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Abstract

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INFRARED SPECTRA OF COMPLEXES OF VINYL ETHERS OF PHENOL, *o*-AMINOPHENOL, AND ANILINE WITH TIN CHLORIDE

The hypothesis of the formation of oxonium complexes of metal halides with simple vinyl ethers in polymerization reactions was proposed about 20 years ago (^1). However, it has not yet been possible to isolate them. A recent attempt by I. P. Goldshtein, E. N. Gur'ianova, and K. A. Kocheshkov to study the processes of complex formation of tin chloride with certain vinyl ethers proved unsuccessful because of polymerization of the products under the experimental conditions (^2). In studying the cationic polymerization of vinylaromatic ethers under the action of $SnCl_2$, $SnCl_4$, $AlCl_3$, $FeCl_3$, and $BF_3 \cdot O(C_2H_5)_2$, we discovered the formation of unstable crystalline precipitates that proved to be active complexes of metal halides with the initial ether (^3). From the literature it is known that, with the aid of infrared spectra, it is possible to establish the type of complex formation of heterocyclic compounds with metal halides (^4). Thus, in the case of donor–acceptor interaction, in the spectrum of a complex of a vinylaromatic ether with tin chloride, in comparison with the spectrum of the pure ether, one should expect a shift of the band assigned to vibrations of the carbon–oxygen bond into the region of lower frequencies. If such interaction does not occur, then the vibrational frequency of the ether group should not change.

In the present work we describe complexes, obtained for the first time, of vinyl ethers of phenol and *o*-aminophenol with tin chloride, and their study by means of IR spectra. Complex compounds of the vinyl ethers of phenol and *o*-aminophenol with tin chloride were obtained at the initial stage of the polymerization process of the corresponding vinylaromatic ethers. Extracted from the reaction medium, they were thoroughly washed with diethyl ether to remove impurities of free tin chloride and monomer, then dried in vacuum and studied by spectral methods. IR spectra were measured for the following substances: $SnCl_4 \cdot C_6H_6OCH{=}CH_2$—white crystals, m.p. 120°; tin content 31.12; 31.67%, calculated 31.86%. $SnCl_4 \cdot 3C_6H_4NH_2OCH{=}CH_2$—white crystals, m.p. 93.2°C; tin found 20.67; 20.77%; calculated Sn 21.34%. $C_6H_5OCH{=}CH_2$—b.p. 31.2°/5 mm; n_D^{20} 1.5222. $C_6H_4 \cdot NH_2OCH{=}CH_2$—b.p. 114°/24 mm; n_D^{20} 1.5716. The vinyl ethers were colorless liquids synthesized from the corresponding phenols and acetylene (^1,5). Spectra were also obtained of aniline ($C_6H_5NH_2$, b.p.

97°/40 mm; n_D^{20} 1.5856) and its complex with tin chloride ($SnCl_4 \cdot 4C_6H_5NH_2$– white powder, m.p. 155°, tin content 15.99, 15.85%; calculated 16.40%).

The infrared spectra of the compounds studied were obtained on a double-beam IKS-14 spectrophotometer, using NaCl and LiF prisms in KBr cells. Solid substances were recorded in Vaseline oil. The thickness of the absorbing layer for the vinyl ethers and aniline was 0.1 mm; for the paste a microsample layer was used. The accuracy of frequency measurement was $\pm5cm^{-1}$ for NaCl, $\pm10cm^{-1}$ for LiF.

Table 1

Infrared spectra of phenol and *o*-aminophenol vinyl ethers and their complexes with tin tetrachloride

Phenol vinyl ether	Complex of phenol vinyl ether with $SnCl_4$	Frequency shift	*o*-Aminophenol vinyl ether	Complex of *o*-aminophenol vinyl ether with $SnCl_4$	Frequency shift
1635 s	1643 med	+ 8	3448 v.s	–	
1621 med	1616 med	– 5	3344 v.s	–	
1588 v.s	1578 weak	–10	3196 s	–	
1454 weak	1451 v.s	– 3	3040 v.s	2870 v.s	–170
1385 med	1382 v.s	– 3	2660 med	2650 s	– 10
1342 med	1340 weak	– 2	1639 s	1620 s	– 19
1303 med	1266 med	–37	1571 weak	1580 med	+ 9
1236 v.s	1172 med	–64	1469 med	1448 v.s	– 21
1220 v.s	1146 med	–74	1394 weak	1376 v.s	– 18
1165 s	1100 med	–65	1324 weak	1320 s	– 4
1024 med	1021 med	– 3	1308 med	1266 s	– 42
			1276 med	1250 s	– 26
			1215 v.s	1192 s	– 23
			1035 s.w	1038 med	+ 3

