STUDIES ON PHOSPHORUS OXYCHLORIDE
AND ALUMINIUM CHLORIDE COMPLEX

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Received December 22, 1959

(Communicated by Dr. M. R. A. Rao, F.A.SC.)

Phosphorus oxychloride has been found to be a versatile solvating liquid for many inorganic compounds. A large number of non-polar halides of the elements of III, IV and V groups of the periodic table react with phosphorus oxychloride and form complexes which are stable and easily isolated. Similarly a large number of solvates of metal oxides with phosphorus oxychloride have been reported in literature. This solvating property of the oxychloride is attributed to its co-ordinating tendency through either oxygen\(^1\) or chlorine\(^2-3\) acting as donor atom.

Earlier reports about the complex formed between phosphorus oxychloride and aluminium chloride indicated the complex to be of composition \(\text{AlCl}_3\cdot\text{POCl}_3\),\(^4\) but recent observations concerning its composition are conflicting. Gutman\(^5\) claims that the complex is \(\text{AlCl}_3\cdot\text{POCl}_3\) while Groeneveld and Zuur\(^6\) report the complex to be \(\text{AlCl}_3\cdot2\text{POCl}_3\) prepared under similar conditions. The latter authors have postulated the possible existence of other complexes with the following compositions: \(\text{AlCl}_3\cdot5\text{POCl}_3\) and \(\text{AlCl}_3\cdot6\text{POCl}_3\).

The preliminary investigations of the present authors indicated that the molar ratio of aluminium chloride and phosphorus oxychloride in the complex formed was 1:2. A detailed investigation was therefore undertaken to throw more light on the composition of the complex and also to study its physico-chemical properties, such as its cryoscopic behaviour, electrical conductivity and absorption spectra in solution.

EXPERIMENTAL

**Phosphorus oxychloride**

Phosphorus oxychloride of C.P. quality (E. Merck) was purified by distilling in an all-glass apparatus in an atmosphere of pure and dry nitrogen. The fraction distilling between 105-106\(^\circ\) C. (683 mm.) was collected and preserved in sealed ampules (about 2.5 g. in each). The purity of the
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Oxychloride was checked by the estimation of the phosphate and the chloride obtained after hydrolysing a known quantity of the sample with dilute alkali. The results indicated that phosphorus oxychloride was 99.9% pure.

Aluminium chloride

Anhydrous aluminium chloride was prepared by passing dry hydrogen chloride over heated aluminium filings (Merck A.R. quality) in a pyrex glass tube maintained at 250°C. The condensed aluminium chloride was resublimed into a series of bulbs in a current of dry hydrogen chloride. The bulbs each containing about 2-3 g. of the anhydrous chlorides were sealed off. A representative sample was analysed by hydrolysing the chloride in a dilute solution of alkali and estimating the aluminium as the hydroxy quinolate and the chlorine by Volhard's method. The analytical results showed that the anhydrous chloride was 99.8% pure.

1. Preparation of the complex

The method followed for the preparation of the complex was essentially the same as described by earlier workers with a few minor improvements. The transfer of materials, etc., was carried out in a 'dry' box and the experiments were conducted in all-glass vessels.

A known quantity of anhydrous aluminium chloride was taken in a dry flask fitted with a phosphorus pentoxide guard tube. A known excess of phosphorus oxychloride was introduced into the same vessel. Considerable heat was evolved during the mixing of the reagents. The anhydrous aluminium chloride dissolved slowly in the oxychloride at room temperature. The reaction could be completed within fifteen minutes by heating at 95°C. The flask was cooled to room temperature and the excess of oxychloride was then removed in two ways: (i) by passing dry air through the solution and (ii) by removing the vapours under vacuum.

(i) Sample obtained by passing dry air.—A portion of the solution of aluminium chloride in phosphorus oxychloride as obtained above was transferred to a dry glass bubbler assembled along with suitable traps and guard tubes. Dry air was slowly drawn through the solution (for 24-36 hours) till a free flowing powder was obtained. The free flowing powder samples (2-3 g.) were preserved in sealed tubes.

(ii) Removal of the solvent by evaporation.—Another portion of the homogeneous solution was transferred to an evaporating dish which was placed in a vacuum desiccator and evacuated slowly at 25°C with occasional stirring till a free flowing powder was obtained. The powder samples were preserved in sealed tubes as mentioned above,
Analysis of the samples.—The estimation of aluminium and phosphorus in presence of each other presents some difficulties. In order to obtain reliable analytical results the method described in an earlier communication was adopted for the determination of both phosphorus and aluminium. The chloride content of the samples was determined after hydrolysing the substance with a cold dilute solution of sodium hydroxide by Volhard's method. This procedure prevented any loss of hydrogen chloride during hydrolysis in water and gave correct analytical results.

