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Abstract

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THE MÖSSBAUER EFFECT IN ASYMMETRIC ORGANOTIN COMPOUNDS CONTAINING ELECTRON-DONOR SUBSTITUENTS

(Presented by Academician M. I. Kabachnik on 25 IV 1964)

The Mössbauer effect on Sn^{119} nuclei has so far been observed for most of the principal types of organic compounds of tetravalent tin. In our earlier works ($^{1-3,4}$) it was shown that, for many compounds, the spectra of resonance absorption of γ-rays exhibit a doublet structure caused by the interaction of the quadrupole moment of the Sn^{119} nucleus with the electric field of the electron shells of organotin molecules.

Quadrupole splittings of the 23.8-keV transition of the Sn^{119} nucleus were observed mainly when the tin atom had valence bonds with at least two different atoms (^{1,2}), and the electronegativity of the substituents considerably exceeded the electronegativity of the tin atom. In addition, quadrupole splitting was observed in those cases in which the electric-field gradient at the Sn^{119} nucleus was caused by the influence of strongly electronegative substituents located beyond the atomic and ionic radius of tin, i.e., not forming direct bonds with the tin atom (^{3}).

In explaining cases of quadrupole splitting it was assumed that a nonzero gradient at the Sn^{119} nucleus arises when the symmetry of the p-components of the electronic wave functions of the tin atom is disturbed.

In the present work we studied the resonance-absorption spectra of γ-quanta for asymmetric organotin compounds containing donor substituents (with respect to the tin atom), as well as the spectra of several other compounds of tetravalent tin. As model compounds, organotin hydrides of the type $R_n\mathrm{SnH}_{4-n}$ and $R'_3\mathrm{SnH}$, hexaalkyldistannanes $R_3\mathrm{Sn}$—$\mathrm{Sn}R_3$, triphenyltin lithium, $R'\mathrm{SnLi}$, and $R_3\mathrm{Sn}R'$ were taken (where $R = C_{nH_{2n+1}} + R' = C_6H_5$).

Results of the measurements and their discussion

The resonance-absorption spectra were measured on a constant-velocity apparatus; registration of the 23.8-keV γ-quanta was carried out with a resonance counter (^{5}). As the source of γ-rays, the Sn^{119} isomer in the form of tin dioxide, SnO_2, was used. All measurements were performed at the temperature of liquid nitrogen. Most of the compounds studied were specially synthesized at the Institute of Organoelement Compounds, Academy of Sciences of the USSR. The constants of the substances corresponded to those given in the literature; judging from elemental-analysis data, the samples studied contained no noticeable impurities that could distort the form of the resonance-absorption spectra.

As is seen from the data of Table 1, the spectra of compounds of the types $R_n\mathrm{SnH}_{4-n}$, $R_3\mathrm{SnLi}$, $R_3\mathrm{Sn}\text{—}\mathrm{Sn}R_3$, $R_3\mathrm{Sn}R'$ are singlets with positions of the absorption maxima 1.45; 1.40; 1.55, respectively, and with line widths in the range 1.15–1.20 mm/sec. Thus, despite the presence of entirely different substituents forming direct bonds

with tin, the quadrupole splitting Δ, within the experimental error, is equal to zero.

In this connection it is necessary to note that in all previously studied cases in which quadrupole splitting was observed in unsymmetrical organotin compounds, the tin atom was bonded to electron-acceptor substituents (compounds of the type $R_{nSnA_{4-n}}$ are meant, where A is an acceptor atom or an acceptor group of atoms). The magnitude of this splitting depended on the acceptor ability of substituent A. If A is an acceptor, then overlap of the electron wave functions disturbs the symmetry of the p-components of the sp^3 wave functions of tin, and a nonzero electric-field gradient arises at the Sn^{119} nucleus.

Table 1

Isomer shifts δ (mm/sec) and quadrupole-interaction constants Δ (mm/sec) of the compounds studied

Absorber of the compound	δ	Δ
$(C_4H_9)_2SnH_2$	1.45 ± 0.07	0
$(C_4H_9)_3SnH$	1.45 ± 0.05	0
$(i\text{-}C_4H_9)_3SnH$	1.45 ± 0.05	0
$(C_3H_7)_3SnH$	1.45 ± 0.05	0
$(C_6H_5)_3SnH$	1.45 ± 0.05	0
$(C_6H_5)_3SnLi$	1.40 ± 0.07	0
$(C_6H_5)_3Sn\text{—}Sn(C_6H_5)_3$	1.55 ± 0.07	0
$(C_2H_5)_3Sn\text{—}Sn(C_2H_5)_3$	1.55 ± 0.05	0
$(C_4H_9)_2Sn(OC_2H_5)_2$	1.30 ± 0.05	2 ± 0.07
$(CH_3)_3SnC_6H_5$	1.25 ± 0.05	0
$(CH_3)_3SnCH{=}CH_2$	1.30 ± 0.05	0
$(CH_3)_3SnC_6H_4CH{=}CH_2$	1.30 ± 0.05	0
$(CH_3)_3SnC_6H_4CH\text{—}CH_2$	1.25 ± 0.05	0
$(C_4H_9)_3SnOCOC(CH_3){=}CH_2$	1.45 ± 0.07	3.70 ± 0.10
$(C_4H_9)_3SnOCOC(CH_3)\text{—}CH_2$, polymer	1.45 ± 0.07	3.10 ± 0.10
$(C_4H_9)_2Sn(OCOC(CH_3){=}CH_2)_2$	1.45 ± 0.07	3.90 ± 0.12

