

## Addition Compounds of Phosphine Oxides

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The formation of addition compounds with phosphine oxides as donor molecules has been studied. The following new compounds have been prepared:  $\text{SbCl}_5 \cdot \text{PO}(\text{C}_6\text{H}_5)_3$ ,  $\text{SbCl}_5 \cdot \text{PO}(\text{CH}_3)_3$ ,  $\text{SbCl}_3 \cdot \text{PO}(\text{CH}_3)_3$ ,  $\text{SbCl}_3 \cdot 2\text{PO}(\text{CH}_3)_3$ ,  $\text{AsCl}_3 \cdot \text{PO}(\text{CH}_3)_3$ ,  $\text{AsCl}_5 \cdot \text{PO}(\text{CH}_3)_3$ , (stabilization of  $\text{AsCl}_5$ ),  $\text{SeOCl}_2 \cdot \text{PO}(\text{CH}_3)_3$ ,  $\text{HgCl}_2 \cdot \text{PO}(\text{C}_6\text{H}_5)_3$ ,  $\text{HgCl}_2 \cdot \text{PO}(\text{CH}_3)_3$ ,  $5\text{HgCl}_2 \cdot 2\text{PO}(\text{CH}_3)_3$  and  $\text{SO}_3 \cdot \text{PO}(\text{C}_6\text{H}_5)_3$ .

The weak interaction between  $\text{HgCl}_2$  and  $\text{PO}(\text{C}_6\text{H}_5)_3$  has been revealed by a study of the infrared spectra of the compounds  $\text{HgCl}_2 \cdot \text{PO}(\text{C}_6\text{H}_5)_3$  and  $\text{HgCl}_2 \cdot \text{PO}(\text{CH}_3)_3$ .

Addition compounds with phosphine oxides were described as early as 1861 by Hofmann<sup>1</sup> who prepared  $\text{ZnI}_2 \cdot 2\text{PO}(\text{C}_2\text{H}_5)_3$ . Sheldon and Tyree<sup>2</sup> have recently studied  $\text{SnCl}_4 \cdot 2\text{PO}(\text{C}_6\text{H}_5)_3$  and  $\text{TiCl}_4 \cdot 2\text{PO}(\text{C}_6\text{H}_5)_3$ , and have shown that the phosphoryl stretching frequency in the infrared decreases 50–55  $\text{cm}^{-1}$  as expected for adduct formation with the oxygen atom in  $\text{PO}(\text{C}_6\text{H}_5)_3$  functioning as donor atom. The donor strength of  $\text{PO}(\text{CH}_3)_3$  has been proved to be greater than that of  $\text{POCl}_3$  with  $\text{SbCl}_5$  as acceptor molecule<sup>3</sup>. In this connection we have found it interesting to investigate further the addition compounds of phosphine oxides in order to compare them with the  $\text{POCl}_3$  adducts.

## EXPERIMENTAL

*Chemicals used.*  $\text{PO}(\text{C}_6\text{H}_5)_3$  was prepared according to Pickard and Kenyon<sup>4</sup>. Yield: 50 % calculated on  $\text{POCl}_3$ . Melting point +152–154°C.

$\text{PO}(\text{CH}_3)_3$  was prepared following McKee and Burg<sup>5</sup> but with use of  $\text{Mg}(\text{CH}_3)_2\text{Br}$  instead of  $\text{Mg}(\text{CH}_3)_2\text{Cl}$ . Yield 75 % calculated on  $\text{POCl}_3$ . The colorless crystals melt at +137–139°C.

$\text{SbCl}_5$  and  $\text{SeOCl}_2$  were purified by vacuum distillation.

$\text{SbCl}_3$  was sublimed directly onto a cool glass bulb placed 3 cm above the bulk of impure solid.