The analytical results indicated that a stable complex is obtained in whatever way the excess of oxychloride is removed from a solution of aluminium chloride in excess of phosphorus oxychloride. The molecular ratio of aluminium chloride and phosphorus oxychloride in the complex was found to correspond to 1:2.

As has been pointed out earlier, Gutman reports a complex of the composition \( \text{AlCl}_3 \cdot \text{POCl}_3 \). But no details of the conditions of preparation and methods of removal of the excess oxychloride are described. Under the specified conditions described above, only one type of complex can be isolated corresponding to the composition \( \text{AlCl}_3 \cdot 2 \text{POCl}_3 \). The physico-chemical properties of the complex are described below.

2. Cryoscopic behaviour of the complex in nitrobenzene

Preliminary investigations indicated that nitrobenzene was the most suitable solvent for the cryoscopic work. The solubility of the complex in nitrobenzene at 25°C was determined and this corresponded to the value 5.91 g. in 100 g. of nitrobenzene whereas other organic solvents like carbon tetrachloride, benzene, etc., could dissolve both aluminium chloride and phosphorus oxychloride separately but the complex was found to be insoluble in such solvents. Therefore all the cryoscopic measurements were carried out in nitrobenzene solutions only.

Preparation of pure and dry nitrobenzene.—Nitrobenzene (C.P. quality) was purified by the method similar to that described by Meisenheimer and Dorner and Roberts and Bury. A pure sample of nitrobenzene was distilled and the middle portion was fractionally crystallised three times, dried over anhydrous calcium chloride and again distilled. The middle portion was stored over phosphoric anhydride and just before commencing the experiment was distilled at 10 mm. pressure into cryoscopic tubes. A carefully dried all-glass distillation apparatus was used for such purposes. The freezing point of such a sample was 5.77°C ± 0.005.

The purity of nitrobenzene and its cryoscopic constant \( (K_f) \) were checked by determining the molecular weight of resublimed naphthalene which is
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known to be a monomer in this solvent. K_f of nitrobenzene was taken to be 6.89 which is in good agreement with the value calculated using latent heat of fusion of nitrobenzene as 22.46 cal./g. as determined by Meyer.

The molecular weights of anhydrous aluminium chloride, and phosphorus oxychloride as well as that of the complex were determined separately and the following values were obtained:

Aluminium chloride: Mol. weight in nitrobenzene 134.6 ± 1
Phosphorus oxychloride ,, 163.7 ± 3.5
"Complex" ,, 345.6 ± 5

It has been observed that aluminium chloride has the formula Al_2Cl_6 up to 400°C. corresponding to all the three states of aggregation. The molecular weight of aluminium chloride in solutions of liquids like carbon disulphide, benzene, etc., also corresponds to the dimeric form; whereas in solvents like pyridine and ether the anhydrous chloride is essentially monomeric. In general, it has been claimed that in any solvent that is known to combine with anhydrous aluminium chloride, aluminium chloride has a molecular weight corresponding to AlCl_3.

Aluminium chloride forms an addition product with nitrobenzene also with the formula (AlCl_3.C_6H_5NO_2). The molecular weight of anhydrous aluminium chloride as determined in the present experiment indicates that it is in monomeric form in nitrobenzene solution at comparatively low concentrations. This result is in agreement with the values reported in literature.

Phosphorus oxychloride has a molecular weight in nitrobenzene corresponding to the monomeric form. While at higher concentrations there seems to be a tendency towards dimerisation. However, the values obtained in the present investigation agree better with the theoretical value than reported earlier.

The determination of the molecular weight of the complex formed between phosphorus oxychloride and anhydrous aluminium chloride in nitrobenzene has been carried out using comparatively dilute solutions. In spite of this the value obtained in the present investigation (345.6) is far from the theoretical value corresponding to the molecular formula AlCl_3.2 POCl_3 (440.1). This deviation of the experimental value from the theoretical value may be attributed to the dissociation of the complex at low concentration into phosphorus oxychloride and a lower complex in the following
One may even expect the complete breakdown of the complex into aluminium chloride and phosphorus oxychloride thus giving rise to three molecules instead of two molecules as suggested in the foregoing. A comparison with the complexes formed between zirconium and hafnium tetrachlorides with phosphorus oxychloride eliminates the probability of getting three molecules.  

3. Electrical conductivity in nitrobenzene

In order to ascertain whether the complex corresponding to the molecular composition of the solid existed in solution, electrical conductivity measurements of the complex in nitrobenzene solution were carried out. A modified form of Freas conductivity cell was used. The electrodes consisted of two circular platinum plates (diameter \( \frac{3}{4} \)") kept apart at a distance of 2 mm. The conductivity cell had an all-glass airtight lid in order to protect the solution from contamination with atmospheric moisture. The measurements of conductivity were carried out with the help of “Electrospezial” conductivity meter (Model GM 4249). The conductivity cell was kept in a thermostat at 25 ± 0.05°C.