The IR spectra of the compounds studied are presented in Fig. 1 and in Tables 1 and 2. As was to be expected, in the spectra of the complexes there is a shift of the frequencies for all groups that take part in their formation ([6]–[10]). In the

Fig. 1

Figure 1: Fig. 1

IR spectrum of the complex of vinyl phenyl ether with $SnCl_4$, in comparison with the spectrum of the original ether, a strong shift of 60 cm^{-1} toward the long-wavelength part of the spectrum is observed for frequencies in the region 1300-1100 cm^{-1}, characteristic of the vibrations of the C–O–C group. An analogous shift of the frequencies of the C–O–C group by approximately 25 cm^{-1} was also observed in the spectrum of the complex of *o*-aminophenol vinyl ether with $SnCl_4$. Such a shift indicates a considerable weakening of the C–O –C bond, occurring as a result of donor-acceptor interaction of $SnCl_4$ with an unshared pair of electrons of the oxygen atom. The magnitude of the lowering of the frequency of the valence vibration of the C–O–C bond is not the same for the complexes of phenol and *o*-aminophenol vinyl ethers. On the basis of the magnitude of the shift, it would seem that a stronger tin–ligand bond should be expected in the complex of vinyl phenyl ether. However, in the case of *o*-aminophenol vinyl ether, the strength

Fig. 1. Solid line –spectrum of the substance before complex formation; dashed line –spectrum of the complex of the substance with tin tetrachloride. **I** –IR spectra of *o*-aminophenol vinyl ether and its complex with tin tetrachloride in the regions 1150-1350 and 2600-3400 cm^{-1}; **II** –IR spectra of phenol vinyl ether and its complex with tin tetrachloride in the region 1150-1350 cm^{-1}; **III** –IR spectra of aniline and its complex with tin tetrachloride in the region 2600-3400 cm^{-1}.

the tin–ligand bond is determined not only by the ether group, but also by the amino group, in which the nitrogen atom is also capable of interacting with the metal ([5]). In the IR spectrum of the complex of the vinyl ether of *o*-aminophenol with tin chloride, in comparison with the spectrum of the vinyl ether of *o*-aminophenol, a strong displacement is observed, of the order of 150 cm^{-1}, of the frequencies of the stretching vibrations of N–H in the region 3500-2600 cm^{-1}. Such a change in the vibrations indicates a weakening of the N–H bond due to donor-acceptor interaction with withdrawal of the free electron pair of nitrogen toward the tin atom.

Table 2

Infrared spectra of aniline and its complex with $SnCl_4$

Aniline	Aniline complex with $SnCl_4$	Aniline	Aniline complex with $SnCl_4$
3424 s	3394 m	1172 s	1166 m
3068 m	–	1150 m	1140 m
3038 m	2892 v.s	1026 m	1029 s
1612 v.s	1581 m	746 v.s	739 s

Aniline	Aniline complex with $SnCl_4$	Aniline	Aniline complex with $SnCl_4$
1598 v.s 1492 v.s	1555 m 1455 v.s	659 m	661 m

This conclusion is confirmed by comparison with the IR spectra of aniline and its complex with $SnCl_4$, obtained under the same conditions as those in which complex formation of the vinyl ether of *o*-aminophenol with $SnCl_4$ took place (see Table 2).

From the data of Table 2 it is evident that the frequencies of the stretching vibrations of the N–H bonds in the complex of aniline with $SnCl_4$ are shifted significantly toward lower values in comparison with the spectrum of free aniline. The spectral investigations carried out indicate complex formation between vinylaromatic ethers and tin chloride and thus confirm the assumptions, expressed earlier by one of the authors, concerning the formation of "onium" complexes with catalysts during the polymerization of simple vinyl ethers.

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