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Abstract

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DIPOLE MOMENTS OF ORGANOTIN CHLORIDES AND THEIR ABILITY TO FORM COMPLEXES

The physicochemical properties of organotin chlorides have been insufficiently studied. In particular, one of the most important parameters characterizing the nature of chemical bonds—the dipole moment—has been determined for only three compounds of this class: $(C_2H_5)_2SnCl_2$ 3.85D (^{1}), $(C_2H_5)_3SnCl$ 3.44D (^{1}), and $(C_6H_5)_3SnCl$ 3.28D (^{2}). Therefore, obtaining new data characterizing the polar properties of these compounds is an independent task. A very interesting and important property of tin tetrachloride is its ability to give molecular compounds of various stability with a number of substances. Apparently, this property determines its catalytic activity in polymerization reactions. It seemed of interest to establish how the ability to form complexes changes when chlorine atoms in $SnCl_4$ are replaced by organic radicals.

In accordance with the foregoing, the present work was carried out in two directions: the dipole moments of organotin chlorides were determined, and their ability to give complexes was investigated by the method of dielectric polarization. The dipole moments μ of the compounds studied, measured in hexane, benzene, and dioxane, are given in Table 1.

Table 1

Compound	μ, hexane	μ, benzene	μ, dioxane	$\mu_b - \mu_g$	$\mu_d - \mu_g$
$SnCl_4$	0 (^{10})	0.87	3.82(^{10})	0.87	3.82
$C_6H_5SnCl_3$	3.99	4.24	5.81	0.25	1.82
$(C_6H_5)_2SnCl_2$	3.65	3.59	4.34	−0.06	0.69
$(C_6H_5)_3SnCl$	(3.30)	3.31	3.93	–	0.63
$(n\text{-}C_4H_9)_2SnCl_2$	4.25	4.22	5.11	−0.03	0.85
$(n\text{-}C_4H_9)_3SnCl$	3.58	3.64	4.03	0.06	0.45

The molecule of tin tetrachloride, according to electron-diffraction data (^{3,4}), has a tetrahedral configuration; consequently, its dipole moment in the vapor and in indifferent solvents should be equal to zero. This has been confirmed experimentally for $SnCl_4$ in the vapor (^{5}), in hexane (^{1}), and in the solid state (^{6}). However, the dipole moment of $SnCl_4$ in benzene differs from zero: $0.8D$ according to (^{6}), $0.96D$ according to (^{7}). The presence of a dipole moment for $SnCl_4$ in benzene, and also in carbon tetrachloride, served as the basis for the conclusion that $SnCl_4$ has a pyramidal configuration (^{7}). We repeated the measurements of the dipole moment of $SnCl_4$ in benzene, taking special precautions against the ingress of moisture, and found it to be $0.87D$. This value agrees well with the data cited above.

In our opinion, the dipole moment of $SnCl_4$ in benzene arises not from a pyramidal configuration of the molecule, as is asserted in (7), but from the formation of a molecular compound of tin tetrachloride with benzene.

The question of the polar properties of molecular compounds of tin tetrachloride and other metal halides with unsaturated hydrocarbons is being studied by us; the results will be published. In considering the dipole moments of organochlorotin compounds it is very important to know whether the tetrahedral configuration of the bonds is retained in these compounds, or whether distortion of the tetrahedron takes place here as a result of another type of hybridization or steric hindrance. According to structural-analysis data, the compounds $Sn(CH_3)_4$, $(CH_3)_3SnJ$, $(CH_3)_3SnCl$, and $(CH_3)_2SnCl_2$ have a tetrahedral configuration (8). Apparently, in the compounds studied by us the tetrahedral direction of the bonds is also retained. If this is so, then the dipole moments of $C_6H_5SnCl_3$ and $(C_6H_5)_3SnCl$ in hexane should be close. The difference of $0.7\,D$ (Table 1) indicates a considerable interaction of the π-electrons of the phenyl rings with the electrons of the Sn—Cl bonds.

The dipole moments of organotin chlorides with aliphatic radicals are higher than the dipole moments of the corresponding compounds with phenyl radicals. If the dipole moment of the Sn—Cl bond in all compounds is taken to be the same, equal to $3.0\,D$ (9), then the dipole moment of the Sn—C bond in aliphatic compounds, according to the data for $(C_4H_9)_3SnCl$, is $0.58\,D$, and according to the data for $(C_4H_9)_2SnCl_2$ is $0.63\,D$, i.e., practically the same, $0.6\,D$.

