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Abstract

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A NEW TYPE OF ORGANOTIN COMPLEX COMPOUNDS

In the chemistry of organotin compounds, rearrangements of the type

$$R_2SnCl_2 + R_2Sn(OOCCH_3)_2 \rightarrow 2R_2Sn(Cl)(OOCCH_3);$$

$$R_2SnCl_2 + R_2SnBr_2 \rightarrow 2R_2SnClBr;$$

$$SnCl_4 + R_4Sn \rightarrow R_3SnCl + RSnCl_3.$$

are well known.

These reactions are often used to obtain mixed organotin compounds (1). The mechanism of such reactions is unclear. It is known that tin halides and mixed organotin compounds are capable of giving fairly stable molecular compounds with substances containing atoms with unshared pairs of valence electrons (O, S, N, etc.).

The complex-forming ability changes in the series $SnX_4 > RSnX_3 > R_2SnX_2 > R_3SnX$ (2). It is of interest to determine how the phenomenon of rearrangements is related to complex formation.

From this point of view, it seemed to us highly important to study the behavior of systems of the type R_2SnX_2—$R_2Sn(OR)_2$. On the one hand, as in the reactions cited above, exchange of groups and formation of $R_2SnX(OR)$ compounds according to the equation

$$R_2SnX_2 + R_2Sn(OR)_2 \rightarrow 2R_2SnX(OR).$$

is possible here. On the other hand, owing to the presence of a methoxy group in the second component, the possibility of formation of donor-acceptor complexes is also not excluded. Moreover, since tin compounds usually give complexes with two donor molecules, in the present case, because of the presence in the molecule of the methoxy derivative of two O atoms, the composition of the complexes may be 1 : 1, i.e., $R_2SnX_2 \cdot R_2Sn(OR)_2$.

One or the other direction of the reaction will be determined primarily by its energetics. It should be noted that compounds of the type $R_2SnX(OR)$ are little known (3). Complex compounds $R_2SnX_2 \cdot R_2Sn(OR)_2$ have likewise not been described in the literature. Therefore, investigations in this field are of undoubted interest.

In the present work, the study of the systems R_2SnX_2—$R_2Sn(OR)_2$, as well as $SnCl_4$—$R_2Sn(OR)_2$, was carried out with the aid of a number of physicochemical methods: cryoscopic titration, dielcometric titration (4), and calorimetric titration (5). In most systems, the products formed were isolated and identified. The isolation of individual compounds was carried out as follows: equimolecular amounts of the starting components were mixed in hexane, the solvent was distilled off in vacuo, and the residue was also distilled in vacuo. Thus were obtained, for example, $(C_4H_9)_2SnCl_2 \cdot (C_4H_9)_2Sn(OCH_3)_2$ (m.p. 25—26°, b.p. 166—167°/1.5 mm) and $(C_4H_9)_2SnBr_2 \cdot (C_4H_9)_2Sn(OCH_3)_2$ (m.p. 49—50°, b.p. 169—170°/3 mm). The dipole moments μ and heats of formation ΔH of the compounds studied were determined. The results are given in Table 1. Since the aggregate of the data obtained, as will be stated below, leads to the conclusion that complexes are formed, Table 1 indicates the formulas of these compounds. In studying processes of intermolecular interaction, it is very important···

Table 1

Dipole moments and heats of formation of the compounds studied

No.	Compound	P_∞	$P_E + P_A^*$	μ	$-\Delta H$
1	$(C_4H_9)_2Sn(OCH_3)_2$	109.6	72.9	1.33	–
2	$(C_4H_9)_2SnCl_2^{**}$	442.4	70.0	4.24	–
3	$(C_4H_9)_2SnBr_2$	390.5	76.2	3.90	–
4	$(C_4H_9)_2SnCl_2 \cdot$ $(C_4H_9)_2Sn(OCH_3)_2$	219.8	142.9	1.93	15.6
5	$(C_4H_9)_2SnBr_2 \cdot$ $(C_4H_9)_2Sn(OCH_3)_2$	231.9	149.0	2.00	15.4
6	$(C_4H_9)_2SnCl_2 \cdot$ $(C_4H_9)_2Sn(OC_4H_9)_2$	–	–	–	14.5
7	$SnCl_4 \cdot$ $(C_4H_9)_2Sn(OC_4H_9)_2$	657.0	144.3	5.00	33.2

* The atomic polarization of tin was taken into account (^{6}).
** Measured previously (^{2}).

