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## Abstract

## Full Text

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# MOLECULAR COMPOUNDS OF TIN TETRACHLORIDE WITH ORGANIC SULFIDES

Complexes of tin tetrachloride with organic sulfides have been little studied. The literature describes the syntheses of only a few compounds of this type: $SnCl_4 \cdot 2(CH_3)_2S$ (1, 2), $SnCl_4 \cdot 2(C_2H_5)_2S$ (1), $SnCl_4(-CH_2-S-CH_3)_2$ (3). Their physicochemical properties, including dipole moments—one of the most important constants characterizing the nature of donor-acceptor bonds—have not been investigated.

In the present work, which is the beginning of a systematic study of complexes of organosulfur compounds with metal halides and organometallic compounds, an attempt has been made to study complex-formation processes in the systems tin tetrachloride—organic sulfides in benzene by the method of dielectric polarization and to investigate a number of properties of the complexes formed.

Judging from the fact that complexes of composition $SnCl_4 \cdot 2D$, where D denotes oxygen- or nitrogen-containing compounds, have large dipole moments (4-6), considerably exceeding the sum of the dipole moments of the components, it could be expected that the formation of donor-acceptor bonds in complexes of organosulfur compounds would also cause significant changes in the polar properties of the systems studied.

We observed the process of complex formation by means of the method of dielectrometric titration (7), which makes it possible to determine not only the composition and stability of the compounds formed, but also their dipole moments under conditions in which dissociation is suppressed.

Figures 1 and 2 show the curves of dielectrometric titration of solutions of $SnCl_4$ in benzene (0.05-0.15 g·mole/l) with the sulfides studied at 25° in an atmosphere of dry nitrogen; Table 1 gives the values of the dipole

**Table 1**

| No. | Complex | $C_{SnCl_4}$ | $\mu_{complex}$ | $\mu_{sulfide}$ in benzene + $SnCl_4$ | $\mu_{sulfide}$ in benzene |
|---|---|---|---|---|---|
| 1 | $SnCl_4 \cdot (C_4H_9)_2S$ | 0.124 | 6.71 | 1.51 | 1.57** |

Fig. 1 and Fig. 2: Dielectrometric titration graphs

Figure 1: Fig. 1 and Fig. 2: Dielectrometric titration graphs

| No. | Complex | $C_{SnCl_4}$ | $\mu_{complex}$ | $\mu_{sulfide}$ in benzene + $SnCl_4$ | $\mu_{sulfide}$ in benzene |
|---:|---|---:|---:|---:|---:|
| 2 | $SnCl_4 \cdot (C_8H_{17})_2S$ | 0.108 | 6.79 | 1.61 | 1.63 |
| 3 | $SnCl_4 \cdot (C_9H_{19})_2S$ | 0.049 | 6.72 | 1.56 | 1.56 |
| 4 | $SnCl_4 \cdot (C_{16}H_{33})_2S$ | 0.049 | 6.83 | – | 1.47** |
| 5 | $SnCl_4 \cdot 2(C_4H_9)_2S$ | 0.124 | 4.10 | – | – |
| 6 | $SnCl_4 \cdot 2(C_8H_{17})_2S$ | 0.049 | 4.10 | – | – |
| 7 | $SnCl_4 \cdot 2(C_9H_{19})_2S$ | 0.049 | 4.13 | – | – |
| 8 | $(C_6H_5)_2S + SnCl_4$ | 0.080 | – | 1.67 | 1.50; 1.57** |
| 9 | (iso-$C_8H_{17})_2S + SnCl_4$ | 0.108 | – | 3.71 | 1.64 |
| 10 | $C_6H_5SC_2H_5 + SnCl_4$ | 0.108 | – | 4.08 | 1.48 |
| 11 | $SnCl_4 \cdot 2(C_4H_9)_2S$* in benzene | – | 4.54 | – | – |
| 12 | $SnCl_4 \cdot 2(C_4H_9)_2S$* in benzene + $(C_4H_9)_2S$ 0.452 g · mole/l | – | 3.93 | – | – |
| 13 | $SnCl_4 \cdot 2(C_4H_9)_2S$* in benzene + $SnCl_4$ 0.12 g · mole/l | – | 6.20 | – | – |

* The dipole moments of the isolated complex were measured.
** Literature data.

moments. The notation is as follows: $\varepsilon$ –dielectric constant, $d$ –density, $C_{SnCl_4}$ –concentration of the initial $SnCl_4$ solution, $C$ –sulfide concentration, $\mu$ –dipole moment.

As can be seen, the process of complex formation in the systems under study depends to a considerable extent on the nature of the organic sulfide.