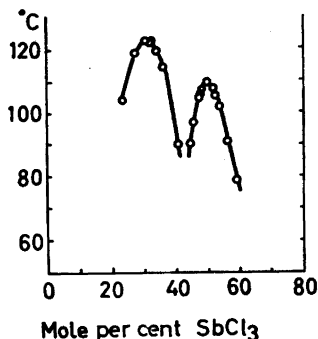
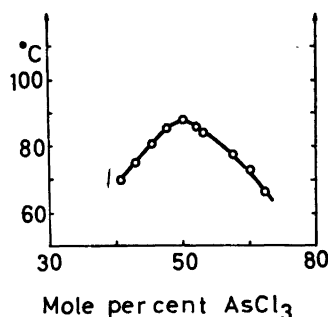
$\text{AsCl}_3$  and  $\text{POCl}_3$  were purified by distillation and collected at +129° and 105°C.

$\text{HgCl}_2$ , Merck *pro analysi*, was not further purified.

$\text{Hg}(\text{C}_6\text{H}_5)_2$  was prepared according to Pfeiffer and Truskier<sup>6</sup> and recrystallized from benzene. Yield 45 % calculated on  $\text{HgCl}_2$ . Melting point +124–125°C.

$\text{Hg}(\text{C}_6\text{H}_5)\text{Cl}$  was prepared following Nesmejanow<sup>7</sup>. Melting point +249–250°C.

*Phase diagrams.* The liquidus curves were studied by the same methods as described earlier<sup>8</sup>. In many cases the sublimation of  $\text{PO}(\text{CH}_3)_3$  or the decomposition of the adduct compounds prevented the study of the liquidus curves in this way.

Fig. 1a. The system  $\text{SbCl}_3\text{-PO}(\text{CH}_3)_3$ .Fig. 1b. The system  $\text{AsCl}_3\text{-PO}(\text{CH}_3)_3$ .

*Preparation of addition compounds.*  $\text{SbCl}_5 \cdot \text{PO}(\text{C}_6\text{H}_5)_3$  was precipitated from cool, dilute solutions of  $\text{SbCl}_5$  and  $\text{PO}(\text{C}_6\text{H}_5)_3$  in  $\text{CCl}_4$  (mole ratio 1:1) and was recrystallized from  $\text{CHCl}_3$  as almost colorless needle-shaped crystals. It is stable in air and can be melted carefully without decomposition at  $+196\text{--}197^\circ\text{C}$ . The crystals are soluble in benzene (colorless solution), ether, chloroform or ethylene chloride. Preparation directly from  $\text{SbCl}_5$  and  $\text{PO}(\text{C}_6\text{H}_5)_3$  gives  $\text{HCl}$  evolution and darkly colored decomposition products (Found: Cl 31.0. Calc. 30.7.)

$\text{SbCl}_5 \cdot \text{PO}(\text{CH}_3)_3$  was precipitated as colorless crystals from a supersaturated solution in ethylene chloride. It is stable in air, melts without decomposition at  $+176\text{--}177^\circ\text{C}$ , and can be dissolved in benzene (no color change). The thermal decomposition with evolution of  $\text{HCl}$  starts at  $+260^\circ\text{C}$  (Found: Cl 44.7. Calc. 45.3.)

$\text{SbCl}_3 \cdot \text{PO}(\text{CH}_3)_3$  and  $\text{SbCl}_3 \cdot 2\text{PO}(\text{CH}_3)_3$  were found in the phase diagram (Fig. 1a). The melting points are  $+110^\circ$  and  $+124^\circ\text{C}$ . Supercooling prevented the study of the system near the eutectic point. Crystals of both compounds prepared directly from the components are stable in air but we could not prepare them from  $\text{CCl}_4$  solutions; only oil drops dispersed in the solution were obtained.

$\text{AsCl}_3 \cdot \text{PO}(\text{CH}_3)_3$  was found in the phase diagram (Fig. 1b). The melting point is  $+88^\circ\text{C}$ . The system cannot be studied at higher phosphine oxide contents because of sublimation. The crystals can also be prepared from  $\text{CCl}_4$  solutions. They are hygroscopic and decompose in air within a few minutes.