It is essential to know the state of the initial components in solution. Cryoscopic determination of the molecular weights of dibutyltin dichloride*, dibutyltin dibromide, and $SnCl_4$ in benzene showed that, over a wide concentration range, these compounds are present in monomeric form, whereas dimethoxydibutyltin and dibutoxydibutyltin are associated in benzene.

Figure 1 gives the curves (2 and 3) characterizing the change in molecular weight of dimethoxydibutyltin and dibutoxydibutyltin, respectively, with concentration. At low concentrations the substance is in the unassociated state; as the concentration increases, association is observed. Curves referring to the heat of solution have an analogous character—for example, curve 1 (Fig. 1) for dibutoxydibutyltin in hexane. At low concentrations dissolution proceeds with absorption of heat; then the thermal effect becomes positive owing to association.

The dipole moments of the starting organotin compounds were measured in benzene at 25°. The results are given in Table 1. Since dipole-moment determinations are carried out in dilute solutions, the values found for μ may be assigned to the monomeric form of the molecules.

Figure 2 gives the curves of dielectrometric (d.m.) titration of solutions of $(C_4H_9)_2SnCl_2$ (1) and $(C_4H_9)_2SnBr_2$ (2) in benzene ($\sim$ 0.06 mole/l) with dimethoxydibutyltin. The corresponding curves of calorimetric titration (3, 4) are given there as well. The course of the curves unambiguously indicates the formation of sufficiently stable compounds of composition 1 : 1. This is also confirmed by cryoscopic titration data.

The unusual course of the dielectrometric titration curves (1, 2, Fig. 2) is explained by the fact that the dipole moments of the starting substances (4.24 and 3.90 D, respectively) are considerably higher than the dipole moments of the compounds formed ($\sim 2.0\,D$).

The displacement of the bend of the experimental curves relative to the straight line corresponding to a 1 : 1 ratio of the components, and the increase in the dielectric permittivity of the solutions in this region, are due to partial dissociation of the complexes formed.

The slope of the straight lines $\varepsilon - C$ after the component ratio 1 : 1 corresponds to the values of the dipole moments of the compounds being added, which indicates completion of the complex-formation process. The molecular weights of the reaction products significantly (almost twofold) exceed those calculated for $R_2SnX(OR)$, and they change somewhat with changes in solution concentration, approaching the value corresponding to the compound $R_2SnX_2 \cdot R_2Sn(OR)_2$ (I) or to the dimer $[R_2SnX(OR)]_2$ (II).

* Everywhere n-C_4H_9.

A very remarkable fact is the increase in molecular weight upon introduction into the solution of one of the initial components (usually R_2SnX_2). This circumstance serves as strong evidence in favor of formation in the system of complex I, whose dissociation is suppressed by addition of one of the components.

The large values of the thermal effects of the reactions studied (Nos. 5, 6, 7,

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Table 1) also testify in favor of the formation of complexes of the donor-acceptor type I. It is known that rearrangement reactions usually proceed without significant thermal effects. Thus, by the method of calorimetric titration we measured the thermal effect of the reaction

$$(C_4H_9)_2SnCl_2 + (C_4H_9)_2Sn(OOCH_3)_2 \rightarrow 2(C_4H_9)_2SnCl(OOCH_3).$$

It proved to be equal to 1.5 kcal. Consequently, if rearrangement reactions occurred in the systems under study and compounds of type II were formed, the thermal effects of the reactions would apparently be small.

It is interesting to note that the stronger acceptor, $SnCl_4$, also gives compounds of composition $1:1$ with dialkoxy derivatives. The heat of formation of $SnCl_4 \cdot (C_4H_9)_2Sn(OC_4H_9)_2$ is 33.2 kcal/g-mol. The analogous compound with the dimethoxy derivative $SnCl_4(C_4H_9)_2Sn(OCH_3)_2$—a more crystalline substance —proved to be insoluble and therefore was not subjected to more detailed study.

Fig. 1. 1 —heat of dissolution of dibutoxydibutyltin, 2 —molecular weight of dibutoxydibutyltin, 3 —molecular weight of dimethoxydibutyltin

Fig. 2. 1 —D.c. titration of a solution of dibutyltin dichloride in benzene with dimethoxydibutyltin, 2 —D.c. titration of a solution of dibutyltin dibromide in benzene with dimethoxydibutyltin, 3 —calorimetric titration of a solution of dibutyltin dichloride in hexane with dimethoxydibutyltin, 4 —calorimetric titration of a solution of dibutyltin dibromide in hexane with dimethoxydibutyltin

A very weighty argument in favor of the complex structure I of the compounds studied is the reaction of displacement of the complex-forming agent by another, stronger one. On treatment of the compound obtained from $(C_4H_9)_2SnCl_2$ and $(C_4H_9)_2Sn(OCH_3)_2$ with a solution of $SnCl_4$, $(C_4H_9)_2SnCl_2$ is separated almost quantitatively (yield 90%). The analytical data and the IR spectrum of the second product formed correspond to the complex $SnCl_4 \cdot (C_4H_9)_2Sn \cdot (OCH_3)_2$. In a similar way, by the action of $SnCl_4$ on the product of the reaction of diethyltin dichloride with dimethoxydibutyltin, we obtained $(C_2H_5)_2SnCl_2$ in 80% yield.

