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Abstract

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Complexes of Tin Tetrachloride with Unsaturated Compounds Containing Heteroatoms

Often, compounds that contain heteroatoms along with double C=C bonds are used as monomers in polymerization reactions catalyzed by metal halides ($SnCl_4$, $TiCl_4$, $FeCl_3$, etc.). Such compounds include vinyl ethers, vinyl sulfides, thiophene, furan, and others. It is known that metal halides form stable donor-acceptor complexes with many compounds containing nitrogen, oxygen, and sulfur atoms. A characteristic feature of such complexes is the presence of large dipole moments.

On the other hand, metal halides are apparently capable of giving π-complexes with unsaturated compounds. The concept of the formation of π-complexes is invoked to explain the catalytic activity of metal halides in polymerization reactions ([1]-[3]).

The existence of such complexes has been detected by spectroscopic methods, for example, for tin tetrachloride and cyclohexene[4], and also for tin tetrachloride and 1,1-diphenylethylene[5] [6]. According to our data[7], the dipole moments of such complexes, in contrast to donor-acceptor complexes, are small. Consequently, from the standpoint of interaction with metal halides, the compounds under consideration possess two reaction centers: the heteroatom on the one hand, and the double C=C bond on the other.

It is of interest to determine what type of complexes metal halides give with such molecules. Are π-complexes formed here with the participation of the π-electrons of unsaturated bonds, or donor-acceptor complexes through the participation of the lone electron pairs of heteroatoms, and how is one or the other type of complex formation related to the structure of the monomer molecules?

To answer these questions, the method of dielectric polarization was used in the present work. The processes of complex formation of tin tetrachloride with furan, 2-methylfuran, thiophene, and diallyl sulfide were studied. For comparison, systems of tin tetrachloride with analogous saturated compounds were investigated: tetrahydrofuran, tetrahydrothiophene, 2,5-dimethylthiophane, and dipropyl sulfide. The work was carried out by the method of dielectrometric titration[8]. Changes in the dielectric constant ε and density d of solutions of tin tetrachloride in benzene or hexane (C = 0.05–0.08 g-mol/l) were studied upon successive addition of small portions of the compounds under investigation. Figure 1 presents the dielectrometric titration curves for a solution of $SnCl_4$ in benzene (C = 0.0561 g-mol/l) with furan and tetrahydrofuran. Similar curves for thiophene, tetrahydrothiophene, 2,5-dimethylthiophane, dipropyl and diallyl sulfides are given in Fig. 2. Since, in the experiments relating to Fig. 2, $SnCl_4$ solutions of different concentrations were taken, the axes show $\Delta\varepsilon/C_{SnCl_4}$ and C/C_{SnCl_4}. The d-C curves are not presented; they are less pronounced, although in a number of cases clear inflections are observed, from which one can judge complex formation and the composition of the complexes.

Table 1

Dipole moments of complexes with tin tetrachloride

No.	Compound	μ	Complex	μ'	$\Delta\mu = \mu' - \mu$	μ''
1	Tetrahydrofuran	1.68	$SnCl_4 \cdot C_4H_8O$	5.94	4.24	1.7
2	Tetrahydrofuran	1.68	$SnCl_4 \cdot 2C_4H_8O$	4.33	–	
3	Tetrahydrothiophene	1.87	$SnCl_4 \cdot C_4H_8S$	4.88	3.01	1.73
4	Tetrahydrothiophene	1.87	$SnCl_4 \cdot 2C_4H_8S$	5.00	–	
5	2,5-Dimethylthiophane	1.86*	$SnCl_4 \cdot C_6H_{12}S$	5.71	3.85	1.83
6	2,5-Dimethylthiophane	1.86	$SnCl_4 \cdot 2C_6H_{12}S$	5.47	–	
7	Dipropyl sulfide	1.55	$SnCl_4 \cdot (C_3H_7)_2S$	6.49	4.94	1.50
8	Dipropyl sulfide	1.55	$SnCl_4 \cdot 2(C_3H_7)_2S$	3.83	–	
9	Diallyl sulfide	1.28*	$SnCl_4 \cdot (C_3H_5)_2S$	6.38		1.28
10	Diallyl sulfide	1.28	$SnCl_4 \cdot 2(C_3H_5)_2S$	5.34	–	
11	Furan	0.67	C_4H_4O	0.99	0.32	
12	2-Methylfuran	0.74	C_5H_6O	1.27	0.53	
13	Thiophene	0.54	C_4H_4S	1.73	1.16	
14	$SnCl_4 \cdot 2C_4H_8S$	–	$SnCl_4 \cdot 2C_4H_8S$	5.05		

* Dipole moments measured by us.