The electrodes were platinised and the cell constant was determined in the usual manner. The cell constant had a value of 0.03865 which enabled the measurement of conductivity of the low conducting non-aqueous solutions. The nitrobenzene used had a specific conductivity of \( 0.6 \times 10^{-7} \) mhos per cm. at 25°C, and this agrees with the value given by Payne (\( 1 \times 10^{-7} \) mho per cm.).

Aluminium chloride in nitrobenzene had a specific conductivity of \( 4 \times 10^{-5} \) mhos/cm. at a concentration of 0.01 mole per litre which increased to \( 148.7 \times 10^{-5} \) mhos with increase in concentration to 1.01 mole per litre. Similarly the specific conductivity of phosphorus oxychloride solution in nitrobenzene increased from \( 1.69 \times 10^{-6} \) mhos/cm. to \( 25.43 \times 10^{-6} \) mhos when the concentration was increased from 0.02 mole/litre to 2.13 moles per litre. These results are presented graphically in the curves A and P of Fig. 1. These experimental values are in agreement with the results reported in literature.

The electrical conductivity of different mixtures of aluminium chloride and phosphorus oxychloride in nitrobenzene prepared by mixing the individual components to give suitable molar ratios at different concentrations were measured. The change in conductivity of the mixture of the reactants in nitrobenzene while keeping the concentration of aluminium chloride complex isolated (\( \text{AlCl}_3 \cdot 2 \text{POCl}_3 \)) were also measured.
It is known that anhydrous aluminium chloride conducts electricity in all the three states of aggregation except at the melting-point. The ionic species responsible for conducting the current are reported\textsuperscript{22} to be \( \text{Al}_2\text{Cl}_6 \rightleftharpoons \text{Al}^{+3} + (\text{AlCl}_6)^{-3} \). In solvents like ethyl chloride the aluminium cation is observed\textsuperscript{23} to be heavily solvated\textsuperscript{6} as \([\text{Al} (\text{C}_2\text{H}_5\text{Cl})_n]^+\). It is also known that in aqueous medium the aluminium ion is solvated corresponding to a co-ordination number six. From the cryoscopic data, it has already been indicated that the monomeric form of aluminium chloride, is associated with nitrobenzene but the extent of solvation is not known. It is very difficult to distinguish from the cryoscopic data whether the two particles correspond to 2 AlCl\(_3\) or Al\(^{+3}\) and (AlCl\(_6\))\(^{-3}\) owing to autoionisation. It is reasonable to attribute the electrical conductivity of aluminium chloride in nitrobenzene to these ionic species.

Phosphorus oxychloride is not a very good conductor in nitrobenzene when compared with aluminium chloride. Even this feeble conductance which is not very much different from the solvent itself may be attributed to the ionic species formed by the autoionisation of phosphorus oxychloride into: \( 2 \text{POCl}_3 \rightleftharpoons \text{POCl}_2^+ + \text{POCl}_4^- \) as suggested by earlier workers.\textsuperscript{18, 24}
Many of the electrolytic properties of phosphorus oxychloride have been explained on the basis of such an ionisation.

The conductivity of various mixtures of aluminium chloride and phosphorus oxychloride in nitrobenzene in different proportions is higher than the sum of the individual conductivities of the two components calculated from the graph. For instance, the specific conductivity of a mixture of equal volumes of 0.6 M AlCl₃ and 0.6 M POCl₃ (the resulting mixture will have 0.3 M AlCl₃ and 0.3 M POCl₃) was found to be $11.04 \times 10^{-4}$ mhos/cm, which is nearly double the value of the sum of the individual conductivities at the corresponding concentrations in solution ($6.75 \times 10^{-4}$ mhos for AlCl₃, $0.079 \times 10^{-4}$ for POCl₃).

In another case when equal volume of 0.4 M solution of aluminium chloride was mixed with 0.6 M solution of phosphorus oxychloride in nitrobenzene, the conductivity was found to be $12.47 \times 10^{-4}$ mhos/cm. Whereas the sum of the conductivities of individual components corresponding to 0.2 M aluminium chloride and 0.3 M phosphorus oxychloride is equal to $4.78 \times 10^{-4}$ mhos/cm.

Similar observations are made in other cases also. It can be inferred from the above results that the contribution of phosphorus oxychloride to the electrical conductivity is very small when compared with that of aluminium chloride. However, the mixture shows a marked increase in the conductivity indicating thereby the conducting species are very much different from either AlCl₃ or POCl₃.

