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A Spectroscopic Study of Some Acceptor-Donor Systems

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The liquidus curves have been studied for the systems $BiCl_3-POCl_3$, $AsCl_3-(CH_3)_2CO$ and $SbCl_3-(CH_3)_2CO$. One compound has been found in each system: $BiCl_3 \cdot 2POCl_3$, $AsCl_3 \cdot (CH_3)_2CO$ and $SbCl_3 \cdot 2(CH_3)_2CO$.

Infrared and Raman spectra of the three systems have been investigated. The infrared spectra of the following compounds have been studied: $SbCl_3 \cdot (CH_3)_3PO$, $SbCl_3 \cdot 2(CH_3)_3PO$, $SbCl_5 \cdot (CH_3)_3PO$, $5HgCl_2 \cdot 2(CH_3)_3PO$, $HgCl_2 \cdot (CH_3)_3PO$ and $2HgCl_2 \cdot (C_2H_5)_2S$.

The relative acceptor strengths of the acceptor molecules $SbCl_3$, $SbCl_5$ and $HgCl_2$ with $(CH_3)_3PO$ as donor molecule have been measured. The results are briefly discussed.

A preceding paper [1] dealt with a study of molecular interaction with phosphoryl chloride. It was there suggested that the interaction in the systems $AsCl_3-POCl_3$ and $SbCl_3-POCl_3$ was a dipole-dipole interaction, caused by favourable charge distribution. Phosphoryl chloride is however known to function as a donor molecule [2] and $AsCl_3$ and $SbCl_3$ are possible acceptor molecules.

$SnCl_4$ and $SbCl_5$ were given as examples of acceptor molecules which give adduct formation with $POCl_3$ by acceptor-donor reactions. In those cases the acceptor molecules change their spectra as can be expected from the change in their coordination and symmetry. It was suggested that intermediate cases could possibly also exist.

It was also assumed that the magnitude of the shift of the symmetrical phosphoryl bond vibration frequency could be a rough measure of the acceptor strength if the acceptor molecules compared are under similar conditions.

In order to obtain a better foundation for a discussion of those problems we decided to study some more acceptor-donor systems.

For systems with melting points lower than room temperature it was possible to obtain Raman spectra at every composition. The systems containing compounds with higher melting points have been studied by infrared spectroscopy in the spectral range 2—35 μ. Unfortunately the lower frequencies of the acceptor molecules are not situated in this range.

As it is difficult to avoid moisture during infrared absorption measurements it was preferred to study compounds stable in air.

EXPERIMENTAL

Chemicals. $AsCl_3$, $POCl_3$, $(CH_3)_2CO$ and $(C_2H_5)_2S$ were purified by distillation (B. p. 129°, 105°, 92° and 57°C). $SbCl_5$ was distilled at reduced pressure. $SbCl_3$ was purified by sublimation. $HgCl_2$, Merck *pro analysi*, was not further purified. $(CH_3)_3PO$ and its addition compounds were prepared as described earlier [3]. Anhydrous $BiCl_3$ was prepared from $BiCl_3 \cdot H_2O$, Mallinkrodt analytical reagent, according to Inorganic Syntheses [4]. $2HgCl_2 \cdot (C_2H_5)_2S$ was precipitated from alcoholic solutions of the components.

Spectroscopic measurements. The Raman spectra were obtained photographically as described earlier [1] (in the institute of Physical Chemistry). The infrared spectra were recorded on a Perkin-Elmer Model 21 Spectrophotometer equipped with NaCl and CsBr prisms (in the institute of Biochemistry). The spectra were run with the solutions in thin layers and the solids dispersed in Nujol between NaCl plates in the range 2—15 μ and between TlBr—TlI plates in the range 15—35 μ.

Phase diagrams. The liquidus curves were obtained by the same methods as described earlier [5].

Thermochemical measurements. The method used for measuring relative enthalpy changes has been described very recently [6].

