# 213. *The Electrolytic Conductance of Solutions of Phosphorus Pentachloride.*

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The electrolytic conductances at 25° of phosphorus pentachloride dissolved in phosphorus oxychloride, benzoyl chloride, nitrobenzene, benzonitrile, and acetonitrile have been measured. The solutions in the last solvent have larger specific conductances than similar solutions in the other solvents. Transport-number experiments support the existence of the ions $PCl_4^+$ and $PCl_6^-$ in solution. Attempts to prepare salts containing the latter ion have been unsuccessful.

The conductance of a solution of phosphorus pentachloride in nitrobenzene was reported by Holroyd, Chadwick, and Mitchell (*J.*, 1925, **127**, 2492). No measurements of its conductance in other solvents except bromine (Plotnikov and Jakubson, *Z. phys. Chem.*, 1928, **138**, 235) and phosphorus oxychloride (Gutmann, *Monatsh.*, 1952, **83**, 39) had been made. The ionic nature of solid phosphorus pentachloride was established by *X*-ray investigation (Clark, Powell, and Wells, *J.*, 1942, 642); however, in the liquid phase the very low conductance (Voigt and Biltz, *Z. anorg. Chem.*, 1924, **133**, 277) together with other data suggested that the condition was primarily a molecular one. No consideration has been given to the state of phosphorus pentachloride in solution, where under certain conditions the simple molecular form might predominate, whilst under others considerable ionisation might occur. Measurements of the specific and equivalent conductivities in various solvents under strictly anhydrous conditions are given in the Table. In each case the solvent and phosphorus pentachloride were purified thoroughly before the solutions were prepared. Measurements were made as soon as possible (within a few hours) after the start of the experiment, since in many cases the readings were inclined to drift when the solutions were kept, probably owing to reaction between the halide and the solvent. The effects of the addition of small amounts of water (0·1 ml. per 10—15 g. of solvent) and of change of temperature were noted for each solution. The former led to a marked change in the results, usually an increase in the conductance, presumably owing to the presence of the products of hydrolysis. Increase in temperature resulted in an increase in the conductance in benzonitrile and a decrease in benzoyl chloride, nitrobenzene, acetonitrile, and phosphorus oxychloride. It seemed of importance to establish the complete absence of reaction between the phosphorus pentachloride and the solvent within the time required for the experiment, and this was achieved in the case of acetonitrile by the quantitative recovery of pure phosphorus pentachloride from the solution, after the solution had been kept for a few hours, during which time the conductance remained unchanged. Longer storage (24 hours) resulted in slight reaction, as shown by the appearance of hydrogen chloride in the solution, the presence of readily volatile phosphorus compounds, and a marked change in the conductance. The application of this method (*i.e.*, recovery of the solute) was impossible in the case of the higher-boiling solvents such as nitrobenzene, but in these cases the reproduceability and constancy of the conductance results, coupled with the absence of hydrogen chloride, suggested that no reaction had occurred. Hydrogen chloride, an expected product of any reaction which might occur, was shown to be absent in all cases by pumping out the solutions and examining any volatile materials obtained. De Konnick and Marquart (*Ber.*, 1872, **5**, 11) had shown that phosphorus pentachloride and nitrobenzene do not react to any appreciable extent.

*Electrolytic conductance of phosphorus pentachloride at* 25°.

| Solvent | $PCl_5$, mole/l. | $\kappa$, mho/cm. | Equivalent conductivity | |
|---|---|---|---|---|
| | | | based on $PCl_5$ | based on $(PCl_5)_2$ |
| $POCl_3$ * | 0·409 | $1{\cdot}99 \times 10^{-4}$ | 0·49 | 0·98 |
| Ph·COCl | 0·0325 | $5{\cdot}09 \times 10^{-5}$ | 1·57 | 3·14 |
| Dioxan | 0·0825 | $<10^{-7}$ | 0 | 0 |
| $Et_2O$ | *ca.* 0·05 | $<10^{-7}$ | 0 | 0 |
| $Ph{\cdot}NO_2$ | 0·0517 | $1{\cdot}77 \times 10^{-4}$ | 3·43 | 6·86 |
| | 0·0470 | $1{\cdot}57 \times 10^{-4}$ | 3·39 | 6·78 |
| | 0·0174 | $5{\cdot}75 \times 10^{-5}$ | 3·29 | 6·58 |
| | 0·0137 | $4{\cdot}51 \times 10^{-5}$ | 3·30 | 6·60 |
| | 0·00480 | $1{\cdot}63 \times 10^{-5}$ | 3·40 | 6·80 |
| | 0·00137 | $5{\cdot}00 \times 10^{-6}$ | 3·64 | 7·28 |
| Ph·CN | 0·0301 | $3{\cdot}08 \times 10^{-5}$ | 1·03 | 2·06 |
| Me·CN | 0·1870 | $4{\cdot}92 \times 10^{-3}$ | 26·3 | 52·6 |
| | 0·0722 | $2{\cdot}16 \times 10^{-3}$ | 29·2 | 58·4 |
| | 0·0495 | $1{\cdot}41 \times 10^{-3}$ | 30·0 | 60·0 |
| | 0·00554 | $1{\cdot}91 \times 10^{-4}$ | 34·5 | 69·0 |