Absorber of the compound	δ	Δ
$(C_4H_9)_2Sn(OCOC(CH_3){—}CH_2)_2$, polymer	1.40 ± 0.07	3.25 ± 0.10
$C_4H_9Sn(OCOC(CH_3){=}CH_2)_3$	1.40 ± 0.07	4.25 ± 0.20
$C_4H_9Sn(OCOC(CH_3){—}CH_2)_3$, polymer	1.55 ± 0.10	3.45 ± 0.15

In the molecule $(C_6H_5)_3SnLi$, the Li atom, on the contrary, is an electron donor with respect to Sn. Thus, the introduction of an electron-donor substituent does not cause any noticeable disturbance of the symmetry of the p-components of all four tin bonds*, and the gradient at the Sn^{119} nucleus, within the experimental error, is equal to zero. It may be assumed that, upon overlap of the Sn—Li wave functions, displacement of electron charge toward Sn leads to symmetrization of all four hybridized orbitals of tin. Since for R'_3SnLi $\delta = 1.40$, whereas for R'_4Sn $\delta = 1.20$, it may be said that introduction of a donor substituent leads only to a slight increase in the density of s-electrons in the region of the Sn^{119} nucleus in comparison with R'_4Sn.

For organotin hydrides $R_{nSnH_{4-n}}$ and R'_3SnH, $\Delta = 0$ at $\delta = 1.45$; that is, in this case as well hydrogen is not an acceptor with respect to the tin atom, and the Sn—H bond does not have the character of $\overset{\delta+}{Sn}—\overset{\delta-}{H}$, i.e., it is predominantly homopolar. This agrees well with the chemical behavior of organotin hydrides, which are not inclined to transfer a hydride ion; in most reactions the Sn—H bond is cleaved homolytically. It should be noted that with an increase in the number of hydrogen atoms in the hydride molecule there is no change in δ. Apparently, some change in the s-electron density occurs upon replacement of only one organic group by hydrogen, and the subsequent introduction of hydrogen does not produce a substantial change in the isomer shift.

The resonance absorption spectra of γ-quanta for hexaethyl- and hexaphenyldistannanes also consist of single lines. Consequently, replacement of an organic group by trialkyl- and triarylstannyl groups also does not cause distortions in the symmetry of the p-components of the wave functions of the atom

* Nevertheless, for dibutyltin ethoxide a quadrupole splitting $\Delta = 2$ mm/sec was observed.

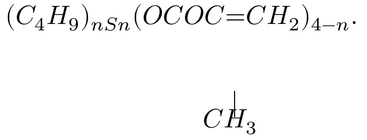
tin; there is only a certain increase in the density of s-electrons in the region of the Sn^{119} nucleus.

From consideration of the experimental data obtained by us, the following conclusions may be drawn.

The quadrupole splitting in the case of different donors D in molecules $R_{nSnD_{4-n}}$ is equal to zero, while the value of the isomer shift depends only very weakly on the type of donor and is fairly close to δ for the case of an ideal tetrahedral environment. At the same time, for molecules of the type $R_{nSnA_{4-n}}$, the value of the quadrupole splitting changes strongly as a function of the type of acceptor A and lies in the range from 0 to 4.8 mm/sec.

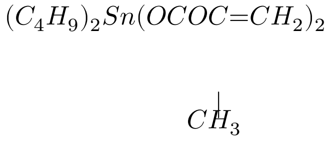
Let us note certain features of the isomer shift in all the organotin and inorganic tin compounds studied. In compounds of the types $R_{nSnA_{4-n}}$, $R_{nSnD_{4-n}}$, and R'_4Sn, the isomer-shift values lie in a rather narrow interval, with a deviation from $\delta = 1.30$ for the symmetric environment (R_4Sn) within ±50%. In inorganic compounds, where the C—Sn bond is absent, the isomer-shift value varies from 0 to 4.0 (compounds of tetravalent tin are also meant). It may be assumed that in organotin compounds the change in the isomer shift caused by electron-acceptor groups is to a considerable extent compensated by electron-donor organic substituents. It was shown earlier that the isomer shift in the series $R_{nSnCl_{4-n}}$ (^{1,2}) changes to a lesser degree with decreasing n than in the series $(C_6H_5)_{nSnCl_{4-n}}$ (^{4}). This can evidently be connected with the fact that the donor properties of alkyl substituents are more pronounced than the analogous properties of aryl groups.