THE SYSTEM $BiCl_3$—$POCl_3$

The liquidus curve (Fig. 1) has a maximum at the composition $BiCl_3 \cdot 2POCl_3$ with the melting point 37°C. The system can not be studied at higher $BiCl_3$ concentrations than 50 mole per cent by this method, because of the distillation of $POCl_3$ at the high temperature required to dissolve $BiCl_3$.

The Raman spectra are given in Fig. 2. The mixture $BiCl_3 \cdot POCl_3$ 1:2 is studied as supercooled liquid. The spectrum of $BiCl_3$ has earlier only been studied in solid state (*cf.* Kohlrausch, *Hand- und Jahrbuch der Chemischen Physik*, 9:IV, Leipzig 1943) and can therefore not be used for comparison. It differs appreciably from the spectrum of $BiCl_3$ dissolved in $POCl_3$.

The shifts of the phosphoryl chloride spectrum are very similar to those caused by $SbCl_3$ except for a splitting of the symmetrical P—Cl bond vibration frequency, 486 cm^{-1}, not observed with $SbCl_3$.

The lowest frequency of $BiCl_3$ shows an obvious continuous shift.

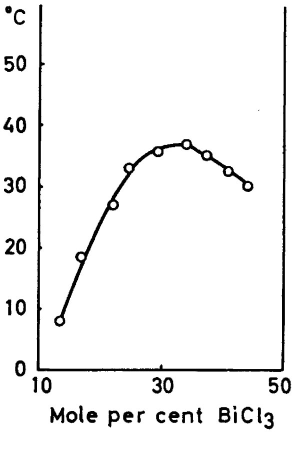

Fig. 1. Liquidus curve for the system $BiCl_3$—$POCl_3$.

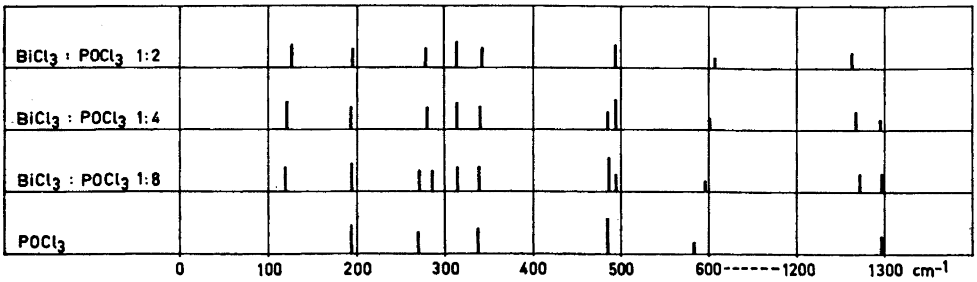

Fig. 2. Raman spectra of the system $BiCl_3-POCl_3$.

THE SYSTEMS $AsCl_3-(CH_3)_2CO$ AND $SbCl_3-(CH_3)_2CO$

The liquidus curves (Figs. 3 a and b) have maxima at the compositions $AsCl_3 \cdot (CH_3)_2CO$ and $SbCl_3 \cdot 2(CH_3)_2CO$ with melting points −35° and −24°C. The tendency of $AsCl_3$ to form 1:1 compounds and of $SbCl_3$ to form 1:2 compounds has been observed before [7]. Studies in the whole range were prevented by supercooling. The reaction vessels were cooled during the measurements. At room temperature a reaction begins in both cases and the liquids darken. (The reaction is probably a condensation of acetone molecules catalysed by the metal halides.)

As the reaction is more rapid in solutions of $AsCl_3$, Raman spectra could not be obtained but the infrared spectra could be recorded.

The solutions of $SbCl_3$ gave a rather dark background in the Raman spectra. The spectrum of the composition 1:1 could not be measured with sufficient accuracy.