**Fig. 1.** Dielectrometric titration of $SnCl_4$ in benzene: **1** –with dibutyl sulfide, **2** –with dinonyl sulfide, **3** –with dioctyl sulfide, **4** –with dihexadecyl sulfide, **5**

–with diphenyl sulfide, **6** –density of $SnCl_4$+ dioctyl sulfide solutions

**Fig. 2.** Dielectrometric titration of $SnCl_4$ in benzene: **1** –with dioctyl sulfide, **2** –with diisooctyl sulfide, **3** –with ethyl phenyl sulfide

In the case of diphenyl sulfide (Fig. 1, 5), over a wide concentration range a rectilinear dependence of $\varepsilon$ on $C$ is observed; its dipole moment in the presence of $SnCl_4$ is 1.67 D (compound No. 8, Table 1) and is close to the moment in benzene: 1.57 D.

Another type of $\varepsilon$-$C$ curve is observed in the systems tin tetrachloride–diisooctyl sulfide (7,9-dimethyl-8-thiapentadecane) (Fig. 2, 2) and tin tetrachloride–ethyl phenyl sulfide (Fig. 2, 3).

The considerable increase in the dielectric constant of the solutions indicates the formation in these systems of compounds with dipole moments substantially greater than the dipole moments of the added sulfides; however, the nature of the $\varepsilon$-$C$ and $d$-$C$ curves does not allow the composition of the complexes to be determined. The dipole moments of these sulfides in the presence of $SnCl_4$, found by extrapolation of the initial portions of the curves, proved to be 2–2.5 times higher than the dipole moments in benzene (Table 1, compounds Nos. 9 and 10). A completely different type of $\varepsilon$-$C$ curve is observed for systems with $n$-aliphatic sulfides (Fig. 1, 1–4 and Fig. 2, 1). All aliphatic sulfides, irrespective of the length of the alkyl radical ($n$-$C_4H_9$, $n$-$C_8H_{17}$, $n$-$C_9H_{19}$, and $n$-$C_{16}H_{33}$)* behave identically toward $SnCl_4$. Three concentration regions are distinguished, in which the dependence of $\varepsilon$ on $C$ is different. In the first, up to the ratio $C_{SnCl_4} : C_{R_2S} = 1 : 1$,

* The complex of tin tetrachloride with diethyl sulfide is insoluble in benzene.

there is a sharp increase in the dielectric constant of the solutions; in the second, at a concentration ratio between 1 : 1 and 1 : 2, the dielectric constant of the solutions decreases; in the third, after the ratio 1 : 2, a linear dependence of $\varepsilon$ on $C$ is observed.

Such a course of the $\varepsilon$–$C$ curves makes it possible to conclude that sulfide molecules add stepwise to $SnCl_4$. First one sulfide molecule adds, forming the complex $SnCl_4 \cdot R_2S$ with a large dipole moment; then a second sulfide molecule adds, forming the complex $SnCl_4 \cdot 2R_2S$ with a considerably smaller dipole moment. At this point the complex-formation process is completed; the change in the dielectric constant of the solution upon further addition of sulfide corresponds to the addition of the individual compound.

In this respect the behavior of the systems investigated differs markedly from the systems $SnCl_4$–alcohols (7) and $SnCl_4$–acids (7), where two donor molecules add at once to the $SnCl_4$ molecule, giving $SnCl_4 \cdot 2D$, and the complex-formation process is completed only after the addition of four and three donor molecules, respectively.

It should be noted that the maxima of the $\varepsilon$–$C$ curves in the systems investigated are, as a rule, shifted toward higher concentrations than corresponds to the composition 1 : 1. This shift is due to dissociation of the complexes. The shift of the minimum on passing from the curve to the straight line after formation of the 1 : 2 complex is explained in the same way.

The $d$–$C$ curves for the systems investigated are less pronounced. Fig. 1 gives the values of the densities of $SnCl_4$ solutions on titration with $n$-octyl sulfide (curve 6). Approximately the same $d$–$C$ curves were obtained for the other sulfides as well. Characteristic of them is a rectilinear course after a concentration ratio of 1 : 2.

The dipole moments of all complexes of $SnCl_4$ with $n$-aliphatic sulfides of composition 1 : 1 (extrapolation of the first branch of the $\varepsilon$–$C$ and $d$–$C$ curves) are close to one another; by $\sim 5.2\,D$ they exceed the sum of the dipole moments of the components. The question of whether this increase may be attributed entirely to the formation of a donor-acceptor bond, or whether this value includes a dipole moment connected with a change in the spatial configuration of $SnCl_4$ during complex formation, still remains open, since the structure of such complexes is unknown. We are attempting to solve this question by means of X-ray structural analysis.

