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COMPLEXES OF DIPHENYLETHYLENE WITH TIN TETRACHLORIDE AND ORGANOTIN CHLORIDES

The catalytic activity of tin tetrachloride in cationic polymerization reactions is explained by the formation of π-complexes with monomers ([1,2]). The nature of these complexes is still unclear. In the present work an attempt has been made to study complexes of asymmetrical diphenylethylene with tin tetrachloride, phenyltin trichloride, and diphenyltin dichloride by methods of electronic and infrared spectra, as well as by the method of dielectric polarization. Unsymmetrical diphenylethylene (DPE) is a convenient object for investigations of this type, since it forms only a dimer and does not give a polymer ([3]); moreover, the dimerization reaction under the influence of catalytic agents proceeds slowly, which makes it possible to investigate intermediate products of the interaction. The use, along with $SnCl_4$, of organotin chlorides as complex-forming agents was of interest from the standpoint of elucidating the influence of organic radicals on the catalytic activity of compounds of this type.

In work ([4]), by the method of dielectric polarization, it was shown that, according to their ability to form complexes with dioxane, the compounds studied are arranged in the series

$$SnCl_4 > C_6H_5SnCl_3 \gg (C_6H_5)_2SnCl_2.$$

It was important to establish whether this sequence is retained in complexes with monomers.

The infrared spectra of the systems: $SnCl_4$ + DPE, $C_6H_5SnCl_3$ + DPE, $(C_6H_5)_2SnCl_2$ + DPE, $SnCl_4$ + DPE+ DPE dimer, $C_6H_5SnCl_3$ + DPE+ DPE dimer were recorded on an H-800 double-beam spectrophotometer in fluorite cells with Teflon gaskets ($20\,\mu$). The electronic spectra of these systems were recorded on an SF-4 spectrophotometer in benzene solution. The polar properties of the complexes formed were determined by measuring the dipole moment of DPE in benzene containing a definite amount of $SnCl_4$. Preparation of the mixtures and filling of the cells were carried out in a sealed chamber in an atmosphere of dry nitrogen. Tin chloride and $C_6H_5SnCl_3$ give, with DPE, solutions colored green with an absorption band at 610 mμ, and also with intense absorption below 500 mμ (Fig. 1).

In the infrared spectra of the systems $SnCl_4$ + DPE and $C_6H_5SnCl_3$ + DPE, significant changes are observed in comparison with the spectrum of pure DPE (Table 1, Fig. 2), namely:

1. Absorption bands in the regions 1612, 1420-1400, and 1335 cm^{-1} disappear, and the intensity of the 1578 cm^{-1} band is greatly reduced. All these bands are associated with the presence of a double bond in the diphenylethylene molecule. The 1615 cm^{-1} band is assigned to stretching vibrations of the C = C double bond, whose frequency is lowered owing to conjugation with the phenyl rings (^{5}). The bands in the regions 1400 and 1330 cm^{-1} are assigned to deformation vibrations of the methylene group at the double bond (^{6}). The 1578 cm^{-1} band is assigned

Table 1

Infrared spectra of DPE, DPE dimer, and DPE systems with $SnCl_4$ and $C_6H_5SnCl_3$

DPE	$SnCl_4$ + DPE	$C_6H_5SnCl_3$ + DPE	$C_6H_5SnCl_3$	DPE + DPE dimer	$SnCl_4$ + DPE + DPE dimer	$C_6H_5SnCl_3$ + DPE + DPE dimer	DPE	$SnCl_4$ + DPE	$C_6H_5SnCl_3$ + DPE	$C_6H_5SnCl_3$	DPE + DPE dimer	$SnCl_4$ + DPE + DPE dimer	$C_6H_5SnCl_3$ + DPE + DPE dimer
	–	–	–	1665			1420				1420		
	–	1640	1640	–			1400				1400		
1612	–	–	–	1612				1376	1372	1372		1378	1378
1605	–	–	–	1605			1335		1338	1337	1335	1333	1341
	1595	1595	–	–	1595	1595	1328						
1578	1575	1572	1570	1578	1578	1578		1307	1310	1310			
					1522	1525					1285	1295	
1495	1490	1490		1495	1495	1495		1250				1222	1219
	1480	1480	1480	1480	1480	1480		1222	1213				
1450	1445	1445		1450	1447	1450	1185	1190	1190	1195	1185	1190	1197
		1436	1436			1437	1166	1166	1166	1167	1160	1160	1167

to vibrations of the phenyl ring, and its intensity increases significantly because of interaction with the conjugated double bond (^{7}). 2. New absorption bands appear in the region of 1376, 1250, and 1220 cm^{-1}. 3. A slight shift of the benzene-ring vibration band at 1605 cm^{-1} is observed

Fig. 1

Fig. 2

Fig. 1. Electronic spectra of benzene solutions of the systems. *a* $-C_6H_5SnCl_3$ + DPE: 1 $-C_6H_5SnCl_3 + (C_6H_5)_2C{=}CH_2$, 2 $-C_6H_5SnCl_3$, 3 $-(C_6H_5)_2C{=}CH_2$; $C_{C_6H_5SnCl_3} = 0.082$ mol/l. *b* $-SnCl_4$ + DPE: 1 $-SnCl_4 + (C_6H_5)_2C{=}CH_2$, 2 $-SnCl_4$, 3 $-(C_6H_5)_2C{=}CH_2$; $C_{SnCl_4} = 0.056$ mol/l