The only detectable shifts referred to the spectrum of pure acetone are a decrease of the carbonyl bond stretching frequency and an increase of the antisymmetrical C—C chain vibration frequency. (Only these two frequencies of the acetone spectrum have been listed in Table 1 a.) The same effects were found earlier in addition compounds with acetone as donor and BF_3[8] and $AlBr_3$[9] as acceptors. They are also comparable with the decrease of the phosphoryl band and the increase of the P—Cl bands in the mixtures studied with $POCl_3$.

The infrared spectrum of $AsCl_3$ does not change appreciably.

For comparison the Raman spectra of $SbCl_3$ are tabulated together with the Raman spectra of $SbCl_3$ in $POCl_3$ (Table 1 b).

THE SYSTEM $SbCl_3-(CH_3)_3PO$

The liquidus curve[3] shows maxima at the compositions $SbCl_3 \cdot (CH_3)_3PO$ and $SbCl_3 \cdot 2(CH_3)_3PO$.

The infrared spectrum of $(CH_3)_3PO$ was investigated by Daasch *et al.*[10] (2—22 μ). We have taken the infrared spectra in the range 2—35 μ and our results are in fairly good agreement with the earlier ones. We have not found

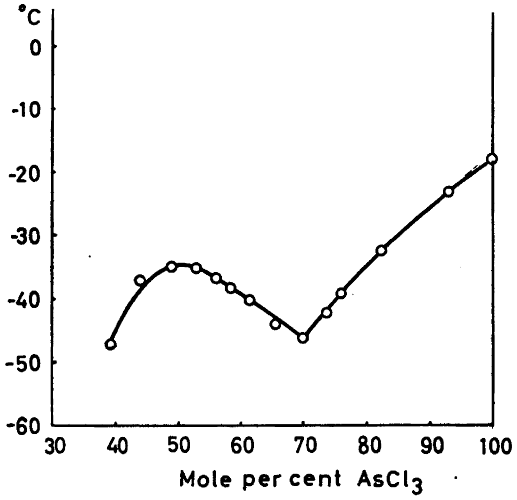

Fig. 3a. Liquidus curve for the system $AsCl_3-(CH_3)_2CO$.

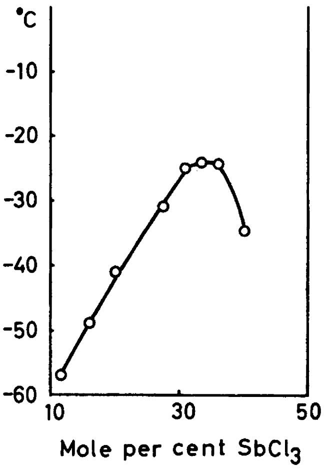

Fig. 3b. Liquidus curve for the system $SbCl_3-(CH_3)_2CO$.

the weak peak at 671 cm^{-1} in the pure substance but it appears in some of the addition compounds. Two new peaks were found in the range 15—35 μ.

(The previous investigators found peaks at 3 410 and 1 672 cm^{-1} and explained the former as arising from reaction with moisture because the substance was very hygroscopic. The latter peak could have the same cause or be a combination frequency. We have also found peaks in those regions but these

Table 1 a.

	I R								Raman		
	$(CH_3)_2CO$	$AsCl_3:(CH_3)_2CO$				$SbCl_3:(CH_3)_2CO$			$(CH_3)_2CO$	$SbCl_3:(CH_3)_2CO$	
		1:4	1:2	1:1	2:1	1:4	1:2	1:1		1:4	1:2
ν (C=O)	1 728	1 712	1 710	1 706	1 700	1 720 1 702	1 718 1 698	1 718 1 695	1 712	1 693	1 691
ν_a(C—C)	1 222	1 228	1 227	1 229	1 228	1 232	1 232	1 234	1 223	1 232	1 230

Table 1 b. Raman.

$SbCl_3$ in $(CH_3)_2CO$		$SbCl_3$ in $POCl_3$	
1:4	1:2	1:4	1:2
134	131	133	133
154	155	156	157
314	319	323	321
351	353	362	363

Table 2.

