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Abstract

Full Text

Chemistry

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Spectroscopic Study of the Complexes of Thiophane and Thiophene with Tin Tetrachloride

Using the method of dielectrometric titration it was shown ([1]) that the interaction of certain heterocyclic compounds with metal halides leads either to the formation of donor–acceptor complexes (thiophane), or to the formation of π-complexes (furan, thiophene). In the present work this question was investigated spectroscopically. The infrared spectra of the systems thiophane + $SnCl_4$ and thiophene + $SnCl_4$ were measured on an H-800 double-beam spectrophotometer in sealed NaCl cells in the region 1800–650 cm^{-1}. The electronic spectra of these systems were recorded in benzene solution on an SF-4 spectrophotometer. Preparation of the mixtures and filling of the cells were carried out in a sealed chamber under an argon atmosphere. The complex of thiophane with $SnCl_4$ is a white crystalline substance of composition $SnCl_4 \cdot 2C_4H_8S$ with a melting point of 154–155°C. For measurement of the infrared spectra, the samples were prepared as a paste in Vaseline oil.

The thiophene + $SnCl_4$ system was studied in solution in excess $SnCl_4$. Several days after preparation, the pale-yellow solution turned bright orange, and then a red precipitate of composition $SnCl_4 : C_4H_4S = 1 : 4$ separated from the solution. In order to remove $SnCl_4$, the precipitate was dissolved in dioxane (with which $SnCl_4$ gives stable complexes), and then a yellowish precipitate was again deposited from the dioxane solution by hexane. The infrared spectra of these precipitates were measured in Vaseline oil.

In the spectrum of the complex of thiophane with $SnCl_4$, in comparison with the spectrum of pure

Table 1

Infrared spectra of thiophane and of a solution of thiophane in $SnCl_4$

Thiophane	Thiophane + $SnCl_4$	Thiophane	Thiophane + $SnCl_4$
685 v.s.*	660 v.s.	1140 med.	1131 weak
824 med.	810 strong	1200 strong	1200 weak
885 strong	880 strong	1218 med.	1216 med.

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Thiophane	Thiophane + $SnCl_4$	Thiophane	Thiophane + $SnCl_4$
–	890 strong	1265 v.s.	1265 v.s.
965 strong	965 strong	1315 med.	1315 strong
1040 weak	1040 weak	1445 v.s.	1450 v.s.
1067 weak	1067 med.		

* Estimate of band intensity: v.s. –very strong, strong –strong, med. –medium, weak –weak.

thiophane (Table 1), a shift of the band at 685 cm^{-1} into the region of 660 cm^{-1} is observed. The band at 685 cm^{-1} belongs to vibrations of the C–S bond in the thiophane ring ([2]). The lowering of the vibration frequency of this bond by 25 cm^{-1} in the complex indicates that the complex is formed through donor-acceptor interaction of $SnCl_4$ with the unshared electron pair of the sulfur atom. This conclusion agrees with the conclusion drawn from measurements of dipole moments

Table 2

Infrared spectra of thiophene, an aged* solution of thiophene in $SnCl_4$, and the complex of thiophene oligomers with $SnCl_4$

Thiophene	Aged solution of thiophene in $SnCl_4$	Complex of thiophene oligomers with $SnCl_4$	Thiophene	Aged solution of thiophene in $SnCl_4$	Complex of thiophene oligomers with $SnCl_4$
–	690 weak	687 v. strong	–	1170 weak	1175 weak
716 v. strong	714 v. strong	708 v. strong	1260 v. strong	1260 v. strong	1260 medium
–	–	803 weak	1290 medium	1275 medium	1275 weak
835 v. strong	835 v. strong	821 medium	1418 v. strong	1418 v. strong	1427 weak
875 medium	865 medium	865 strong	–	1440 v. strong	1445 v. strong
909 weak	905 weak	897 weak	–	1504 medium	1500 medium
–	980 weak	980 medium	1560 weak	1560 weak	–
1045 weak	1040 medium	1025 medium	1596 strong	1586 medium	1585 strong

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Figure 1

Figure 1: Figure 1

Thiophene	Aged solution of thiophene in $SnCl_4$	Complex of thiophene oligomers with $SnCl_4$	Thiophene	Aged solution of thiophene in $SnCl_4$	Complex of thiophene oligomers with $SnCl_4$
1090 strong	1085 strong	1085 medium			

* Measured two days after preparation.

([1]). In the infrared spectrum of a freshly prepared solution of thiophene in $SnCl_4$ (Fig. 1a, Table 2), the position of the 715 cm^{-1} band, assigned to vibrations of the C–S bond in the ring ([3]), does not change in comparison with the position of this band in the spectrum of pure thiophene. This fact gives grounds for asserting that the complex of thiophene with $SnCl_4$ is not formed through donor-acceptor interaction of $SnCl_4$ with the sulfur atom in the ring. All the other absorption bands in the infrared spectrum of this solution likewise do not change, except for the 1595 cm^{-1} band, whose intensity increases and whose maximum is shifted by approximately 10 cm^{-1} toward the low-frequency region. The 1595 cm^{-1} band is assigned to vibration of the thiophene ring ([3]).

