289. *Electrolytic Conductance of Solutions of Halogenotrifluoromethylphosphoranes.*

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Dichlorotristrifluoromethylphosphorane, $PCl_2(CF_3)_3$, is a conductor, and trichlorobistrifluoromethylphosphorane, $PCl_3(CF_3)_2$, a non-conductor, in acetonitrile. Values of molar conductance are given. The infrared spectra of the vapours of the two phosphoranes are recorded. Conductometric titration of tristrifluoromethylphosphine $P(CF_3)_3$ with bromine in acetonitrile provides evidence for the existence of an ionic compound of composition $P(CF_3)_3,Br_2$.

MANY derivatives of phosphine readily add a halogen molecule to produce, formally at least, a compound in which a phosphorus(V) atom is attached by covalent bonds to five univalent atoms or groups: $PX_3 + Y_2 \longrightarrow PX_3Y_2$. When these groups about the phosphorus atom are electron-attracting, the adduct may, under certain conditions, display well-defined ionic properties. An example of this dual behaviour is afforded by phosphorus pentachloride, which exists as trigonal bipyramidal molecules in the vapour phase [1] and as ions, PCl_4^+ PCl_6^-, in the solid state; [2] the same ions are also present in solutions in solvents of high dielectric constant.[3] When X is an electronegative organic group (*e.g.*, phenoxy-), the adduct containing quinquevalent phosphorus may also undergo ionic dissociation. For example, the following equilibria occur in acetonitrile: [4]

$$2P(OPh)_3 + 2Br_2 \rightleftharpoons 2P(OPh)_3Br_2 \rightleftharpoons P(OPh)_3Br^+ + P(OPh)_3Br_3^-$$

Compounds of the general type PX_nY_{5-n} in which X is the trifluoromethyl group have recently been prepared.[5,6] Account being taken of the strongly electronegative character of the trifluoromethyl group, and its pseudo-halogenoid behaviour in certain derivatives,[5] it was of interest to study the halogenotrifluoromethylphosphoranes more fully to find out if their properties followed the general pattern outlined above for phosphorus(V)

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[1] Rouault, *Compt. rend.*, 1938, **207**, 620.
[2] Clark, Powell, and Wells, *J.*, 1942, 642.
[3] Payne, *J.*, 1953, 1052.
[4] Harris and Payne, *J.*, 1956, 3038.
[5] Bennett, Emeléus, and Haszeldine, *J.*, 1953, 1565.
[6] Emeléus, Haszeldine, and Ram Chand Paul, *J.*, 1955, 563.

halides and related compounds. We now report an investigation of the properties of halogenotrifluoromethylphosphoranes of the types $P(CF_3)_3Hal_2$ and $P(CF_3)_2Hal_3$.

Dichlorotristrifluoromethylphosphorane, which at room temperature is a colourless solid, dissolves readily in acetonitrile, a solvent that has been widely used as an ionising medium for non-metallic halides and polyhalides.[7,8] Measurement of the conductance of the solutions immediately after their preparation gave a very low value (*ca.* 1×10^{-5} ohm^{-1} cm.$^{-1}$) for their specific conductance, but on standing, the conductance increased gradually and after 48 hr. a steady high value (*ca.* 3×10^{-3} ohm^{-1} cm.$^{-1}$) was observed. Solutions covering a range of concentration were examined and the values of " steady " molar conductance obtained are given in the table below. When molar conductance is plotted against the square root of the molar concentration the points fall nearly on a straight line which, on extrapolation to zero concentration, gives a value of 66 ohm^{-1} cm.^{2} mole^{-1} for the molar conductance at infinite dilution ($\Lambda_{m,\infty}$). This is a significantly high figure, being greater than that for acetonitrile solutions of phosphorus pentabromide ($\Lambda_{m,\infty} = 20$ ohm^{-1} cm.^{2} mole^{-1}) [8] and pentachloride ($\Lambda_{m,\infty} = 35$ ohm^{-1} cm.^{2} mole^{-1}),[9] and less than that for solutions of dichlorotriphenoxyphosphorane ($\Lambda_{m,\infty} = 105$ ohm^{-1} cm.^{2} mole^{-1}).[4] Thus the high conductance of these solutions leads to the conclusion that in acetonitrile, dichlorotristrifluoromethylphosphorane ionises with the probable occurrence of solvation of the ions. The mode of ionisation has not been determined directly, but by analogy with phosphorus pentachloride and pentabromide,[3,8] and dibromotriphenoxyphosphorane,[4] the ionisation occurring in the solution may be of the overall form,

Conductance of dichlorotristrifluoromethylphosphorane in acetonitrile at 15°.

