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A. Yu. Aleksandrov, K. P. Mitrofanov, O. Yu. Okhlobystin,

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Abstract

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**A. Yu. Aleksandrov, K. P. Mitrofanov, O. Yu. Okhlobystin,
L. S. Polak, V. S. Shpinel**

FEATURES OF THE MÖSSBAUER EFFECT ON Sn^{119} NUCLEI IN ORGANOTIN OXIDES

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The study of isomer shifts and quadrupole splitting values of the 23.8 keV γ transition of the Sn^{119} nucleus in organotin compounds, carried out by the method of resonant absorption of gamma rays (^{1,2}), makes it possible to obtain important information on changes in the distribution of electronic charge in molecules as a function of the structure and the characteristics of their chemical bonds.

In addition to the information obtained in Mössbauer spectra from hyperfine structure, supplementary data may be obtained from a study of the magnitude of the probability of recoil-free absorption of γ quanta. This probability, in particular, should depend on the structure of the organotin compounds being studied. In the present work, in addition to studying quadrupole splittings and isomer shifts, the probability of the Mössbauer effect f' was investigated in compounds of the homologous series R_2SnO (where R is an alkyl of the type C_nH_{2n+1}).

Experimental part

The isomer Sn^{119m} in the form of the compound SnO_2 was used as the gamma-ray source. Measurements were carried out on an apparatus with constant velocity (^{4}). In all measurements the source was at room temperature, and the absorbers were at the temperature of liquid nitrogen. The γ quanta were recorded with a resonance counter (^{4}) having selective sensitivity to γ quanta with an energy of 23.8 keV. For the absorbers, weighed portions of the compounds under study were taken in such a way that the tin content remained constant (for all substances the tin content was 33.5 mg/cm^2). Chemical analysis of the samples showed that the absorbers contained no impurities that could noticeably affect the shape of the resonant-absorption spectrum. To determine the magnitude of the effect ε, measurements were made with the source vibrating (at a frequency sufficient to destroy the resonance between detector and source). In this case the nonresonant background, N_b, is measured. The magnitude of the effect was determined by the formula:

$$\varepsilon = \frac{N_\infty - N(v_p)}{N_\infty - N_b},$$

where N_∞ is the count at absorber velocities for which resonance is absent, $N(v_p)$ is the count at the velocity of maximum resonance, and N_b is the number of nonresonant quanta. Determination of ε by this method makes it possible to calculate the absolute value of the effect directly from the experiment without introducing a background correction, which requires additional measurements and calculations. The probability of resonant absorption of γ quanta was determined from the dependence curve $\varepsilon(C)$ for the case of lines of natural width, where $C = \sigma_0 n f'$ is the effective absorber thickness; σ_0 is the resonant-absorption cross section; and n is the number of Sn^{119} nuclei per 1 cm^2.

Since the spectra of the compounds studied have the form of well-resolved symmetric doublets, the values of f' were taken to be twice f', determined from the above dependence $\varepsilon(C)$.

To calculate the absolute value of f', it is necessary to introduce a correction for the broadening of the lines of the source and absorber, which requires additional calculations. Since the line widths for all compounds are, within the limits of error, identical (1.2±0.05 mm/sec), the correction is the same for all compounds, and therefore the relative value of f' determined by this method will be valid.

X-ray structural analysis showed that all compounds of the series R_2SnO have no crystalline structure.

Results and discussion

In the present work, compounds of tetravalent tin of the type R_2SnO (gross formula) were investigated. The values of the isomer shifts δ, the quadrupole-interaction constants Δ, and the values of ε and f' are given in Table 1. The values of δ and Δ for all the compounds are identical with good accuracy.