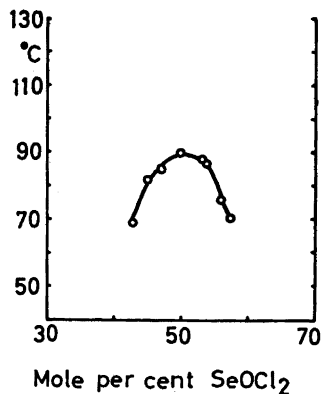
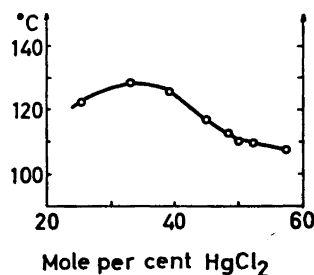
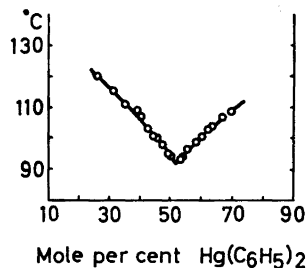
$\text{AsCl}_5 \cdot \text{PO}(\text{CH}_3)_3$  is formed when dry chlorine gas is led at  $25^\circ\text{C}$  through a liquid mixture of  $\text{AsCl}_3$  and  $\text{PO}(\text{CH}_3)_3$  (mole ratio 3:1). The color of the solution changes to orange, and orange crystals form upon cooling. They decompose near  $+50^\circ\text{C}$  with loss of color. They also decompose in air with color disappearance. A rapid analysis of four different samples gave an average Cl content of 51.1% (Calc. 51.5%).

$\text{SeOCl}_2 \cdot \text{PO}(\text{CH}_3)_3$  was found in the phase diagram (Fig. 2a). Its melting point is  $+90^\circ\text{C}$ .

$\text{HgCl}_2 \cdot 2\text{PO}(\text{C}_6\text{H}_5)_3$  was found in the phase diagram (Fig. 2b). The existence of the  $\text{HgCl}_2 \cdot \text{PO}(\text{C}_6\text{H}_5)_3$  1:1 compound was confirmed by powder photographs. The 1:2 compound can be precipitated from ethylene chloride solution and has been described earlier<sup>4</sup>. Both compounds are stable in air. The melting points are  $+110^\circ$  and  $+126^\circ\text{C}$ . The latter was measured with precipitated 1:2 crystals; the value  $+128^\circ\text{C}$  found in the liquidus curve is less accurate.

$\text{HgCl}_2 \cdot \text{PO}(\text{CH}_3)_3$  and  $5\text{HgCl}_2 \cdot 2\text{PO}(\text{CH}_3)_3$  were precipitated from acetone or alcohol solutions with excess of  $\text{PO}(\text{CH}_3)_3$  and  $\text{HgCl}_2$ , respectively. They can be recrystallized with unchanged compositions. Their melting points are  $+137^\circ\text{C}$  and  $+187^\circ\text{C}$ . Phase diagrams cannot be studied because of the sublimation of  $\text{PO}(\text{CH}_3)_3$ . (Found: Hg 55.2. Calc. for  $\text{HgCl}_2 \cdot \text{PO}(\text{CH}_3)_3$ : 55.1.) (Found: Hg 64.9. Calc. for  $5\text{HgCl}_2 \cdot 2\text{PO}(\text{CH}_3)_3$ : 65.0.)

$\text{HgCl}_2$  does not give any addition compounds with  $\text{POCl}_3$  as checked by us in a series of preparations.

Fig. 2a. The system  $\text{SeOCl}_2\text{-PO}(\text{CH}_3)_3$ .Fig. 2b. The system  $\text{HgCl}_2\text{-PO}(\text{C}_6\text{H}_5)_3$ .Fig. 2c. The system  $\text{Hg}(\text{C}_6\text{H}_5)_2\text{-PO}(\text{CH}_3)_3$ .

$\text{Hg}(\text{C}_6\text{H}_5)_2$  and  $\text{Hg}(\text{C}_6\text{H}_5)\text{Cl}$  do not give any addition compounds as shown by the phase diagram for  $\text{Hg}(\text{C}_6\text{H}_5)_2$  (Fig. 2c) and by repeated melting and precipitation experiments for  $\text{Hg}(\text{C}_6\text{H}_5)\text{Cl}$ .

