L. M. Krizhanskii, O. Yu. Okhlobystin, A. V. Popov, B. I. Rogozov

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Abstract

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L. M. Krizhanskii, O. Yu. Okhlobystin, A. V. Popov, B. I. Rogozov

MÖSSBAUER SPECTRA OF ORGANOTIN COMPOUNDS CONTAINING ACYLOXY GROUPS

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In the present work, using the Mössbauer spectrometer described by us earlier in paper (^{1}), we investigated organometallic compounds obtained in reactions of carboxylic and ω-chlorocarboxylic acids with dibutyltin oxide.

As the source of γ-quanta, tin dioxide SnO_2 containing the isomer Sn^{119} was used. The source was at room temperature; the absorbers were cooled to the temperature of liquid nitrogen (77°K).

The following were measured: the chemical shift of the absorption line relative to the emission line of the source (δ) and the quadrupole splitting of the absorption line (Δ), characterizing, respectively, the magnitude of the electron density and the gradient of the electric field at the tin nucleus.

Mössbauer spectra of 14 different compounds were obtained. The results of the measurements are presented in Tables 1 and 2.

1. As is seen from the data of Table 1, for compounds obtained by the reaction

$$(C_4H_9)_2SnO+HOOC(CH_2)_nCH_3 \rightarrow (C_4H_9)_2Sn[OOC(CH_2)_nCH_3]_2+H_2O, \quad (1)$$

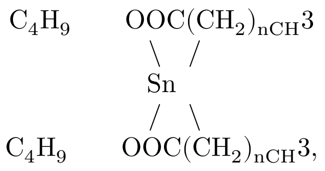
when stoichiometric ratios are observed, the quadrupole splitting found for $n = 1, 3, 5, 8$ is approximately constant and in magnitude is $\cong 3.65$ mm/sec.

Table 1

No.	Acid	n	Weight ratio of components in reaction (1)	Chemical shift of the absorption line relative to β-Sn, δ, mm/sec	Quadrupole splitting of absorption line Δ, mm/sec	Proposed structure of the compound
1	Propionic	1	Stoichiometric	1.21 ± 0.04	3.70 ± 0.06	(A)
2	Valeric	3	Stoichiometric	1.23 ± 0.02	3.23 ± 0.04	(A)
3	Enanthic	5	Stoichiometric	1.24 ± 0.02	3.64 ± 0.04	(A)
4	Capric	8	Stoichiometric	1.21 ± 0.02	3.61 ± 0.03	(A)
5	Lauric	10*	Stoichiometric	1.22 ± 0.02	3.41 ± 0.05	(mixture A and B)
6	Tridecanoic	13	2–2.5-fold excess of $(C_4H_9)_2SnO$	1.46 ± 0.06	3.10 ± 0.02	–
7	Stearic	16*	Stoichiometric	1.19 ± 0.05	3.25 ± 0.04	(B)
7	Stearic	16*	2–2.5-fold excess of $(C_4H_9)_2SnO$	1.22 ± 0.05	3.26 ± 0.04	(B)
8	Valeric	3	2–2.5-fold excess of $(C_4H_9)_2SnO$	1.17 ± 0.06	3.28 ± 0.05	(B)

* Data for $n = 10$ and 16 are also given in paper (3) and, within the measurement error indicated by the author ($±$5%), coincide with ours.

In compounds of this type, whose structural formula has the form

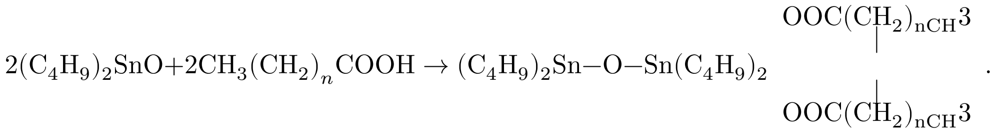


$$\begin{array}{ccc} C_4H_9 & & OOC(CH_2)_{nCH}3 \\ & \diagdown \quad \diagup & \\ & Sn & \\ & \diagup \quad \diagdown & \\ C_4H_9 & & OOC(CH_2)_{nCH}3, \end{array}$$

(A)

two butyl radicals are always present, and the change in Δ in this series of compounds is completely determined by the fields of the atoms of the acid residues bound to the Sn atom.

We found that, when carboxylic acids are reacted with dibutyltin oxide in excess of the latter, organotin compounds are formed for which Δ is appreciably lower and amounts to $\simeq 3.25$ mm/sec. This can be explained if it is assumed that two moles of dibutyltin oxide dissolve in two equivalents of acid with the formation of a compound containing two tin atoms in the molecule. The structure of such compounds should have the form (B)*



$$2(C_4H_9)_2SnO + 2CH_3(CH_2)_nCOOH \rightarrow \begin{array}{c} OOC(CH_2)_{nCH}3 \\ | \\ (C_4H_9)_2Sn{-}O{-}Sn(C_4H_9)_2 \\ | \\ OOC(CH_2)_{nCH}3 \end{array} .$$

(B)

The smaller value of Δ in compounds of group B as compared with group A is qualitatively explained by the absence in compounds of group A of an electron-acceptor carboxyl group at the second oxygen atom bound to tin, which leads to an increase in the electron density on Sn along the Sn–O bond in the chain –Sn–O–Sn (a decrease in the mesomeric effect).