The conductivities of the solution (Table I) prepared from the isolated complex AlCl₃·2 POCl₃ in nitrobenzene also show a higher value than the sum of the conductivities of the individual components at corresponding concentrations. However, the solubility of the isolated complex, which corresponds only to 0.53 molar, restricts the choice of higher concentration. Heating the mixtures of the two components in nitrobenzene solution to 95°C had little effect on conductivity indicating that the reaction between aluminium chloride and phosphorus oxychloride on mixing was complete even at room temperature.

4. Conductometric titration of aluminium chloride with phosphorus oxychloride in nitrobenzene

A solution of aluminium chloride in nitrobenzene (0.37 M) was titrated against a standard solution of phosphorus oxychloride in nitrobenzene conductometrically and it was found that the specific conductivity of the resulting system attained a limiting value at a point corresponding to the
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TABLE I

Electrical conductivity of the complex AlCl₃·2POCl₃ in nitrobenzene at 25°C.

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<th>Concentration in mole per litre</th>
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<th>Sp. conductivity in mho./per cm.</th>
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<td>3.18</td>
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molecular ratio of the components in solution AlCl₃·POCl₃ 1:2. Conductometric titration curve (C) is given in Fig. 1. This value clearly indicated the formation of the complex corresponding to a definite composition AlCl₃·2POCl₃.

It has already been pointed out that the conductivity of the complex in solution is very much higher than the sum of the conductivities of the two components at corresponding concentrations. This may be attributed to the formation of AlCl₄⁻ and POCl₂⁺ ions and the tendency of the additional phosphorus oxychloride to dissociate into POCl₂⁺ and Cl⁻ ions. All these species are likely to bring about a perceptible increase in specific conductivity of the solutions of the complex formed between aluminium chloride and phosphorus oxychloride in nitrobenzene.

5. Absorption spectra of the systems AlCl₃·POCl₃ in nitrobenzene

The absorption spectrum of pure and dry nitrobenzene showed a peak at 4150 Å with an optical density of 9.25×10⁻³. This is in agreement with the value reported in literature. Absolute alcohol was used as a standard while measuring the absorption of nitrobenzene. The absorption spectrum of phosphorus oxychloride in nitrobenzene, using nitrobenzene itself as a standard, did not show any characteristic absorption maximum.

Pure and dry nitrobenzene has a straw yellow colour, whereas even a dilute solution of aluminium chloride is deep yellow. The intensity of the colour depends on the concentration. The absorption maximum is found to shift towards longer wavelengths with increase in concentration. The absorption maximum changed from 4400 Å to 4620 Å when the concentration of the solution was changed from 0.02 M to 0.4 M. Beer's law was found to be valid between concentrations 0.016 M and 0.025 M of aluminium chloride in nitrobenzene at a wavelength of 4400 Å. The optical density of aluminium chloride solution in nitrobenzene reached a limiting value of 0.825 at 0.22 M.

The optical density measurements of the mixtures containing various proportions of aluminium chloride and phosphorus oxychloride (corres-
ponding to solutions of concentration in the range where Beer's law is valid) indicated that there was another range of maximum absorption between 6950 Å and 7200 Å which is not observed in case of either nitrobenzene or the individual solutions of aluminium chloride or oxychloride. It could therefore be inferred that there was complex formation between aluminium chloride and phosphorus oxychloride when mixed in nitrobenzene solution even at room temperature.

The solutions of the isolated solid complex in nitrobenzene also exhibited a similar peak in the range 6900 Å-7200 Å. The complex whether it is formed in solution by the addition of aluminium chloride and phosphorus oxychloride in nitrobenzene or prepared separately and then dissolved in nitrobenzene appear to be the same.

**SUMMARY**

1. Anhydrous aluminium chloride reacts with phosphorus oxychloride to give a complex with a composition $\text{AlCl}_3\cdot2\text{POCl}_3$ which can be prepared in the form of a free flowing powder.

2. The phosphorus oxychloride-aluminium chloride complex in nitrobenzene dissociates into $\text{AlCl}_3\cdot\text{POCl}_3$ and $\text{POCl}_3$ as indicated by the cryoscopic measurements.

3. The solution of the complex in nitrobenzene has a higher specific conductivity than the corresponding electrical conductivities of individual components. Similar higher electrical conductance is observed when the two components are mixed in nitrobenzene in different proportions.

4. When a solution of anhydrous aluminium chloride in nitrobenzene is titrated conductometrically against a solution of phosphorus oxychloride in nitrobenzene, a limiting value in the conductivity is reached at point corresponding to the molecular composition, the components in the ratio of 1:2 $\text{AlCl}_3: \text{POCl}_3$ in solution.

5. The absorption maxima of the complex in nitrobenzene solution differ from the absorption maximum of the individual components.

**ACKNOWLEDGMENT**

The authors wish to express their grateful thanks to Professor K. R. Krishnaswami and Professor M. R. A. Rao for their keen interest in the work.
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