The values of the dipole moments found from the experimental data (μ') are given in Table 1. In those cases where the composition of the complexes is known (from the ε—C and d—C curves), the table gives the dipole-moment values for these complexes (Nos. 1–10, Table 1); if, however, the character of the curves does not make it possible to determine the composition of the complex, the

Fig. 1: plot of ε versus C for tetrahydrofuran and furan

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table gives the values of the dipole moments of the compounds under study, measured in the presence of $SnCl_4$ (Nos. 11–13, Table 1). For comparison, the table gives the dipole moments of the compounds under study (μ). Some of them were measured by us, and some were taken from the literature.

Fig. 1

As can be seen (Figs. 1, 2, Table 1), the interaction of unsaturated compounds—furan, 2-methylfuran, and thiophene—with tin tetrachloride has a quite different character than the interaction of analogous saturated compounds: tetrahydrofuran, tetrahydrothiophene, and 2,5-dimethylthiophane. The latter, like other saturated compounds of oxygen and sulfur (^{9}), form stable complexes of composition $SnCl_4$: donor $= 1 : 1$ and $1 : 2$. The dipole moments of such complexes exceed by 3–5 D the sum of the dipole moments of the components (Table 1, $\Delta\mu$). The complex-formation process here ends with complexes of composition $1 : 2$. This is indicated by the values of the dipole moments of the compounds under study found from the last branch of the ε—C and d—C curves (μ'', Table 1).

In the case of furan, 2-methylfuran, and thiophene, only a small increase in the dipole moment is observed, analogous to that which was observed (^{7}) in the case of interaction of unsaturated hydrocarbons with tin tetrachloride.

Consequently, the presence of two carbon atoms in the sp^2-state adjacent to the heteroatom almost completely suppresses the ability of the latter to give donor-acceptor type complexes. Judging from the increase in dipole moments (Table 1, Nos. 11, 12, 13), these compounds give π-complexes. The formation of π-complexes in the thiophene–$SnCl_4$ system was confirmed by us by infrared spectroscopy (the results will be published). The decrease in the donor ability of heteroatoms in α—β-unsaturated-

in such compounds is apparently explained by the fact that the unshared pair of valence electrons responsible for complex formation is not free in these compounds.

According to quantum-chemical calculations, for example, it is known for the thiophene molecule (^{10}) that the $3p^2$ unshared electron pair of the sulfur atom, being excited into the $3pd$ state, takes a direct part in the π-electron interaction of the system. It was of interest to determine: 1) how far along the chain this effect of unsaturated $C = C$ bonds extends, and 2) how the properties of the heteroatom change if adjacent to it there is not two, but one $C = C$ bond; the second group being an alkyl radical (vinyl ethers, vinyl sulfides).

Fig. 2

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

As regards the first point, from the example of diallyl sulfide (Table 1, No. 9) it is seen that removal of the double bond by one $C = C$ bond, i.e., its transfer from the α–β to the β–γ position with respect to the heteroatom, practically completely eliminates the effect of the $C = C$ bond on the donor properties of the sulfur atom. Diallyl sulfide gives with $SnCl_4$ donor-acceptor complexes of the same type as dialkyl sulfides and, in particular, dipropyl sulfide (Fig. 2, Table 1, No. 7).

Since the course of the $\Delta\varepsilon$–C/C_{SnCl4} curve for diallyl sulfide differs from that of the corresponding curve for dipropyl sulfide, and its interpretation from the standpoint of establishing the composition of the complexes (1 : 1 or 1 : 2) is difficult, we carried out an additional investigation of these systems by the method of cryoscopic titration.

Fig. 3

Figure 3 presents the results of cryoscopic titration of a solution of $SnCl_4$ in benzene (0.35 g-mol/liter) with diallyl and dipropyl sulfides. As can be seen, both compounds behave identically toward $SnCl_4$. The process ends with the formation of a complex of composition 1 : 2, which agrees with the result of dielectric titration (μ'', Table 1).

As regards the second question, there is as yet no clarity. Our attempt to study the processes of complex formation of $SnCl_4$ with certain vinyl ethers proved unsuccessful because of polymerization of the products under the experimental conditions. However, judging from the fact that in the case of ethyl phenyl sulfide, in contrast to diphenyl sulfide, a significant increase in the dipole moment is observed (^{9}) in the presence of $SnCl_4$, it may be assumed that in such compounds the ability of the heteroatom for acceptor-donor interaction is partially retained.