Table 1

Isomer shifts δ, quadrupole-interaction constants Δ, magnitude of the effect ε, and effect probability f' of the compounds studied

Compound	δ, mm/sec	Δ, mm/sec	ε	f'
$(C_2H_5)_2SnO$	1.05 ± 0.05	2.10 ± 0.10	0.68 ± 0.07	0.22 ± 0.02
$(C_4H_9)_2SnO$	1.00 ± 0.05	2.00 ± 0.10	0.59 ± 0.06	0.17 ± 0.02
$(C_6H_{13})_2SnO$	1.00 ± 0.05	2.00 ± 0.10	0.51 ± 0.05	0.14 ± 0.01
$(C_8H_{17})_2SnO$	1.00 ± 0.05	2.00 ± 0.10	0.42 ± 0.04	0.10 ± 0.01
$(CH_3)_2SnO$	1.00 ± 0.05	2.00 ± 0.10	0.29 ± 0.03	0.06 ± 0.01

Compound	δ, mm/sec	Δ, mm/sec	ε	f'
$(C_4H_9)_3SnOCCCH_2$ with CH_3 above the central C and O below	1.45 ± 0.1	3.70 ± 0.15	–	–
$(C_2H_5)_3SnCH_2COCH_3$	1.45 ± 0.1	1.00 ± 0.05	–	–

This means, first, that the distribution of electron density and the field gradient at the tin nucleus in this series are determined mainly by the atoms nearest to the tin atom, CH_2 and O, and, second, that the bonds of the tin atom with C and O are identical in all the compounds. According to the generally accepted point of view, compounds of this type have a polymeric structure of the form

$$-O - Sn - O - Sn-$$

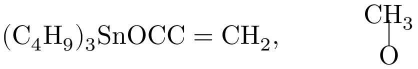
with R groups above and below each Sn atom (^{3,5}). In this case the tin atom directly forms valence bonds with two oxygen atoms and two carbon atoms. Let us compare the values of the quadrupole splittings and isomer shifts of the compounds studied with the corresponding values for the series

$$(C_4H_9)_2Sn\left(OCC_{nH_{2n+1}}\right)_2,$$

in which the tin atom also forms σ-bonds with two O and two C atoms. As can be seen from the data of Table 1, for organotin oxides $\Delta = 2$, and $\delta = 1$; for

$$(C_4H_9)_2Sn\left(OCC_{nH_{2n+1}}\right)_2$$

$\Delta = 3.40$–3.50 and $\delta = 1.45$ (^{2}). Such a large difference in Δ and δ may indicate that the SnO bond in compounds of this type is different, if one assumes that the distribution of electron density and the field gradient at the tin nucleus are determined mainly by the nearest bonds and atoms. However, such a conclusion cannot be drawn, taking into account the following fact. For tributyltin oxide $(C_4H_9)_3SnOSn(C_4H_9)_3$, in the molecules of which the tin atom forms σ-bonds with one oxygen atom and three carbon atoms, $\Delta = 1.2$ mm/sec, $\delta = 1.1$ mm/sec (^{2}). In the monomeric compound



$$(C_4H_9)_3SnOCC = CH_2, \qquad \overset{CH_3}{\underset{O}{|}}$$

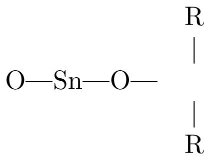
Fig. 1. Dependence of the probability of the effect f' on the mass of the radical M_R for a series of organotin oxides

Figure 1: Fig. 1. Dependence of the probability of the effect f' on the mass of the radical M_R for a series of organotin oxides

in the molecule of which the tin atoms likewise form analogous bonds with three carbon atoms and one oxygen atom, Δ proved to be equal to 3.70 mm/sec, and $\delta = 1.45$ mm/sec, i.e., the presence in the compound of a second type of carbonyl group, not forming a direct bond with tin, leads to polarization of the bond, which is also reflected in a change of the field gradient and, to a lesser degree, of the electron density at the tin nucleus. The influence on the electric-field gradient and the isomer shift of the Sn^{119} nucleus of various groups of atoms that do not form direct bonds with the tin atom is most clearly manifested when comparing Δ and δ for the compounds $(\mathrm{C_2H_5})_4\mathrm{Sn}$ and $(\mathrm{C_2H_5})_3\mathrm{SnCH_2{—}COCH_3}$. For tetraethyltin $\delta = 1.30$ and $\Delta = 0$ (^{2}), and, as was shown in that work, δ is the same for the entire series $(\mathrm{CH}_{2n+1})_4\mathrm{Sn}$. In the molecules $(\mathrm{C_2H_5})_3\mathrm{SnCH_2{—}COCH_3}$, the nearest neighbors of tin and the bonds of the tin atom with them are analogous; however, the presence of an acyl group leads to an increase in the electron density at the tin nucleus, $\delta = 1.45$, and in the gradient, $\Delta = 1$ mm/sec.