$(CH_3)_3PO$	$SbCl_3$ in $POCl_3$	$SbCl_3$: $(CH_3)_3PO$ 1:2	$SbCl_3$: $(CH_3)_3PO$ 1:1	$SbCl_5$: $(CH_3)_3PO$ 1:1	$HgCl_2$	$HgCl_2$: $(CH_3)_3PO$ 1:1	$HgCl_2$: $(CH_3)_3PO$ 5:2
(3 325 w)							
(1 640 vw)							
1 425 vw		1 428 vw	1 420 vw	1 420 vw			1 425 vw
1 410 vw			1 410 vw	1 408 vw		1 415 vw	1 415 vw
1 333 vw		1 342 vw				1 333 vw	1 336 vw
1 298 w		1 310 w	1 310 w	1 310 w		1 307 vw	1 308 vw
1 280 w		1 298 w	1 298 w	1 300 w		1 292 w	1 292 w
			1 098 w				
1 158 vs		1 063 vs	1 045 ms	1 037 vs		1 093 vs	1 082 vs
			1 025 s				
945 vs		950 s	948 s	953 s		940 s	943 s
869 ms							
862 ms		868 ms	865 ms	863 ms		860 ms	858 ms
778 vw							755 w
740 s		758 ms	758 w	763 w		749 w	
		670 vw	684 vw	678 vw			749 w
			673 vw				
		596 vw	520 vw				
			438 ms	446 s			
364 vs	363 w	394 vs	403 ms	363 ms	371 s	388 s	397 s
318 ms	333 ms	363 s	359 w	347 ms		359 s	377 ms
		326 ms	338 w	323 w		314 vw	345 s
		317 w	308 vw	296 vw			314 vw
			296 vw				

disappeared completely after adduct formation. This certainly should be the result if the absorption arose from hydrate formation.)

Antimony trichloride has not been investigated by infrared spectroscopy earlier and an attempt failed because the substance reacted with the TlBr—TlI plates. For comparison, the spectrum of $SbCl_3 \cdot 2POCl_3$ was taken. When the peaks from $POCl_3$ were excluded, two peaks remained.

The results from the infrared study are given in Table 2. The phosphoryl bond vibration frequency 1 158 cm^{-1} is split and shows a larger shift in the 1:1 compound than in the 1:2 compound. (The largest shift is 131 cm^{-1}.) In the range 15—35 μ the two addition compounds show great diversities. The spectra of the components seem not to be very much changed in the 1:2 compound but the 1:1 compound shows new absorption peaks.

THE SYSTEM $SbCl_5-(CH_3)_3PO$

Relative enthalpy measurements (carried out in 0.4 M ethylene chloride solutions in mole ratio 1:1) show that $SbCl_5$ is a much stronger acceptor than $SbCl_3$ with $(CH_3)_3PO$ as donor molecule.

The results in Table 2 show that the phosphoryl bond frequency has decreased 126 cm^{-1}. The shift is thus in the same order of magnitude as in the compound $SbCl_3 \cdot (CH_3)_3PO$ in spite of the large difference between enthalpy changes of the two reactions.

The infrared spectrum of $SbCl_5$ has not been investigated, which prevents any comparisons.

THE SYSTEM $HgCl_2-(CH_3)_3PO$

Thermochemical measurements carried out in 0.4 M alcoholic solutions show that $SbCl_3$ gives larger enthalpy change than $HgCl_2$ in reacting with $(CH_3)_3PO$ in the mole ratio 1:1.

Two addition compounds are found in this system: $5HgCl_2 \cdot 2(CH_3)_3PO$ and $HgCl_2 \cdot (CH_3)_3PO$.[3] The symmetrical phosphoryl bond vibration frequency has the largest shift in the 5:2 compound but not as large as in the compounds with $SbCl_3$.