In the systems considered by us, competition between two reaction centers in complex-formation reactions with metal halides led to two limiting cases: either to the formation of donor-acceptor type complexes (diallyl sulfide), or to the formation of π-complexes (furan, thiophene, 2-methylfuran). Depending on the structure of the molecules, other intermediate states may apparently also be realized.

The polymerization activity of monomers of this type depends substantially on the kind of complexes that they form with metal halides. The formation of π-complexes promotes polymerization reactions. The polymerization of furan and 2-methylfuran under catalysis by $SnCl_4$ was studied in work ([11]).

Taking into account the results of experiments on dielectric titration, we attempted to isolate some of the complexes established by us, characterize them, and measure their dipole moments in solution by the usual method.

The following complexes were isolated.

$SnCl_4 \cdot 2C_4H_8S$—a white crystalline substance, comparatively stable in air, m.p. 154-155°, tin content 27.3; 28.1%, calculated 27.2%; molecular weight in benzene, determined by the cryoscopic method, is 432, calculated 436.7.

$SnCl_4 \cdot 2(C_3H_7)_2S$—a white crystalline substance, m.p. 54-55°, partially decomposing, distills in vacuum at 80-83° at 5 mm Hg.

$SnCl_4 \cdot C_4H_8O$—a white crystalline substance, hydrolyzing in air, melts with decomposition at 175-180°. The data agree with the literature ([12]).

The dipole moment of the complex $SnCl_4 \cdot 2C_4H_8S$, measured in benzene containing tetrahydrothiophene (0.643 g-mol/l) to suppress dissociation, proved to be 5.05 D (Table 1, No. 14). This value agrees well with the data obtained by the dielectric titration method (Table 1, No. 4).

To confirm the fact of formation of complexes of composition 1 : 1, the dipole moment of $SnCl_4 \cdot 2C_4H_8S$ was measured in the presence of an excess of $SnCl_4$ (0.12 g-mol/l). The course of the curve ϵ—C indicates the presence of the reaction

$$SnCl_4 \cdot 2C_4H_8S + SnCl_4 \rightarrow 2SnCl_4 \cdot C_4H_8S.$$

Analogous results were obtained by us for the complex of $SnCl_4$ with dibutyl sulfide ([9]).

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REFERENCES

[1] P. H. Plesh, *Cationic Polimerisation and Related Complexes*, London, 1953.
[2] E. B. Lyudvig, A. R. Gantmakher, S. S. Medvedev, *Vysokomol. soed.*, **1**, 1342 (1959).
[3] M. F. Shostakovskii, E. N. Prilezhaeva, V. M. Karaeva, *Vysokomol. soed.*, **1**, 582 (1959).
[4] A. N. Terenin, V. N. Filimonov, D. S. Bystrov, *Izv. AN SSSR, ser. fiz.*, **22**, No. 9, 1100 (1958); V. N. Filimonov, D. S. Bystrov, A. N. Terenin, *Optika i spektroskopiya*, **3**, 480 (1957).
[5] A. G. Evans, J. Lewis, *J. Chem. Soc.*, **1957**, 2975; A. G. Evans, R. M. Jones, J. H. Thomas, *J. Chem. Soc.*, **1957**, 105; A. G. Evans, N. Jones et al., *J. Chem.*

Soc., **1956**, 2737.
[6] I. P. Goldshtein, N. Kh. Faizi et al., *DAN*, **138**, 839 (1961).
[7] I. P. Goldshtein, E. N. Gur'yanova, K. A. Kocheshkov, *ZhOKh*, **32**, 317 (1962).
[8] E. N. Gur' yanova, I. P. Goldshtein, *ZhOKh*, **32**, 12 (1962).
[9] I. P. Goldshtein, E. N. Gur' yanova, K. A. Kocheshkov, *DAN*, **138**, 1099 (1961).
[10] H. C. Longuet-Higgins, *Trans. Farad. Soc.*, **45**, 173 (1949).
[11] V. V. Korshak, A. S. Sultanov, A. A. Abduvaliev, *Uzb. khim. zhurn.*, No. 4, 39 (1959).
[12] H. H. Sisler, H. H. Batey et al., *J. Am. Chem. Soc.*, **70**, 3818 (1948).

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