* Gutmann (*loc. cit.*) gives $\Lambda = 0{\cdot}49$ at 20° and a concentration of 0·596 mole of $PCl_5$/l.

The results show that in the solvents investigated phosphorus pentachloride varies considerably in the extent of its dissociation into ions. The determining factor would appear to be the ability of the solvent to stabilise the ionisation by complex formation, rather than the effect of its dielectric constant. The data for the equivalent conductance shown in the Table (col. 4) are expressed on the basis of moles of phosphorus pentachloride ($PCl_5$) per l. of solution. An alternative and more precise presentation is in terms of the ionisation

$$2PCl_5 \rightleftharpoons PCl_4^+ + PCl_6^- \quad \ldots\ldots\ldots \quad (A)$$

and is expressed as moles of $(PCl_5)_2$ per litre. Data for acetonitrile solutions on this basis are shown in col. 5. It was not possible to obtain results at a sufficiently low concentration to make feasible the extrapolation of the equivalent conductivity to infinite dilution, so no reliable comparison with other uni-univalent electrolytes ($\Lambda_\infty$ 150—200) is possible. Failure to obtain conductance data at low concentrations was in the main due to the difficulties arising from traces of water and impurities.

Electrolysis of a solution of phosphorus pentachloride in acetonitrile, by means of smooth platinum electrodes and a cell designed to prevent mixing by diffusion, leads to concentration changes in the anolyte and catholyte which are completely in accord with ionisation (A). Thus, if it is assumed that no phosphorus or chlorine is lost from the solution during electrolysis, then $\Delta_{Cl} = x(10n^+ - 6)$ and $\Delta_P = x(1 - 2n^+)$, where $\Delta_{Cl}$ and $\Delta_P$ are the changes in g.-atoms of chlorine and phosphorus in the catholyte and anolyte respectively, $x$ is the number of Faradays passed during the electrolysis, and $n^+$ is the transport number of the cation at the concentration studied. The corresponding changes for the ionisation $PCl_5 \rightleftharpoons PCl_4^+ + Cl^-$ are $\Delta_{Cl} = x(5n^+ - 1)$ and $\Delta_P = -xn^+$.

The electrode processes occurring during the electrolysis are envisaged as

Anode : $PCl_6^- - e \longrightarrow [PCl_6] \longrightarrow PCl_5 + [Cl]$

$[Cl] + CH_3{\cdot}CN \longrightarrow$ Chlorinated compounds

Cathode : $PCl_4^+ + e \longrightarrow [PCl_4] \longrightarrow PCl_3 + PCl_5$.

The presence of phosphorous acid in the hydrolysed catholyte and of free chlorine in the anolyte confirms the suggested electrode reactions. A transport experiment in nitrobenzene has given results which are also in agreement with the ionisation (A).

In view of the absence of information, other than the conductances reported above, on the state of phosphorus pentachloride in solution, an attempt was made to measure the molecular weight in a variety of solvents. Only nitrobenzene possessed suitable properties for a sufficiently precise molecular-weight determination. Acetonitrile is unsuitable, having too low a melting point for cryoscopic measurements and being too reactive at the boiling point for ebullioscopic measurements. Results for the molecular weight by depression of freezing point in nitrobenzene, carried out under strictly anhydrous conditions, show that the association to double molecules occurs to a negligible extent in this solvent.

The occurrence of the $PCl_6^-$ ion in acetonitrile solution suggested that this solvent might be a suitable one for the preparation of other salts containing this anion and other alkali-metal cations. These attempted preparations and others involving direct interaction of phosphorus pentachloride and an alkali-metal halide were unsuccessful. Similar experiments by Gutmann (*Monatsh.*, 1952, **83**, 583) were also unsuccessful. It thus appears that compounds based on a lattice comprising $PCl_6^-$ and a simple cation are unstable under the conditions examined. Compounds which are essentially ionic, based on the $PCl_4^+$ ion, have been prepared and will be reported in a later communication.