Fig. 2. Infrared spectra of DPE (*1*), $SnCl_4$ + DPE (*2*), $C_6H_5SnCl_3$ + DPE (*3*), $C_6H_5SnCl_3$ (*4*)

and a simultaneous increase in its intensity. To prove that these changes in the spectrum of diphenylethylene are not connected with the appearance of a dimer in the systems studied, the spectrum of the DPE dimer in a DPE solution was measured (Fig. 3). In the spectrum of this system there are two additional bands that are absent from the spectrum of the monomer. The band at 1665 cm^{-1} evidently belongs to va-

vibrations of the C=C bond in the dimer. The band at 1285 cm^{-1} possibly belongs to deformation vibrations of CH at the double bond ([6]). Neither of these bands is observed in the IR spectra of DPE systems with $SnCl_4$ and $C_6H_5SnCl_3$; this is a reliable criterion that the above-mentioned changes in the IR spectra are due to intermediate products of the interaction of DPE with tin halides, and not to the dimer. In the spectra of the three-component systems $SnCl_4$ + DPE + DPE dimer (Fig. 3) and $C_6H_5SnCl_3$ + DPE + DPE dimer, the bands associated both with the double bond in the monomer, 1612, 1400, 1335 cm^{-1}, and with the double bond in the dimer, 1665 and 1285 cm^{-1}, disappear, and, in addition to new bands in the regions 1376 and 1220 cm^{-1}, an additional band appears in the region 1525 cm^{-1}. This indicates that the dimer also forms complexes with $SnCl_4$ and $C_6H_5SnCl_3$.

In a series of studies Evans and co-workers ([8]) investigated the dimerization of DPE in the presence of $SnCl_4$. They assigned two absorption bands (480 and 600 mμ) to two types of intermediate products supposedly formed in these systems: a carbonium ion of the type CR_2Me^+, the first, and a π-complex, the second. We measured the dipole moment of DPE in the presence of excess $SnCl_4$ in benzene and found it to be equal to 1D. This value is approximately 0.7-0.8D higher than the dipole moment of DPE in benzene ([9]). Approximately the same dipole moment (0.87D) is possessed by the complex of $SnCl_4$ with benzene ([4]). If a significant fraction of the DPE complex with $SnCl_4$ were present in the form of ionic compounds, the dipole moment would be considerably higher. Consequently, the assignment of the 480 mμ band to the presence of carbonium ions ([7]) is not convincing.

Fig. 3. Infrared spectra of DPE + DPE dimer (a), $SnCl_4$ + DPE + DPE dimer (b)

The absorption band in the region of 610 mμ in the systems studied may be assigned to a π-complex. According to A. N. Terenin et al. ([10]), when a complex of cyclohexene with $SnCl_4$ is formed, the frequency of the valence vibration of

Fig. 3. Infrared spectra of DPE + DPE dimer (a), SnCl4 + DPE + DPE dimer (b)

Figure 1: Fig. 3. Infrared spectra of DPE + DPE dimer (a), SnCl4 + DPE + DPE dimer (b)

the double bond is lowered by 115-195 cm^{-1}, and, in addition, absorption bands appear in the regions 1400-1340 and 1220 cm^{-1}.

In the IR spectrum of the systems $SnCl_4$ + DPE + DPE dimer and $C_6H_5SnCl_3$ + DPE + DPE dimer there is an absorption band in the region of 1525 cm^{-1}; evidently it should be assigned to the frequency of the double-bond vibration in the π-complex of the dimer with tin halides, lowered by 140 cm^{-1}. If it is assumed that the frequency of the double-bond vibration in the π-complex of the monomer with tin tetrachloride and phenyltrichlorotin is lowered by approximately the same amount, then the band corresponding to this vibration should lie in the region 1470-1500 cm^{-1}. Unfortunately, in the system $C_6H_5SnCl_3$ + DPE this region is covered by the absorption bands of the pure components and is very difficult to analyze. In the spectrum of the system $SnCl_4$ + DPE an intense broad absorption band at 1480-1490 cm^{-1} with two maxima is observed. One component of this doublet is the absorption band of DPE itself, while the second component may be regarded as a shifted band of the C=C bond in the π-complex of DPE with $SnCl_4$.

The appearance of new bands in the regions 1376 and 1220 cm^{-1}, analogous to the bands of the π-complex of cyclohexene with $SnCl_4$ ([10]), may serve as an additional indication of the formation of π-complexes in the systems studied. In contrast

from the systems $SnCl_4$ + DPE and $C_6H_5SnCl_3$ + DPE, in the system $(C_6H_5)_2SnCl_2$ + DPE we found no indications whatever of the formation of π-complexes. Solutions of $(C_6H_5)_2SnCl_2$ + DPE in benzene are colorless, and in the IR spectrum no changes are observed in comparison with the spectra of the components.

Consequently, the previously established series of compounds with respect to complex formation with dioxane is also preserved in the case of complexes with monomers. The material presented makes it possible to conclude that, among the compounds studied, not only tin tetrachloride but also, probably, phenyltin trichloride can be active in olefin polymerization reactions. In contrast to them, diphenyltin dichloride, apparently, will be practically inactive. This conclusion is consistent with the data of work [4].

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