The dipole moments of complexes of composition 1 : 2 (extrapolation of the values of $\varepsilon$ and $d$ at the points $M$ (Fig. 2) to zero concentration) are also close to one another; they are $\sim 2.7\,D$ lower than the dipole moments of complexes of composition 1 : 1.

In the last two columns of Table 1 are given the dipole moments of the sulfides in the presence of the corresponding complexes (extrapolation of the third rectilinear section of the curves) and the dipole moments of the sulfides investigated, measured by us in benzene.

On the basis of the results of dielectrometric titration, we carried out several experiments on the isolation of a number of complexes in pure form and studied in more detail the processes of their transformations in solution.

The complex $SnCl_4 \cdot 2(C_4H_9)_2S$ is a white crystalline substance, m.p. 41–42°, soluble in hydrocarbon solvents, recrystallized from petroleum ether, distills in vacuum without decomposition, b.p. 93° at 5 mm Hg, hydrolyzes rather slowly on contact with air; sulfur analysis: found 11.75; 11.23%, calculated 11.57%.

The complex $SnCl_4 \cdot 2(C_9H_{19})_2S$ is a colorless viscous liquid, $n_D^{20}$ 1.5158, partially decomposes on distillation in vacuum, b.p. 174–175° at 2–3 mm Hg.

The molecular weights of these complexes in benzene (cryoscopy) correspond to monomeric, partially dissociated molecules (504 instead of 553 for the first, and 787 instead of 833 for the second).

Measurement of the dipole moment of the isolated complex $SnCl_4 \cdot 2(C_4H_9)_2S$ in benzene by the usual method showed a deviation of $\varepsilon - C$ from linear dependence, characteristic of dissociating compounds. As was to be expected, upon dissociation according to the scheme:

$$\mathrm{SnCl_4 \cdot 2(C_4H_9)_2S \rightleftharpoons (C_4H_9)_2S + SnCl_4 \cdot (C_4H_9)_2S},$$

an elevated value of the dipole moment was obtained (Table 1, compound No. 11).

The dipole moment of $SnCl_4 \cdot 2(C_4H_9)_2S$, measured in the presence of a large excess of dibutyl sulfide, i.e., under conditions of suppressed dissociation (Table 1, compound No. 12), proved to be close to the moment found by the method of dielectrometric titration (3.93 and 4.11 D).

For additional confirmation of the formation in the systems studied of complexes of composition 1 : 1, dielectrometric titration of a solution of $SnCl_4$ with the complex $SnCl_4 \cdot 2(C_4H_9)_2S$ (compound No. 12) was carried out. The course of the $\varepsilon - C$ and $d - C$ curves indicates the presence of the reaction:

$$\mathrm{SnCl_4 \cdot 2(C_4H_9)_2S + SnCl_4 \rightleftharpoons 2SnCl_4 \cdot (C_4H_9)_2S}.$$

The dipole moment found, 6.2 D, proved to be close to the dipole moment of the 1 : 1 complex.

If such a reaction did not occur, we would obtain a rectilinear dependence of $\varepsilon$ on $C$ and a dipole moment equal to 3.9–4.1 D.

In order to determine the mobility and equivalence of the dibutyl sulfide molecules in the complex $SnCl_4 \cdot 2(C_4H_9)_2S$, exchange experiments were carried out with dibutyl sulfide labeled with $S^{35}$. For this purpose, a weighed portion of the complex was dissolved in an equimolar amount of labeled dibutyl sulfide, after which the mixture was treated with petroleum ether. The precipitated complex was recrystallized from petroleum ether (m.p. 42°) and analyzed for radioactive sulfur content. It was found that at 18–20° the exchange reaction reaches equilibrium in 10–15 min; both sulfide molecules undergo exchange.

As mentioned above, the complex-forming ability of sulfides depends to a significant degree on the structure of the molecules. The difference in the behavior of di-*n*-octyl and di-*iso*-octyl sulfides is apparently due to steric hindrance in the latter. The differences in the behavior of aliphatic and aromatic sulfides are probably determined by the different donor ability of the sulfur atom. The unshared $3p^2$ electron pair responsible for the donor properties of the sulfur atom in aromatic compounds interacts (being in the excited $^3pd$ state) with the $\pi$-electrons of neighboring carbon atoms, which is absent in aliphatic compounds.

According to preliminary data, thiophene, like diphenyl sulfide, does not give donor-acceptor complexes with $SnCl_4$. It probably forms low-polarity $\pi$-complexes. In contrast to thiophene, thiophane behaves analogously to alkyl sulfides. It is interesting to note that replacement of one chlorine atom in $SnCl_4$

by a phenyl group considerably reduces the acceptor properties. Phenyltin trichloride does not give complexes with dibutyl sulfide.

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