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Abstract

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THE MÖSSBAUER EFFECT IN ORGANIC COMPOUNDS OF DIVALENT TIN

Although organic compounds of divalent tin have been known for more than 60 years, their structure is still being discussed at the present time ([1–3]). Some additional information about this structure can be obtained on the basis of the characteristics of the Mössbauer spectra of divalent tin compounds ([4]).

The most specific such characteristic, sharply distinguishing divalent and tetravalent tin, is the magnitude of the chemical shift of the Mössbauer spectral line δ.

For the isotope Sn^{119} this chemical shift is equal to:

$$\delta_{Sn} = 1.55 \cdot 10^{-29} \frac{\Delta R}{R} \{|\psi(0)|^2_{absorber} - |\psi(0)|^2_{emitter}\} \text{ eV},$$

where $\Delta R = R_e - R_0$ is the positive difference between the nuclear charge radii of Sn^{119} in the excited (R_e) and ground (R_0) states, and $|\psi(0)|^2$ is the total density of all s-electrons of tin in the region of the Sn^{119} nucleus for the absorber ($|\psi(0)|^2_{absorber}$) and the emitter ($|\psi(0)|^2_{emitter}$) of resonant γ-quanta.

The electronic configuration of the free tin atom is $5s^2p^2$, which corresponds to the ^3P state; transition to the divalent tin ion occurs by removal of two $5p$-electrons and formation of the $5s^2$ configuration.

For wholly covalent bonds of tetravalent tin, $5sp^3$-hybridization occurs, corresponding to ^5S; transition to the Sn^{+4} ion occurs by removal of all four electrons with $n = 5$.

Within these ideas, wholly covalent bonds of Sn(IV) correspond to the presence of one $5s$-electron; real (i.e., partially ionic) bonds of Sn(IV), to a number of $5s$-electrons from 0 to 1; and the corresponding bonds of Sn(II), to the presence of

two $5s$-electrons with the number of $5p$-electrons varying from 0 to 2. Neglecting the effect of shielding of the inner s-electrons by the action of $5p$-electrons, we conclude from what has been said that the inequality holds:

$$|\psi(0)|^2(\text{Sn II}) > |\psi(0)|^2(\text{Sn}_{\text{covalent}}\ \text{IV}) > |\psi(0)|^2(\text{Sn}_{\text{ionic}}\ \text{IV}).$$

Indeed, for inorganic compounds of divalent and tetravalent tin, as a rule, the opposite sign of the chemical shift is observed relative to such an emitter, which may be regarded as Sn(IV) with wholly covalent bonds–α-Sn (gray tin) ([4,5–8]). In this case, for Sn(II) it was found that $\delta > 0$, and for Sn(IV) with partial ionic character of the bonds $\delta < 0$, whence also follows the positivity of the difference ΔR for Sn^{119}.

It might have been expected that for organic compounds of divalent tin a positive chemical shift relative to α-Sn would also be observed. The experiments described below showed, however, an entirely different picture.

We investigated the Mössbauer spectra of absorbers–diphenyl- and dibutyltin. The spectra were recorded with the absorbers cooled by liquid

with nitrogen, according to the procedure described earlier ([9]). The $^{119m}SnO_2$ source was kept at room temperature. The chemical shift of SnO_2 relative to gray tin is equal to $\delta(SnO_2) = -2.1$ mm/sec; thus, the range of expected δ values for compounds of divalent tin corresponded to the observed values $\delta = \delta(\text{Sn II}) - \delta(SnO_2) > +2.1$ mm/sec. The Mössbauer spectra of all the organotin compounds studied are singlet, unbroadened lines.

Table 1

Values of chemical shifts in the Mössbauer spectra of the organotin compounds studied*

No.	Compound	δ, mm/sec
1	$(Ph_2Sn)_n$	1.42
2	$(Bu_2Sn)_n$	1.55
3	Bu_4Sn	1.35
4	Ph_4Sn	1.35
5	$Et_3Sn - SnEt_3$	1.45

* The values of the chemical shifts (δ mm/sec) are given relative to the 23.8-keV γ transition in SnO_2. The accuracy of measuring the chemical shift is everywhere ± 0.08 mm/sec.

The measurement results are given in Table 1, where, for comparison, the values of the chemical shifts of some organic compounds of tetravalent tin are also presented.

It follows from the data in Table 1 that there is no noticeable difference in the chemical-shift values for organic compounds of divalent and tetravalent tin. Apparently, in the case of organic compounds of divalent tin, a polymer $(R_2Sn)_n$ with $Sn-Sn$ and $Sn-C$ bonds is formed ([3]). This assumption is confirmed by the closeness of the chemical-shift values for $(Ph_2Sn)_n$ and $(Bu_2Sn)_n$ to the analogous value for the spectrum of hexaethyldistannane ($Et_3Sn-SnEt_3$), measured by us, in which there are both $Sn-Sn$ bonds and $Sn-C$ bonds. Like the compounds $R_3Sn-SnR_3$, the compounds $(R_2Sn)_n$ are readily oxidized in air ([1]) at room temperature. Figure 1 shows the corresponding change in the Mössbauer spectrum of $(Bu_2Sn)_n$ with the formation of a doublet. The final oxidation product of $(Bu_2Sn)_n$ is $(Bu_2SnO)_n$, as is proved by the identity of the Mössbauer spectra of the oxidation product of $(Bu_2Sn)_n$ with the spectrum of pure $(Bu_2SnO)_n$. The position of the line of the initial $(Bu_2Sn)_n$ accidentally coincides with one of the lines of the compound being formed, $(Bu_2SnO)_n$. In this case the Debye–Waller factor for $(Bu_2SnO)_n$ proves to be approximately twice as large as for the initial compound $(Bu_2Sn)_n$. Therefore, in Fig. 1 the position and length of one of the lines remain practically unchanged, whereas the length of the other line, proportional to the magnitude of the Mössbauer effect observed for the reaction product $(Bu_2SnO)_n$, increases as oxidation of dibutyltin proceeds.

Fig. 1. Positions of the lines in the Mössbauer spectra of the same sample $(Bu_2Sn)_n$ as a function of the time of its oxidation in air at room temperature. The magnitude of the effect is proportional to the line length. Channel width 0.124 mm/sec. Zero velocity relative to SnO_2 corresponds to channel No. 49.5.

On the basis of these data, a complete kinetic curve for the oxidation of $(Bu_2Sn)_n$ can easily be constructed.

The results obtained once again confirm the great possibilities offered by the application of a new method of chemical physics—Mössbauer molecular spectroscopy—for investigating the structure and kinetics of transformations of organotin compounds.

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