

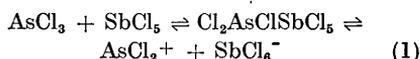
On the Reactions in Solutions of Phosphorus Oxychloride

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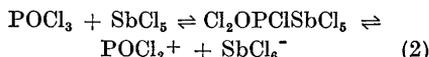
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The acid-base concept suggested by Gutmann and Lindqvist¹ has already been applied in a discussion² of solutions in arsenic trichloride, AsCl_3 . This short communication will deal with the differences in behaviour, compared with that in AsCl_3 , which might be expected in phosphorus oxychloride, POCl_3 . The main difference between these two solvents is that only POCl_3 contains oxygen. The reaction between bases like $(\text{CH}_3)_4\text{NCl}$ and the solvent cannot be much influenced by the presence of an oxygen atom, but it may be mentioned that POCl_3 has a very small tendency to react with bases, that is, to function as an acid (a detailed comparison will be made in a subsequent paper³). The reason for this is probably that the phosphorus atom in POCl_3 cannot easily increase its coordination. This is possible for As in AsCl_3 and Se in SeOCl_2 , and those solvents react much better with bases.

With chlorides like SbCl_5 , SnCl_4 and TiCl_4 which are acids in AsCl_3 there are certain changes in the reactions with oxychlorides. The important factor is always the increase in coordination. In AsCl_3 this increase can only take place in this way:

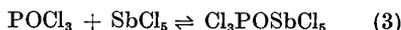


The analogous reaction in POCl_3 is:



The dissociations to AsCl_2^+ or POCl_2^+ and SbCl_6^- have been established through potentiometric measurements^{4,5}.

In POCl_3 a competing reaction is possible, however:



The further dissociation to PCl_3^{2+} and SbOCl_5^{2-} is very improbable because it would require the breaking of the strong P—O bond and would lead to the forma-

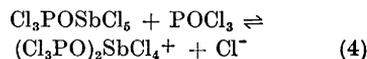
tion of bivalent ions in a solvent with a very low dielectric constant.

Reaction (3) would not change the chloride ion activity but the occurrence of the reaction would decrease the apparent strength of SbCl_5 as an acid in POCl_3 .

The structure of the solid compound $\text{POCl}_3 \cdot \text{SbCl}_5$ which has recently been determined⁶, is built up by $\text{Cl}_3\text{POSbCl}_5$ molecules (contrary to the conclusions drawn from Raman spectroscopic work⁷). This is not in conflict with the assumption of different competitive equilibria in solution, because the equilibrium system can easily be shifted by the precipitation of the energetically most favourable solid phase.

The ionic compounds obtained by reactions (1) and (2) do not seem to have very favourable lattice energies compared with the compound found by reaction (3) and SbCl_5 , SnCl_4 and TiCl_4 give crystalline compounds with POCl_3 and SeOCl_2 while only eutectic points are obtained with AsCl_3 ³.

The reactions discussed so far involve only *addition* of solvent molecules, giving increased coordination. With an excess of solvent *substitution* reactions of the type:



cannot be quite excluded. It is true that potentiometric measurements have shown that reaction (4) does not take place⁵ with SbCl_5 but it remains to be seen whether reactions of type (2), (3) or (4) are most important for other chlorides, *e. g.* SnCl_4 and TiCl_4 .

It is obvious that investigations along the same lines as earlier drawn up for AsCl_3 ² are also of importance for the study of POCl_3 as a solvent.

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