(C_6H_5)_3SnCl$	2.5	1.32

* The chemical shift is given relative to the γ-transition in β-Sn; for SnO_2 the value $\delta = -2.7$ mm/sec was adopted. Conversion to energy values (eV) may be obtained by multiplying the values of δ and Δ by $7.9 \cdot 10^{-8}$. The accuracy in determining δ and Δ is throughout ± 0.08 mm/sec.

where $R = n\text{-}C_4H_9$, $R' = CH_3CO$, or of distannane derivatives of the type:



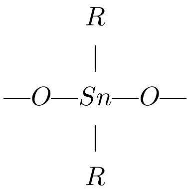
$$\begin{array}{c} C_2H_5 \quad C_2H_5 \\ \vert \qquad \vert \\ Cl—Sn—Sn—Cl \\ \vert \qquad \vert \\ C_2H_5 \quad C_2H_5 \end{array} \tag{5}$$

In the latter case, it is true, the atom adjacent to tin is chlorine rather than oxygen; however, in electronegativity these elements are close to one another, and the position of the lines in the Mössbauer spectra depends relatively little on the replacement of Cl by O, as is evident, in particular, from comparison of the data given in Table 1 for R_3SnOH and R_3SnCl, where $R = C_6H_5$. However, as is also seen from the data of Table 1, the values of the quadrupole splitting Δ and the chemical shift $-\delta$ for the compounds R_2SnO differ strongly from the corresponding values for compounds (3), (4), and (5).

For organotin carboxylates and distannane derivatives one might have supposed that such a difference is due to an appreciable dependence of the characteristics of the Mössbauer spectra of tin in bonds of the type

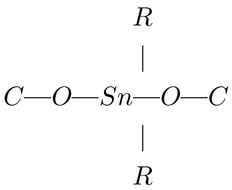
Fig. 2. Probability of the Mössbauer effect (in relative units) for some organotin oxides R_2SnO. The designations R are given in the figure

Figure 1: Fig. 2. Probability of the Mössbauer effect (in relative units) for some organotin oxides R_2SnO. The designations R are given in the figure



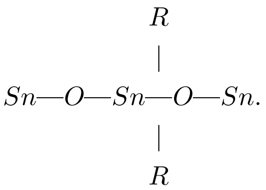
$$\begin{array}{c} R \\ | \\ —O—Sn—O— \\ | \\ R \end{array}$$

on the nature of the atoms providing the second valence bonds of oxygen and, in particular, to a strong change in the form of the spectra on passing from



$$\begin{array}{c} R \\ | \\ C—O—Sn—O—C \\ | \\ R \end{array}$$

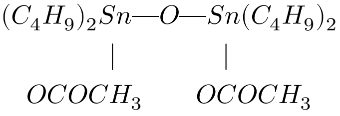
to



$$\begin{array}{c} R \\ | \\ Sn—O—Sn—O—Sn. \\ | \\ R \end{array}$$

Fig. 2. Probability of the Mössbauer effect (in relative units) for some organotin oxides R_2SnO. The designations R are given in the figure.

However, quite apart from the obvious lack of foundation for such an assumption, it is also refuted by the fact that—as is seen from the data of Table 1—the spectrum of the compound



$$\begin{array}{cc} (C_4H_9)_2Sn—O—Sn(C_4H_9)_2 & \\ | \qquad\qquad | & \\ OCOCH_3 \qquad OCOCH_3 & \end{array}$$

also differs strongly from

from the spectra of R_2SnO, but is close to the spectra of structures of types (3) and (5). It follows from this that the structure of the molecules of organotin oxides R_2SnO does not correspond to the usual structure of a linear polymer, represented by formulas (1) and (2), or to rings with the same bonds between tin atoms.

It should be noted that the magnitude of the quadrupole splitting Δ, obtained in the organotin oxides R_2SnO, proves to be the smallest of all those found for asymmetric organotin compounds. This indicates that in R_2SnO compounds the symmetry of the p-electrons around the tin nucleus is higher than the symmetry of the p-electrons in other asymmetric organotin compounds.

The reason for this difference may be supposed to be that in R_2SnO there is sp^2 hybridization, whereas in the molecules of other asymmetric organotin compounds sp^3 hybridization occurs. In the case of sp^2 hybridization the p_π-electrons belong almost equally to oxygen and to tin, as a result of which the symmetry of the p-electrons proves to be higher than in sp^3 hybridization.

It may also be assumed that polymeric organotin oxides have the structure of a network coordination polymer, with a coordination number of tin equal to 5 (see, for example, (5)).

It is interesting to note that replacement of alkyl by aryl in organotin oxides leads to a decrease in the magnitude of the quadrupole splitting, i.e., to an additional symmetrization of the p-electrons around the tin nucleus.

Introduction of a halide into the phenyl group in the para position does not change the magnitude of the quadrupole splitting or the chemical shift, but does exert some influence on the asymmetry of the peaks. At the same time, introduction of halogen atoms into the para position of the phenyl group has a noticeable effect on the probability of the Mössbauer effect f'. As can be seen from Fig. 2, the value of f' increases with increasing molecular weight of the aryl substituents in Ar_2SnO, although the structure of the molecule does not change substantially in this process.

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Note: Figure translations are in progress. See original paper for figures.