An argument in favor of such an interpretation may be provided by the resonance-absorption spectra of monomeric and polymeric compounds of the type



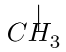
$$(C_4H_9)_{nSn}(OCO\underset{CH_3}{\underset{|}{C}}{=}CH_2)_{4-n}.$$

X-ray diffraction patterns of the monomeric and polymeric compounds showed the absence of a crystalline structure, and in the IR spectra a characteristic absorption band was found, indicating rupture of the C—C double bond. It is seen from Table 1 that, in polymeric molecules of this type, rupture of the C—C double bond leads to a noticeable change in the γ-ray resonance-absorption spectra, despite the fact that the rupture occurs at a rather large distance from the tin atom. In contrast to the resonance-absorption spectra considered above, the spectra of compounds of this type have a doublet structure (the compound



$$(C_4H_9)_2Sn(OCO\underset{CH_3}{\underset{|}{C}}{=}CH_2)_2$$

was studied by us earlier (^{2}) and has now been investigated again). The presence of two absorption lines is due to the appearance of an electric-field gradient at the Sn^{119} nucleus as a result of replacement of the alkyl radical by the strongly polar group $OCOC{=}CH_2$,



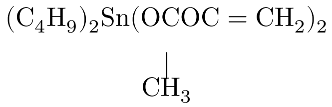
$$\underset{CH_3}{|}$$

which in this case plays the role of an electron acceptor with respect to the tin atom.

As is seen from Table 1, the magnitude of the quadrupole splitting depends on the number of substituted radicals and increases with increasing number of substituents. It should be noted that an analogous dependence of the change in Δ was observed in the series $(C_4H_9)_{nSnCl_{4-n}}$ (^{1,2}).

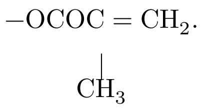
The quadrupole-interaction constants for polymeric molecules are appreciably smaller than the Δ values of the corresponding monomeric compounds and are equal to: 3.10; 3.25; 3.50, i.e., rupture of the double bond leads to a decrease in the gradient by ∼ 18%, which considerably exceeds the experimental error. The dependence of the splitting on the number of acceptor groups is in this case analogous to the dependence for monomeric compounds. In this connection, it is of interest

compare Δ and δ for the polymer



$$(\mathrm{C_4H_9})_2\mathrm{Sn}(\mathrm{OCO}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}} = \mathrm{CH_2})_2$$

with the corresponding values for compounds of the type $(\mathrm{C_4H_9})_2\mathrm{Sn}(\mathrm{OCO}(\mathrm{CH_2})_n\mathrm{CH_3})_2$ (2), in which there is likewise no double bond located at the same distance from the tin atom. It turns out that, within the limits of error, Δ and δ for these compounds are identical. This may serve as an additional argument in favor of the view that rupture of the double bond during polymerization of molecules of this type decreases the electric-field gradient at the Sn^{119} nucleus. As is seen from Table 1, the magnitude of the isomer shift δ for all compounds, monomeric and polymeric, is the same within the limits of error: $\delta = 1.45$ mm/sec. This value is rather close to the shift $\delta = 1.30$ for the tetrahedral environment $(\mathrm{C_4H_9})_4\mathrm{Sn}$, i.e., it depends only weakly on replacement of an alkyl group by an electron-acceptor group and practically does not change with an increase in the number of these substituents. These results may serve as some confirmation of the supposition that in these compounds as well the alkyl groups compensate the electron-acceptor action of



$$-\mathrm{OCO}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}} = \mathrm{CH_2}.$$

We note that the experimental results obtained indicate that the study of resonance absorption spectra of γ-quanta can provide useful information on the character of the distribution of electronic charges in the initial stage of the polymerization process of similar molecules.

We also studied compounds of the type $(CH_3)_3SnC_6H_5$, $(CH_3)_3SnCH = CH_2$, and $(CH_3)_3SnC_6H_4CH = CH_2$, polymer and monomer. The resonance absorption spectra of these substances consist of single lines with the position of the absorption maximum in the interval 1.25–1.35 mm/sec, with line widths of the order of 1.20 mm/sec. The magnitude of the isomer shift for these compounds, within the limits of error, coincides with the isomer shift of $(CH_3)_4Sn$. Thus, replacement of the CH_3 radical by C_6H_5 and the presence of a conjugated bond at the vinyl radical do not change the electron density and do not lead to an electric-field gradient at the Sn^{119} nucleus. An analogous result was obtained also for compounds of the type $(CH_3)_3SnC_6H_4CH = CH_2$, for which $\delta = 1.30$ in the case of monomeric and polymeric molecules. In contrast to the polymeric and monomeric compounds considered earlier, rupture of the double bond during polymerization of the compounds under consideration does not cause changes in the resonance absorption spectra.

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