In view of the existence of numerous addition compounds of halides with nitriles and nitro-compounds, and the possibilitity of obtaining evidence for the stabilisation of the ionised form of phosphorus pentachloride, the formation of solvates of phosphorus pentachloride was of interest. No evidence for solvates of phosphorus pentachloride with acetonitrile or nitrobenzene was obtained, a surprising fact in view of the existence of $SbCl_5,CH_3{\cdot}CN$ (Henke, *Annalen*, 1858, **106**, 281) and $2SbCl_5,3C_6H_5{\cdot}NO_2$ (Rosenheim and Stellman, *Ber.*, 1901, **34**, 3382).

The conductance of phosphorus pentabromide in bromine (Plotnikov, *Z. phys. Chem.*, 1904, **48**, 220) in liquid sulphur dioxide and arsenic trichloride (Walden, *ibid.*, 1903, **43**, 434) and in nitrobenzene (Finkelstein, *ibid.*, 1925, **115**, 303) has been measured. An exploratory experiment using acetonitrile, but without intense purification of the phosphorus pentabromide, gave a value of $\kappa = 0{\cdot}53 \times 10^{-4}$ mho/cm. at a concentration of 0·0078 mole of ($PBr_5$) per l. of solvent at 20°, corresponding to an equivalent conductance of 6·9. Acetonitrile reacts more readily with phosphorus pentabromide than with the pentachloride. Preliminary experiments show that phosphorus pentafluoride in acetonitrile gives a conducting solution.

## EXPERIMENTAL

*Materials.*—Phosphorus pentachloride was prepared by reaction of pure phosphorus trichloride (b. p. 75—76°) with an excess of pure dry chlorine. The resulting solid was stored in a glass-stoppered bottle in a desiccator until required, and was sublimed in a vacuum on to a cold finger before use. Solvents were ordinary commercial chemicals purified by storage over suitable drying agents followed by fractionation or distillation until a material of sufficient purity was obtained. Nitrobenzene and acetonitrile were purified according to the methods of Kraus and Taylor (*J. Amer. Chem. Soc.*, 1947, **69**, 1731) and of Smith and Witten (*Trans. Faraday Soc.*, 1951, **47**, 1304), respectively. All the solvents except phosphorus oxychloride and nitrobenzene were finally distilled from phosphoric oxide before use. Pure solvents had the following specific conductances ($\kappa$) in mho/cm.: phosphorus oxychloride $10^{-6}$, benzoyl chloride $10^{-5}$, dioxan $<10^{-7}$, diethyl ether $<10^{-7}$, nitrobenzene $10^{-7}$, benzonitrile $2{\cdot}5 \times 10^{-6}$, acetonitrile $4 \times 10^{-6}$.

*Measurement of Conductance.*—The various solutions were prepared by distilling the solvent in a vacuum on to the solid phosphorus pentachloride, which had previously been kept at room temperature under vacuum to remove any traces of volatile impurities. Dissolution was speeded in most cases by gentle agitation by means of a current of thoroughly dry air, and the solution was then transferred by a difference in pressure to a cell of the pipette type with smooth platinum electrodes each 1 sq. cm. in area (cell constant 0·463). Measurements of conductance were made by using a Mullard conductance bridge, type B 7566, and are considered to be accurate to ±2%. The cell and adjoining tubes were kept at a constant temperature in a water thermostat.

Concentrations were determined by weighing a sample of solution and adding it to an excess of water or dilute alkali. The procedure which followed varied from solvent to solvent but was essentially the removal of any unwanted solvent, followed by an adjustment of the solution to the correct conditions for precipitation. The phosphorus pentachloride was then usually determined by precipitation of the chloride as silver chloride. Where this was impossible the pentachloride was determined as phosphorus and weighed as $P_2O_5,24MoO_3$.

*Transport Experiments.*—Solutions of phosphorus pentachloride were prepared as in the experiments described above. The solution was transferred by a slight pressure difference to a cell in the form of an H. The two compartments were separated by a sintered plate, the arms of the cell having at their ends the electrodes, which were of smooth platinum, 1 sq. cm. in area. Taps were provided to empty the two compartments into sampling vessels. The cell was connected in series with a milliammeter and silver coulometer, and connected to a 20-v battery supply. The amounts of phosphorus and chlorine in the anolyte and catholyte were determined by standard procedures after the solutions had been fully hydrolysed and oxidised. The results of a series of experiments lead to values for the transport number of the cation, $n^+ = 0{\cdot}37, 0{\cdot}40, 0{\cdot}41$, and $0{\cdot}41$ measured at 20° in acetonitrile ($\text{M} \sim 0{\cdot}05$—$0{\cdot}1$) and $n^+ = 0{\cdot}65$ in nitrobenzene under similar conditions. In both cases ionisation (A) fits the results completely.

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