$\text{SO}_3 \cdot \text{PO}(\text{C}_6\text{H}_5)_3$  was prepared by leading  $\text{SO}_3$  through a U-tube filled with  $\text{PO}(\text{C}_6\text{H}_5)_3$  dissolved in ethylene chloride. A white precipitate formed which dissolved in an excess of  $\text{SO}_3$ . It melts with decomposition at  $+102^\circ\text{C}$ . (Found: S 8.63. Calc. 8.94.)

$\text{SO}_3 \cdot \text{PO}(\text{CH}_3)_3$  which has earlier been described by McKee and Burg<sup>5</sup> was also prepared and found to dissolve in an excess of  $\text{SO}_3$ .

*Infrared spectra.* The infrared spectra of  $\text{HgCl}_2 \cdot \text{PO}(\text{C}_6\text{H}_5)_3$  and  $\text{HgCl}_2 \cdot 2\text{PO}(\text{C}_6\text{H}_5)_3$  were recorded on a Perkin-Elmer Model 21 Spectrophotometer equipped with NaCl and CsBr prisms (in the Institute of Biochemistry). The crystals were dispersed in Nujol and studied between KBr and TlBr-TlI plates. The phosphoryl stretching frequency was found at  $1149$  and  $1161\text{ cm}^{-1}$  and the antisymmetrical Hg-Cl bond stretching frequency at  $352$  and  $345\text{ cm}^{-1}$  respectively. The corresponding values for pure  $\text{PO}(\text{C}_6\text{H}_5)_3$  and  $\text{HgCl}_2$  were  $1186$  and  $371\text{ cm}^{-1}$ .

#### DISCUSSION

1. In a paper on the addition compounds of sulfoxides and sulfones<sup>9</sup>, a qualitative discussion of the cohesion energies in the solid state was attempted. The results were successful in so far as the principal predictions about the structures of the adduct molecules between  $\text{SbCl}_5$  and sulfoxides or sulfones have later been confirmed by X-ray crystallography<sup>10</sup>. Spectroscopic investiga-

tions<sup>11</sup> indicate, however, that the conditions of interaction are quite complicated and that the reasonable results obtained in the paper on the sulfoxides and sulfones are rather fortuitous. This suggestion is strongly supported by the results presented here. The melting points of the compounds  $\text{SbCl}_5 \cdot \text{POCl}_3$ ,  $\text{SbCl}_5 \cdot \text{PO}(\text{CH}_3)_3$ , and  $\text{SbCl}_5 \cdot \text{PO}(\text{C}_6\text{H}_5)_3$  are 115, 40, and 43°C higher than the melting points of the pure donor molecules  $\text{POCl}_3$ ,  $\text{PO}(\text{CH}_3)_3$ , and  $\text{PO}(\text{C}_6\text{H}_5)_3$ . The same argument as the one applied to  $\text{SbCl}_5 \cdot \text{SOCl}_2$ ,  $\text{SbCl}_5 \cdot \text{SO}(\text{CH}_3)_2$ , etc. would here lead to the conclusion that the structures of  $\text{SbCl}_5 \cdot \text{POCl}_3$  and  $\text{SbCl}_5 \cdot \text{PO}(\text{CH}_3)_3$  have quite different bond angles at the donor atom oxygen (cf. Fig. 3 of Ref.<sup>9</sup>). We have, however, been able to show<sup>12</sup> that the structure of  $\text{SbCl}_5 \cdot \text{PO}(\text{CH}_3)_3$  is very similar to the structure of  $\text{SbCl}_5 \cdot \text{POCl}_3$ <sup>13</sup>. The discussions of the resulting dipole moments and the melting point relations which were proposed<sup>9</sup> tentatively should therefore now be considered as too crude simplifications to permit any safe predictions.

2. It is difficult to express any opinion about the structures of  $\text{SbCl}_3$  and  $\text{AsCl}_3$  adducts. Structure determinations would be of great interest because of the labelling of the similar reactions of  $\text{SbCl}_3$  or  $\text{AsCl}_3$  with  $\text{POCl}_3$  as weak electrostatic interaction, on the basis of the spectroscopic data<sup>11</sup>.