Compound No. 7 ($n = 16$) was obtained by two different methods: a) with stoichiometric ratios observed, b) with a 2-2.5-fold excess of $(C_4H_9)_2SnO$. However, both compounds obtained gave similar Mössbauer spectra, which should be assigned to the spectra of compounds of structure (B).

Thus, even complete dissolution of dibutyltin oxide in a benzene solution of the acid cannot serve as an indication of completion of reaction (1), and an estimate of the relative content of compounds (A) and (B) in the reaction mixture can be made on the basis of the value of Δ.

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* Apparently, the tendency to form compounds of type (B) increases with increasing molecular weight of the acid; this, in particular, may explain the decrease in Δ at $n = 10$. In this case, broadening of the spectral lines was also observed. However, for complete confirmation of this it is necessary to obtain spectra of compounds with $n > 16$. The splitting value (Δ) for the compound with $n = 13$ falls sharply outside the general pattern. The reasons for this are still unclear.

2. Reaction with ω-chlorocarboxylic acids. Spectra of compounds obtained by the reaction

$$(C_4H_9)_2SnO + HOOC(CH_2)_nCH_2Cl, \tag{2}$$

were measured in parallel with reactions of type (1). The results are presented in Table 2.

For compounds obtained by reaction (2), with stoichiometric ratios observed, Δ is systematically lower by $\simeq 0.20$ mm/sec than the values of Δ for compounds of type (A).

This decrease in Δ cannot be explained by the inductive influence of the chlorine atom located at the end of the chain, since in that case a sharp decrease of this influence with increasing n would be observed. The independence of the influence of the chlorine atom on the Mössbauer atom from the chain length indicates—

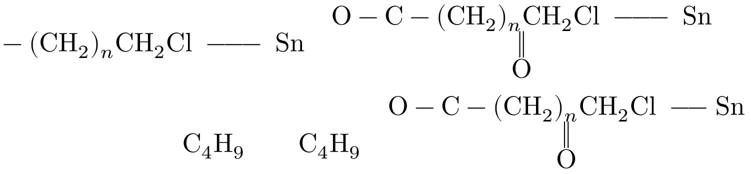
* When the present work had been completed, we learned that similar compounds had recently been described by Kocheshkov, Zemlyanskii, and others (2).

Table 2

No.	Acid		Weight ratio of components in reaction (2)	Chemical shift relative to β-Sn, δ, mm/sec	Quadrupole splitting, Δ, mm/sec	Structure of compound
1	ω-Chlorovaleric	3	Stoichiometric	1.20 ± 0.05	3.41 ± 0.03	(C)
2	ω-Chloroenanthic	5	Stoichiometric	1.27 ± 0.02	3.35 ± 0.02	(C)
3	ω-Chloropelargonic	7	Stoichiometric	1.15 ± 0.05	3.39 ± 0.06	(C)
4	ω-Chlorotridecanoic	13	Stoichiometric	1.40 ± 0.03	2.89 ± 0.04	(C)
5	ω-Chloroenanthic	5	2–2.5-fold excess of $(C_4H_9)_2SnO$	1.22 ± 0.02	3.25 ± 0.05	(D)

No.	Acid		Weight ratio of components in reaction (2)	Chemical shift relative to β-Sn, δ, mm/sec	Quadrupole splitting, Δ, mm/sec	Structure of compound
6	ω-Chloropelargonic	7	2-2.5-fold excess of $(C_4H_9)_2SnO$	1.26 ± 0.02	3.25 ± 0.04	(D)

corresponds rather to the formation of associative bonds leading to an increase in the coordination number of tin. One of the possible structures of this type is the following:

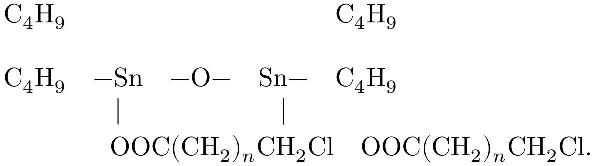


$$\begin{array}{llll} -(CH_2)_nCH_2Cl \text{ —— } Sn & & O-\underset{\overset{\|}{O}}{C}-(CH_2)_nCH_2Cl \text{ —— } Sn & \\ & & O-\underset{\overset{\|}{O}}{C}-(CH_2)_nCH_2Cl \text{ —— } Sn & \\ C_4H_9 & C_4H_9 & & \end{array}$$

(*C*)

If this or an analogous structure is admitted, it becomes clear why the chain length does not affect the value of Δ of the Mössbauer spectra.

The compounds obtained by reaction (2) with an excess of $(C_4H_9)_2SnO$ practically do not differ in their Mössbauer spectra from analogous compounds of type B. This makes it possible to suppose that, in the case of dimeric compounds, the formation of bridging bonds through the chlorine atom becomes impossible, and the reaction products have the form:



$$\begin{array}{ccccc} C_4H_9 & & & & C_4H_9 \\ C_4H_9 & -Sn & -O- & Sn- & C_4H_9 \\ & | & & | & \\ & OOC(CH_2)_nCH_2Cl & & OOC(CH_2)_nCH_2Cl. & \end{array}$$

(*D*)

Solutions of all the compounds were prepared with a threefold dilution in benzene. Mössbauer spectra were obtained for these solutions, sharply cooled to the temperature of liquid nitrogen (77°). No substantial difference from the spectra of the corresponding compounds was found.

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