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Abstract

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STUDY OF THE STRUCTURE OF COMPOUNDS WITH A STANNOXANE BOND BY THE METHODS OF DIPOLE MOMENTS AND INFRARED SPECTRA

The nature of the Sn–O bond is unclear. In the literature, for example, two points of view are expressed concerning the character of this bond in alkyltin acylates R_3SnOOCR and R_2Sn(OOCR)$_2$. On the basis of an analysis of infrared spectra, a number of works (^{1,2}) conclude that these compounds have an ionic structure. The authors (^{3,4}) regard alkyltin acylates as covalent compounds constructed analogously to organic esters.

A very substantial characteristic of the type of bond is the magnitude of the dipole moment. However, the data available in the literature on the dipole moments of organotin compounds are very scanty and do not make it possible to characterize with any reliability the polar properties of these bonds.

In the present work, measurements have been made of the dipole moments of a series of organotin compounds containing Sn-O bonds. The list of compounds studied and the results of the d.m. measurements are given in Table 1.

Table 1

No.	Compound	Formula	Mol. wt., found	Mol. wt., calculated	P_∞	R_D	μ	Solvent
1	Methoxy-tri-*n*-butyltin	$(C_4H_9)_3SnOCH_3$	311, 325, 327	321	184.6	35.5	2.18	Octane
2	Ethoxytriethyltin	$(C_2H_5)_3SnOC_2H_5$	253, 256, 257	251	151.7	62.4	2.19	»
3	Triethyltin acetate	$(C_2H_5)_3SnOOCCH_3$	265, 270	265	149.4	62.4	2.05	Benzene

No.	Compound	Formula	Mol. wt., found	Mol. wt., calculated	P_∞	R_D	μ	Solvent
4	Tri-*n*-butyltin acetate	$(C_4H_9)_3SnOOCCH_3$	335 338 340	349	175.0	90.1	2.03	»
5	Di-*n*-butyltin diacetate	$(C_4H_9)_2Sn(OOCCH_3)_2$	330 350	351	122.2	82.5	1.39	»
6	Di-*n*-butyltin dilaurinate	$(C_4H_9)_2Sn(OOCC_{11}H_{23})_2$	562 576	631	218.5	174.9	1.45	»
7	Hexaethyldistannoxane	$(C_2H_5)_3SnOSn(C_2H_5)_3$	385 397	428	140.6	102.4	1.36	Octane
8	Hexa-*n*-butyldistannoxane	$(C_4H_9)_3SnOSn(C_4H_9)_3$	535	596	200.4	157.9	1.43	Hexane
9	Tet-*n*-butyldistannoxane dichloride	$[ClSn(C_4H_9)_2OSn\cdot(C_4H_9)_2Cl]_2$	1011 1048 1045	1115	364.8	261.3	2.24	»
10	Tet-*n*-butyldistannoxane diacetate	$[CH_3COOSn(C_4H_9)_2\cdot OSn(C_4H_9)_2OOCCH_3]_2$	1086 1184 1217	1198	455.9	285.4	2.87	»
11	Same		1217	1198	449.4	285.4	2.82	Benzene
12	Tet-*n*-butyldistannoxane dilaurinate	$[C_{11}H_{23}COOSn(C_4H_9)_2\cdot OSn(C_4H_9)_2\cdot OOCC_{11}H_{23}]_2$	1770 1830 1720	1760	696.2	470.1	3.31	»

Here P_∞ is the molar polarization of the substance at infinite dilution, R_D is the molar refraction for the sodium D-line, and μ is the dipole moment (in debyes), calculated from the formula $\mu = 0.22\sqrt{P_\infty - R_D}$. The molar refraction of the compounds studied was calculated according to an additive scheme. The

Fig. 1. IR spectra: a —tetrabutyltin, b —hexabutyldistannoxane, c —methoxytributyltin

Figure 1: Fig. 1. IR spectra: a —tetrabutyltin, b —hexabutyldistannoxane, c —methoxytributyltin

refraction increment of the tin atom was taken to be 19.4 (5).