3. The stabilization of  $\text{AsCl}_5$  by complex formation with the strong donor molecule  $\text{PO}(\text{CH}_3)_3$  was successful and can probably be achieved with other similar donors. The non-existence of free  $\text{AsCl}_5$  thus seems to depend upon unfavorable energy conditions in the trigonal bipyramid  $\text{AsCl}_5$ , while the octahedral co-ordination is more favorable. The same difference is found with the very strong Lewis acid  $\text{SbCl}_5$  but in that case the free  $\text{SbCl}_5$  is also stable.

4. The importance of 1:2 adducts of  $\text{SbCl}_3$  is confirmed by the existence of the compound  $\text{SbCl}_3 \cdot 2\text{PO}(\text{CH}_3)_3$  in analogy with  $\text{SbCl}_3 \cdot 2\text{POCl}_3$  and  $\text{SbCl}_3 \cdot 2\text{SO}(\text{CH}_3)_2$ <sup>9</sup>.

5.  $\text{SeOCl}_2$  on the other hand is here exceptional as an acceptor molecule in giving a 1:1 compound  $\text{SeOCl}_2 \cdot \text{PO}(\text{CH}_3)_3$ . The adducts with  $\text{POCl}_3$  and sulfoxides cannot be prepared because of metathetical processes<sup>8</sup> but many 1:2 compounds are known, and the crystal structure of  $\text{SeOCl}_2 \cdot 2\text{NC}_5\text{H}_5$  has recently been determined<sup>14</sup>. A comparative study of  $\text{SeOCl}_2 \cdot \text{PO}(\text{CH}_3)_3$  would be of great interest.

6. The differences between the reactions of  $\text{PO}(\text{CH}_3)_3$ ,  $\text{PO}(\text{C}_6\text{H}_5)_3$ , and  $\text{POCl}_3$  with  $\text{HgCl}_2$  are obvious. We have without success tried to isolate a 1:2 compound with  $\text{PO}(\text{CH}_3)_3$  and a 5:2 compound with  $\text{PO}(\text{C}_6\text{H}_5)_3$ .

7. The interaction between  $\text{HgCl}_2$  and  $\text{PO}(\text{C}_6\text{H}_5)_3$  is of the same weak type as between  $\text{AsCl}_3$  and  $\text{POCl}_3$ <sup>11</sup>. The spectra of  $\text{HgCl}_2$  and  $\text{PO}(\text{C}_6\text{H}_5)_3$  are both preserved and only slightly perturbed in the spectra of the adduct molecules. The band shifts are in the predicted direction and magnitude. The P-O bonds would thus be most perturbed for the highest mole ratio of  $\text{HgCl}_2$ , and the 1:1 adduct actually shows the largest decrease in the phosphoryl band position. The Hg-Cl bond on the other hand must be most perturbed in the 1:2 compound which has the highest  $\text{PO}(\text{CH}_3)_3$  content, and the corresponding stretching frequency is accordingly shifted furthest in that compound.

8. The structure of  $\text{HgCl}_2 \cdot 2\text{PO}(\text{C}_6\text{H}_5)_3$  can thus probably not be characterized by simple tetrahedral co-ordination around Hg but rather by a distorted square

co-ordination of the same type as in  $\text{HgCl}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$ <sup>15</sup>. The structures of the 1:1 and 5:2 adducts are difficult to predict. They will be investigated by Mr. Brändén of this Institute as part of an extensive study on the crystal chemistry of  $\text{HgCl}_2$  adduct molecules.

9. The negative results of the experiments with  $\text{Hg}(\text{C}_6\text{H}_5)_2$  and  $\text{Hg}(\text{C}_6\text{H}_5)\text{Cl}$  confirm earlier suggestions about the negligible or very weak acceptor properties of these compounds<sup>16</sup>. Strohmeier has, however, proved that  $\text{Hg}(\text{C}_2\text{H}_5)_2$  has some acceptor character<sup>17</sup>.

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