$HgCl_2$ has only one infrared active band in the range studied, the antisymmetrical Hg—Cl bond stretching frequency at 371 cm^{-1}. This frequency decreases at adduct formation (*e.g.* with 1,4-dioxane [11] and $(C_6H_5)_3PO$[3]). One of the two compounds gives a more complicated spectrum in this case too.

THE SYSTEM $HgCl_2-(C_2H_5)_2S$

Two compounds in this system have been described earlier [12]: $2HgCl_2 \cdot (C_2H_5)_2S$ and $HgCl_2 \cdot (C_2H_5)_2S$. The 1:1 compound, however, loses ethyl sulfide on grinding [13] and the infrared spectra could not be taken. The ethyl sulfide has no frequency lower than 640 cm^{-1} but the 1:1 adduct has two low frequencies, 343 and 311 cm^{-1} (*cf.* $HgCl_2$, 371 cm^{-1}).

DISCUSSION

1. The spectra of the systems $BiCl_3-POCl_3$, $AsCl_3-(CH_3)_2CO$ and $SbCl_3-(CH_3)_2CO$ show a similar type of interaction, as found earlier [1] in the systems $AsCl_3-POCl_3$ and $SbCl_3-POCl_3$ but the changes in the spectra of the acceptor molecules are larger.

2. In the systems $SbCl_3-(CH_3)_3PO$ and $HgCl_2-(CH_3)_3PO$, where two compounds have been studied in each system, one of the compounds does not change its spectrum very much but the other shows new peaks in the region where the acceptor molecules absorb.

According to the introduction, the spectra of $SbCl_3 \cdot 2(CH_3)_3PO$ and $HgCl_2 \cdot (CH_3)_3PO$ indicate weak dipole-dipole interaction and $SbCl_3 \cdot (CH_3)_3PO$ and $5HgCl_2 \cdot 2(CH_3)_3PO$ strong interaction caused by acceptor-donor reactions. It is however hard to understand how the acceptor-donor bonds could be of different nature in the same acceptor-donor systems.

The present results do not seem to supply evidence for the suggestion that two different types of interaction exist. They indicate rather that the acceptor-donor bond strengths change continuously from weak to strong interaction.

3. The fact that the spectrum of $2HgCl_2 \cdot (C_2H_5)_2S$ has two low frequencies is in agreement with the structure of this compound, very recently determined by X-ray work at this institute [13]. This structure determination shows that the two $HgCl_2$ molecules are bonded in different ways. One of them has changed its coordination and structure by the adduct formation, the other is rather unchanged.

The new peaks in the spectra of the compounds $5HgCl_2 \cdot 2(CH_3)_3PO$ and $SbCl_3 \cdot (CH_3)_3PO$ may also indicate that the acceptor molecules are bonded in different ways or that the chlorine atoms of the same acceptor molecule are not equivalent after the adduct formation. Such structures have already been found: $3HgBr_2 \cdot 2Bu_3As$[14] and $(TiCl_4 \cdot POCl_3)_2$[15].

4. Sheldon and Tyree[16] have interpreted the shifts obtained in the P—O stretching frequency by adduct formation as due to a weakening of the P—O bond. It must be assumed that the magnitude of these shifts is a measure of the weakening if the donor molecule is the same. It might naturally be supposed that this weakening is closely related to the bond strength between the donor and the acceptor atom.

The two adducts $SbCl_3 \cdot (CH_3)_3PO$ and $SbCl_5 \cdot (CH_3)_3PO$ give about the same shifts of the P—O bond frequency but very large difference between the enthalpy changes of the reactions.

If the above assumptions are correct, these results show that the enthalpy changes at the acceptor-donor reactions are not only dependent on the acceptor-donor bond formation but also very much on the gain or loss of energy involved in the structural changes of the acceptor molecules. The reservation in the earlier paper[1], that the magnitude of the shift as a measure of relative acceptor strengths can only be used "if the acceptor molecules to be compared are under very similar conditions" is thus shown to be well justified.

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