We measured the thermal effect of the reaction

$$(C_4H_9)_2SnCl_2 \cdot (C_4H_9)_2Sn(OC_4H_9)_2 + SnCl_4 \rightarrow$$

Fig. 3. IR spectra: 1 –dibutyltin dimethoxide, 2 – $(C_4H_9)_2SnCl_2 \cdot (C_4H_9)_2Sn \cdot (OCH_3)_2$, 3 $-SnCl_4 \cdot (C_4H_9)_2Sn(OCH_3)_2$

Figure 3: Fig. 3. IR spectra: 1 –dibutyltin dimethoxide, 2 $-(C_4H_9)_2SnCl_2 \cdot (C_4H_9)_2Sn \cdot (OCH_3)_2$, 3 $-SnCl_4 \cdot (C_4H_9)_2Sn(OCH_3)_2$

$$\rightarrow (C_4H_9)_2SnCl_2 + (C_4H_9)_2Sn(OC_4H_9)_2 \cdot SnCl_4.$$

It proved to be equal to 18.4 kcal.

If it is taken into account that the heat of formation of the first complex is 14.5 kcal, and the heat of formation of the second is 33.2 kcal (Table 1), then the transition from

from one to another should be accompanied, to a first approximation, by the release of $33.2 - 14.5 = 18.7$ kcal. This value is close to that found experimentally.

In the IR spectrum of dibutyltin dimethoxide, the intense doublet in the region 1045–1080 cm^{-1} evidently belongs to vibrations of the C—O bond in the Sn—O—C group (^{7}) (Fig. 3). In methoxytributyltin this vibration corresponds to a very strong band with a maximum in the region 1075 cm^{-1} (^{6}). In the spectrum of the compound $(C_4H_9)_2SnCl_2 \cdot (C_4H_9)_2Sn(OCH_3)_2$, instead of such a doublet, an intense band is observed in the region 1030 cm^{-1}. This indicates that the complex is formed through the ether oxygen atoms of the methoxy groups; as a result, the O—C bond is weakened and the frequency of its vibration is shifted to the region of lower frequencies. An especially large shift of the O—C-vibration frequency occurs in the complex of dibutyltin dimethoxide with the stronger acceptor–$SnCl_4$. In the spectrum of this complex the maximum of the band assigned to the C—O bond in the C—O—Sn group is shifted to the region 960 cm^{-1}.

Fig. 3. IR spectra: **1** –dibutyltin dimethoxide, **2** $-(C_4H_9)_2SnCl_2 \cdot (C_4H_9)_2Sn \cdot (OCH_3)_2$, **3** $-SnCl_4 \cdot (C_4H_9)_2Sn(OCH_3)_2$

In the 700–400 cm^{-1} region of the spectrum of dibutyltin dimethoxide, complex formation produces very strong changes. However, an exact interpretation of these changes is difficult and requires further investigation, which is being carried out at present.

Thus, the totality of the data obtained makes it possible to draw the unambiguous conclusion that in the systems R_2SnX_2—$R_2Sn(OR)_2$, fairly stable molecular compounds of composition $1:1$ are formed. No phenomena of rearrangement and formation of compounds $R_2SnX(OR)$ are observed.

The comparatively small values of the dipole moments of the complexes studied (1.9—2.0 D) indicate their sufficiently symmetrical structure.

The most probable structure appears to be an octahedral configuration with a trans arrangement of the chlorine atoms and a cis arrangement of two donor oxygen atoms.

The complexes $SnCl_4 \cdot R_2Sn(OR)_2$ apparently have an analogous configuration. Naturally, the heats of formation and dipole moments of the donor-acceptor bonds in the complexes formed by R_2SnX_2 are smaller than the corresponding values in the complexes formed by $SnCl_4$. The considerable difference in the dipole moments of these complexes (2.0 and 5.0 D) is due both to the difference in the polarity of the bonds formed and to the difference in the dipole moments of $Sn—Cl$ and $Sn—R$.

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