This value includes the atomic polarization of tin; therefore it is higher than the average value of 13-14 cm^3 for the tin atom obtained from the data of work (6) and from tabulated data (7).

Measurements of the molecular weights of the compounds under study by the cryoscopic method showed that alkoxytrialkyltin compounds, alkyltin acylates, and hexaalkyldistannoxanes are present in benzene in monomeric form. Compounds of the type $X\mathrm{Sn}(R)_2\mathrm{OSn}(R)_2X$, where X = Cl or OCOR, are dimeric in solution. Changing the concentration of the solutions within the range from 0.01 to 0.1 g-mol/kg had practically no effect on the molecular-weight value (Table 1). In accordance with the above, the dipole moments of the first group of compounds correspond to monomeric molecules, and the dipole moments of the second group correspond to dimers.

Fig. 1. IR spectra: **a** —tetrabutyltin, **b** —hexabutyldistannoxane, **c** —methoxytributyltin

The dipole moments of compounds of the type $R_3\mathrm{SnOR}$ make it possible to estimate the value of the dipole moment of the Sn—O bond. If one starts from a tetrahedral model of the molecule with the tin atom at the center of the tetrahedron and adopts the values of the dipole moments of the bonds $\mathrm{Sn} \rightarrow R_3$, 0.6 D, $\mathrm{O} \leftarrow R$, 1.0 D, the valence angle of the oxygen atom 105°, and takes into account the experimental dipole-moment value of 2.18 D, then by the method of vector additivity the portion of the $\mathrm{Sn} \rightarrow \mathrm{O}$ moment is 2.7 D.

The value of the dipole moment of the Sn—O bond could also have been obtained from the results of determining the dipole moments of hexaalkyldistannoxanes (see Table 1). However, this is difficult because of the uncertainty of the valence angle of the oxygen atom in such compounds. Owing to steric hindrance (the large radius of the tin atom), the valence angle of the oxygen atom here must be considerably larger than usual. If the dipole moment of the Sn—O bond is taken as 2.7 D and the experimentally found value of the dipole moment of hexaalkyldistannoxanes, ~1.4 D, is taken into account, then the valence angle of the oxygen atom in such compounds is 150-160°. Approximately the same value of the Sn—O—Sn angle (150-180°) is proposed (9) for hexaphenyldistannoxane on the basis of analysis of infrared spectra. This circumstance indicates a different valence state of the oxygen atom and a substantially different type of Sn—O bond in compounds of the type $R_3\mathrm{SnOSn}R_3$ as compared with compounds of the type $R_3\mathrm{SnOR}$. This conclusion is consistent with the results of work (10) on the study of organotin compounds by the method of Mössbauer resonance absorption, where a significant deviation was shown in the parameters characterizing the distribution of electron-charge density and quadrupole splitting in $(C_4H_9)_3SnOSn(C_4H_9)_3$ in comparison with the parameters for other organotin compounds. We investigated the IR spectra of tetrabutyltin, methoxytributyltin, and hexabutyldistannoxane (Fig. 1). The absence of intense bands in the region of the symmetric vibration of Sn—O—Sn bonds (500-600 cm^{-1}) in hexabutyldistannoxane indicates—

speaks to the linearity or near-linearity of this group. This conclusion agrees with the dipole-moment data, as well as with the results of work ([9]).

The intense band at 518 cm^{-1} in the spectrum of methoxytributyltin lies approximately in the same region as the band of medium intensity in the spectrum of tetrabutyltin. However, their completely different intensity and the shift by 13 cm^{-1} make it possible to conclude that this band belongs to the stretching vibration of the Sn–O bond in the Sn–O–C group.

In the spectrum of hexabutyldistannoxane, the intense band in the region of 780 cm^{-1} is assigned to the antisymmetric vibration of Sn–O–Sn ([10]). The large difference in the positions of the Sn–O-bond absorption bands in the spectra of methoxytributyltin and hexabutyldistannoxane also indicates a different type of Sn–O bond in these compounds.