A similar change in the intensity of the absorption band of benzene-ring vibrations in the region of 1596 cm^{-1} was observed in the spectrum of the complex of antimony trichloride with benzene ([4]), and it was shown that the $SbCl_3$ complex with benzene belongs to π-complexes. Consequently, the complex formed in a freshly prepared solution of thiophene with $SnCl_4$ may also be regarded as a π-complex. Such an interpretation agrees with the results of measuring the dipole moment of this complex ([1]). Moreover, this is confirmed by the appearance of an absorption band in the region of 510 mμ in the electronic spectrum of a solution of thiophene and $SnCl_4$ in benzene (Fig. 2), since we previously showed ([5]) that, upon formation of the π-complex of $SnCl_4$ with diphenylethylene, an absorption band appears in its electronic spectrum in the visible region. However, in the infrared spectrum of a solution of thiophene in $SnCl_4$ measured several days after its preparation, obser–

Fig. 1. IR spectra: a –solid line –thiophene (d = 40 mμ), dotted line –fresh solution of thiophene in $SnCl_4$ (d = 60 mμ); b –solution of thiophene in $SnCl_4$ two days after preparation.

very substantial changes are observed in comparison with the spectrum of pure thiophene, as well as with the spectrum of a freshly prepared solution (Fig. 1b,

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Figure 2

Figure 2: Figure 2

Table 2): some absorption bands shift and a number of new bands appear at 1500, 1440, 1175, and 980 cm^{-1}, while the intensity of the newly appearing bands at 1500 and 1440 cm^{-1} increases noticeably with time. In the region 1400-1450 cm^{-1} lie the absorption bands of deformation vibrations of the CH bond; in the spectrum of thiophene the corresponding band is in the region of 1415 cm^{-1}, and in the spectrum of thiophane it is in the region of 1445 cm^{-1}. Consequently, the appearance of a band in the region of 1440 cm^{-1} in the spectrum of a solution of thiophene in $SnCl_4$, measured two days after preparation, indicates a strong change in the thiophene molecules during aging of the solution.

Fig. 2. Electronic spectrum of a solution of thiophene and $SnCl_4$ in benzene. $C_{C_4H_4S} = 0.431$ mol/l. Ratio $C_{C_4H_4S} : C_{SnCl_4} = 2$

The spectrum of the solid red precipitate that separated from a solution of thiophene in $SnCl_4$ after several days is very similar to the spectrum of the aged solution, but in addition to the already indicated new bands, a band appears in the spectrum of the precipitate in the region of 687 cm^{-1} (Fig. 3), i.e., in the same region where the band assigned to the C–S bond lies in the spectrum of thiophane. This is also an indication that, in the system under consideration, a process occurs that changes the thiophene ring. Such a process is polymerization, which takes place in thiophene in the presence of $SnCl_4$ ([6]).

As Korsiak et al. ([7]) and also Topchiev et al. ([8]) have shown, during the polymerization of furan and silvan under the influence of $SnCl_4$, the conjugated system of double bonds in the furan ring disappears and a polymer with one isolated double bond in each ring constituting the chain is formed. There is every reason to believe that the polymer formed during the polymerization of thiophene in the presence of the same catalyst must have a similar structure. The intense coloration of the precipitate separating from a solution of thiophene in $SnCl_4$, and its composition, indicate that this precipitate is a complex of thiophene oligomers with $SnCl_4$. Only in this way can one explain the absence, in the infrared spectrum of the precipitate, of the band corresponding to an isolated double bond in the region 1650-1670 cm^{-1}, and the appearance of a new band in the region of 1500 cm^{-1}. The latter band should be assigned to the vibration frequency of the double bond in π-complexes of thiophene oligomers with $SnCl_4$, lowered by 150-170 cm^{-1}, similar to what was observed in the formation of a π-complex of diphenylethylene and its dimer with $SnCl_4$ ([5]). A band in the region of 1650 cm^{-1} appeared in the spectrum of the precipitate after it had been washed with dioxane to remove $SnCl_4$, while the band in the region of 1500 cm^{-1} disappeared. This serves as proof that the precipitate separating from a solution of thiophene in $SnCl_4$ is a complex of thiophene oligomers with $SnCl_4$.

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Figure 3

Figure 3: Figure 3

Fig. 3. IR spectra in the region 800-650 cm^{-1} of thiophene (1) and of the precipitate separated from a solution of thiophene in $SnCl_4$ (2)

The small second maximum in the region of 560 mμ in the electronic spectrum of a solution of thiophene with $SnCl_4$ in benzene (Fig. 2) can also be explained by the formation of complexes of thiophene dimers or trimers with $SnCl_4$.

Consequently, in solutions of thiophene in $SnCl_4$, π-complexes are first formed through interaction of $SnCl_4$ with the π-electrons of the thiophene ring,

which leads to the gradual polymerization of thiophene, and the thiophene oligomers formed also give π-complexes with $SnCl_4$.

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REFERENCES

1. I. P. Goldshtein, E. N. Guryanova, K. A. Kocheshkov, DAN, **144**, No. 3 (1962).

2. P. A. Akishin, N. G. Rambidi et al., Vestn. Moskovsk. Univ., No. 5, 61 (1956).

3. J. Lecomte, Bull. Soc. Chim. France, **92**, 423 (1946).

4. L. W. Daasch, J. Chem. Phys., **28**, 1005 (1958).

5. I. P. Goldshtein, N. Kh. Faizi et al., DAN, **138**, 839 (1961).

6. J. Bruice, F. Challeng r et al., J. Inst. Petrol. Techn., **34**, 226 (1948).

7. V. V. Korshak, A. S. Sultanov, A. A. Abdulvaliev, Uzb. Khim. Zhurn., **4**, 39 (1959).

8. A. V. Topchiev, Yu. Ya. Goldfarb, B. A. Krentsel, Vysokomolek. Soed., **3**, No. 6, 870 (1961).

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