Fig. 1. Dependence of the probability of the effect f' on the mass of the radical M_R for a series of organotin oxides

Thus, the experimental data presented indicate that the form of the spectra of Mössbauer resonant absorption may depend not only on the nearest neighbors and the types of bonds, but also on the features of the structure of the molecules as a whole. And the fact that, for compounds



$$\begin{array}{lc} & \mathrm{R} \\ & | \\ \mathrm{O{—}Sn{—}O{—}} & \\ & | \\ & \mathrm{R} \end{array}$$

Δ and δ are substantially smaller than the corresponding quantities for

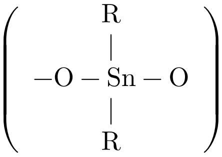
$$(\mathrm{C_4H_9})_2\mathrm{Sn}(\mathrm{OCC}_n\mathrm{H}_{2n+1})_2, \qquad \underset{\mathrm{O}}{\|}$$

makes it possible to suppose that the Sn—O bond in the first case is polarized much more weakly.

Let us now turn to the discussion of the experimental data on the study of the probability of the effect f'. Figure 1 shows the dependence of the probability of the effect f' on the molecular weight of the radical M_R, which proved to be close to linear for compounds with radicals C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}. The value of f' for the compound with the methyl radical falls sharply out of this dependence. Such a dependence is difficult to explain on the basis of the gross formula R_2SnO, i.e., considering these compounds monomeric, since in this case one should rather expect an increase in f' with increasing weight of the radical. On the other hand, the compound with the lightest radical, $(CH_3)_2SnO$, has $f' = 0.06$, which is considerably smaller than for the compound with the heaviest radical. This means that the structures of the compounds of the R_2SnO series are not identical. The following qualitative interpretation of the observed dependence may be proposed. From the fact that the probability of the effect increases with decreasing radical mass, it may be concluded that the vibrational spectrum of the tin atom in the system changes with decreasing radical mass in such a way that the amplitudes of tin-atom vibrations at high frequencies increase.

Soleri showed that, for polymeric structures of the oxides R_2SnO, the degree of condensation decreases with increasing radical weight (6). Therefore, the observed

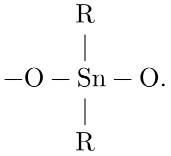
the observed increase in the probability of the effect can be associated with an increase in the degree of condensation, i.e., with an increase in the number of units



$$\left(\begin{array}{c} \mathrm{R} \\ | \\ -\mathrm{O}-\mathrm{Sn}-\mathrm{O} \\ | \\ \mathrm{R} \end{array}\right)$$

in the macromolecule, which, generally speaking, can take place only at low degrees of condensation.

From the data of Table 1 it is seen that, for the compound with the methyl radical, the values ε and f' are substantially smaller than the corresponding values for compounds with other radicals, whereas, if the structures were identical, one would expect values of ε and f' at least no smaller than for the compound with the C_2H_5 radical. Two different structures may be proposed for the compound with the methyl radical: a monomeric state or a cyclic structure, in contrast to the linear structure of the other compounds in this series. In the first case a double bond Sn=O should be present, which cannot but affect the redistribution of electron density or the field gradient at the tin nucleus in comparison with the bond



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

However, it follows from the experiment that δ or Δ for all compounds are the same within the limits of error. In order for the bonds of tin with O and C in the compound $(CH_3)_2SnO$ to be analogous to the bonds of the other compounds, but not to have a linear structure fitting into the homologous series R_2SnO, it must be assumed that it is thermodynamically more favorable for molecules with the methyl radical to form a cyclic structure. In the case of a cyclic structure of $(CH_3)_2SnO$ molecules, the distribution of electron density and the field gradient at the nucleus should not change substantially in comparison with the linear construction of macromolecules. However, it may be assumed that $(CH_3)_2SnO$ molecules have the structure of a linear oligomer of considerably smaller size than the compounds with heavier radicals. This question requires further investigation.

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Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

Institute of Nuclear Physics
Moscow State University
named after M. V. Lomonosov

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