Proceeding to consideration of the question of the nature of the bonds and the structure of tin alkyl acylates, it should first of all be noted that the comparatively small dipole-moment values obtained by us–2.0 D for trialkyltin acylates and 1.4 D for dialkyltin diacylates–quite unambiguously testify in favor of the covalent character of the Sn–O bonds in these compounds. These results are in complete agreement with the concept of the covalent structure of trialkyltin acylates, developed in ([3]), and do not confirm the view of an ionic structure ([1,2,11]).

Taking the dipole moment of the Sn–O bond to be 2.7 D, we attempted to estimate the most probable spatial configurations of the compounds studied.

The corresponding calculations for trialkyltin acylates (3, 4, Table 1) showed that the dipole-moment values found agree both with conformation I, provided there is free rotation of the –C=OR group about the O–C bond, and with conformation II, with a fixed position of the C–O group due to formation of a donor-acceptor bond of the tin atom with the carbonyl oxygen atom. The considerable lowering of the frequency of the carbonyl-bond vibration observed in the IR spectra of trialkyltin acylates ([3,12]) is a very substantial argument in favor of conformation II. Structure II is also consistent with the IR-spectroscopy data in the frequency region of the vibrations of Sn–C bonds, indicating that these bonds are located in one plane. Finally, conformation II makes it possible to explain the observed phenomenon of association of trialkyltin acylates in concentrated solutions and in the solid state by the fact that the tin atom in such compounds is capable of forming one more donor-acceptor type bond. Such a possibility, as will be shown below, is absent in the case of dialkyltin diacylates. Thus, conformation II appears to be the most probable for trialkyltin acylates.

Calculation by the method of vector additivity of dipole moments for dialkyltin diacylates for different positions of the OCOR groups shows that the values closest to the experimental ones are obtained for conformation III (2.3 D) and especially for IV (1.5 D). Conformation IV appears more probable than III not only because of the closer agreement of the calculated dipole moment with the experimental one, but also because of a number of other circumstances. Among these, first of all, one should point to the observed shift of the vibration frequency of the carbonyl bond in dialkyltin diacylates ([1,2,11]). It is true that, in the cited works, the lowering of the frequency of the $C = O$ bond is explained by the fact that the acyl groups in the compounds studied are in ionic form. However, as already stated above, the results of the present work (small values of the dipole moments) testify in favor of a covalent, rather than ionic, structure of these compounds and, in our opinion, the shift of the $C = O$ bond bands is due to the formation of donor-acceptor bonds between the oxygen atoms of the carbonyl groups and the tin atom.

As is seen from scheme IV, the coordination possibilities of the tin atom are fully utilized here (2 donor-acceptor bonds); therefore it should be expected that dialkyltin diacylates will have a considerably smaller capacity for intermolecular interaction than trialkyltin acylates II, where there is only one coordination bond.

We recorded the IR spectra of dibutyltin diacetate in dilute solutions and in the liquid state and found that, in contrast to tributyltin acetate, its spectrum changes practically not at all on going from dilute solution to the liquid state. Comparing the results of the study of compounds containing Sn—O—Sn bonds (7, 8, 9, 10, 12, Table 1), it should first of all be noted that hexaalkyl derivatives (7, 8, Table 1) have molecular weights corresponding to monomeric forms of the molecules, whereas analogous compounds containing acyl groups or chlorine atoms (9, 10, 12, Table 1) exist in the form of dimers.

This difference in the behavior of distannoxanes is apparently explained by the fact that the presence of electron-acceptor groups at the tin atom increases its acceptor properties and promotes the formation of donor-acceptor bonds. This conclusion is consistent with the data of works ([8,12]), where it is shown that the complex-forming ability of compounds $R_n\mathrm{SnCl}_{4-n}$ decreases with increasing number n. In the literature ([13,14]) two possible structures for the dimer are discussed. It is not difficult to see that the structure with a four-membered ring of covalent Sn—O bonds is unlikely because of steric hindrance. From this point of view, the second of the structures considered is more probable.

The comparatively small magnitudes of the dipole moments of the dimers (if one takes into account that the molecule contains four polar Sn—O bonds and four acetate groups) indicate a high degree of symmetry in the structure of these compounds, which is in full agreement with the indicated conformation.

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