In phenyl derivatives such constancy is not observed; the moment of the Sn—C bond is equal to $1\,D$, $0.2\,D$, and $0.3\,D$ in the mono-, di-, and triphenyl derivatives, respectively. In contrast to the aliphatic compounds, in these compounds a deviation from additivity is observed owing to the mutual influence of the phenyl radicals and chlorine atoms.

The dipole moment of tin tetrachloride in dioxane is $3.82\,D$ (10). The large value of the dipole moment indicates the formation of a complex of the donor-acceptor type. The dipole moments of organotin chlorides in dioxane are also higher (Table 1) than in benzene and hexane. Since the compounds studied do not contain hydrogen atoms capable of forming hydrogen bonds, the dipole moment here cannot be increased because of the usual dioxane effect. The increase in moment in dioxane is explained by interactions of the donor-acceptor type.

Table 2

Measurements in benzene containing phenyl tin trichloride (0.0744 g-mol/l)

Compound	P_∞	R_D	μ_{exp}	μ in benz.
n-C_4H_9SH	73.0	28.4	1.47	1.48
$(n$-$C_4H_9)_2S$	109.4	47.2	1.73	1.57
CH_3OH	229.6	8.3	3.27	1.67
C_2H_5OH	247.3	13.0	3.37	1.67
C_4H_8O	234.2	20.1	3.22	1.71

Table 1 gives the differences in the dipole moments of the compounds studied in dioxane and in hexane. These values can, to a certain extent, characterize the complex-forming ability of the tin compounds studied with dioxane. As can be seen, it is different for different compounds and falls sharply when chlorine atoms are replaced by organic radicals.

According to their ability to form complexes, the substances are arranged in the following series:

$$SnCl_4 > C_6H_5SnCl_3 > (C_4H_9)_2SnCl_2 > (C_6H_5)_2SnCl_2 > (C_6H_5)_3SnCl > (C_4H_9)_3SnCl.$$

First among the organotin compounds studied stands phenyl tin trichloride. We studied the complex-forming ability of this compound with other substances in greater detail by means of the method of dielectrometric titration.

Table 2 gives the values of the dipole moments of a number of compounds, measured in benzene containing phenyltin trichloride (0.0744 g-mol/l).

As can be seen, the dipole moments of butyl mercaptan and dibutyl sulfide, found in the presence of phenyltin trichloride, are close to the dipole moments in benzene. In addition, in these systems a linear dependence of ε (the dielectric constant) on the donor concentration C is observed over a wide concentration range. Consequently, these compounds do not form donor-acceptor complexes with phenyltin trichloride.

A different pattern in the changes of ε with C is observed when methyl alcohol, ethyl alcohol, and tetrahydrofuran are added to the solution. In all systems there is first a sharp increase in the dielectric permittivity of the solutions up to a concentration ratio of phenyltin trichloride—donor of 1 : 2, after which the course of the curve changes. The dipole moments of the compounds, found from extrapolation of the experimental data belonging to the first part of the curve, are almost twice as large as the dipole moments of the corresponding compounds in benzene (Table 2). These facts indicate the formation of donor-acceptor complexes in the systems under investigation.

From analysis of the ε—C data one may conclude that the process of complex formation here does not end with the addition of two donor molecules, but that further interaction of the complex with the added substance takes place.

The dipole moments of the complexes, found from extrapolation of the experimental data belonging to the first part of the curve (ε—C), are:

$$\mathrm{C_6H_5SnCl_3 \cdot 2CH_3OH} = 6.36D, \qquad \mathrm{C_6H_5SnCl_3 \cdot 2C_2H_5OH} = 6.47D,$$

$$\mathrm{C_6H_5SnCl_3 \cdot 2C_4H_8O} = 6.29D.$$

If the catalytic activity of tin tetrachloride in polymerization reactions is in some way connected with its ability to form the corresponding complexes, then on the basis of the results obtained one may expect that some organotin chlorides will also be active in this respect. Of the compounds investigated, this applies above all to phenyltin trichloride. It is possible that the sequence of changes in the catalytic activity of the tin compounds investigated in the present work will be the same as that given above for complex formation.

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