c_m (mole l.$^{-1}$)	0·0248	0·0375	0·0515	0·0704	0·1492	0·2313
$10^4\kappa$ (ohm^{-1} cm.$^{-1}$)	12·19	16·46	21·41	27·17	27·00	29·64
Λ_m (ohm^{-1} cm.^{2} mole^{-1})	49·2	43·9	41·6	38·6	18·1	12·8

$$2P(CF_3)_3Cl_2 \rightleftharpoons P(CF_3)_3Cl^+ + P(CF_3)_3Cl_3^-$$

In solution, molecular equilibrium of the type,

$$P(CF_3)_3Cl_2 \rightleftharpoons P(CF_3)_3 + Cl_2$$

cannot be excluded, but the products of such a dissociation could not account for the high value of conductance since tristrifluoromethylphosphine and halogens are non-conductors in acetonitrile.

Conductometric titration of an acetonitrile solution of dichlorotristrifluoromethylphosphorane with an acetonitrile solution of water resulted in a steep drop in specific conductance from $1{\cdot}3 \times 10^{-3}$ to $2{\cdot}5 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$ at mole ratio 1 : 1. Thereafter the conductance rose very slowly as further volumes of the aqueous acetonitrile were added. This result is in accord with the accepted mode of hydrolysis of dichlorotristrifluoromethylphosphorane:

$$P(CF_3)_3Cl_2 + H_2O \rightleftharpoons P(CF_3)_3O + 2HCl$$

and precludes the possibility that the high values of the conductance of the phosphorane solutions are due to traces of moisture in the measuring system. The stability of acetonitrile as a solvent for $PCl_2(CF_3)_3$ has been demonstrated by recovery of the solute after 24 hours' standing.

The variation of conductance with time is an interesting but not unique feature of this system. A similar drift in conductance has been observed by Popov and Deskin [10] in acetonitrile solutions of iodine halides, where the effect is thought to be due to a slow

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[7] Popov and Skelly, *J. Amer. Chem. Soc.*, 1954, **76**, 5309.
[8] Harris and Payne, *J.*, 1956, 4617.
[9] *Idem*, unpublished results.
[10] Popov and Deskin, *J. Amer. Chem. Soc.*, 1958, **80**, 2976.

conversion of the solvated covalent molecule into a solvated ion-pair: $CH_3{\cdot}CN,IX \longrightarrow CH_3{\cdot}CNI^+X^-$. The "slow ionisation" of dichlorotristrifluoromethylphosphorane may be due to a similar type of process in which a change from a covalent molecule to an ion-pair occurs, and it has been shown that dichlorotrifluorophosphorane (PF_3Cl_2) behaves in much the same way.[11]

The conductance of trichlorobistrifluoromethylphosphorane in acetonitrile was studied under the same conditions as applied to dichlorotristrifluoromethylphosphorane. In this case, however, the values of conductance were about fifty times lower ($\Lambda_{m,\infty} < 1$). This compound must therefore, in relation to the other PX_nHal_{5-n} derivatives so far discussed, be regarded as a non-conductor in acetonitrile.

The difference in behaviour of the two phosphoranes under discussion, when dissolved in an ionising medium, may possibly be connected with differences between the structures of the covalent molecules. Although a direct structural determination has not been carried out, the molecule of trichlorobistrifluoromethylphosphorane appears, from the absorption in the carbon–fluorine stretching region of its infrared spectrum, to have the symmetrical trigonal bipyramidal structure in which the apices are occupied by the trifluoromethyl groups. It has also been postulated that ionisation of phosphorus pentahalides in a suitable environment occurs through a mechanism involving ionisation of the apical bond.[12,13] This, together with the fact that the CF_3^- ion has not been observed in any system, appears to explain the non-ionic behaviour of trichlorobistrifluoromethylphosphorane. The infrared spectrum of the dichloro-analogue does not lead to the assignment of a definite structure to the compound. It seems probable that there is present a mixture of configurations, at least one of which contains an apical phosphorus–chlorine bond which is the site of ionisation.

Attempts to prepare dibromotristrifluoromethylphosphorane were not successful. However, there is evidence to suggest that in acetonitrile an ionic compound of composition $P(CF_3)_3,Br_2$ does exist, since the stepwise addition of bromine to an acetonitrile solution of $P(CF_3)_3$ causes the conductance of the latter to increase steadily until the mole ratio 1 : 1 is reached: thereafter, the conductance of the solution rises only slowly. This behaviour resembles closely that of the system phosphorus tribromide–bromine (leading to PBr_5),[8] but at the 1 : 1 ratio the molar conductance is higher ($\Lambda_m = 9{\cdot}75$ ohm^{-1} cm.^{2} mole^{-1} at molar concentration 0·20; PBr_5, $\Lambda_m = 1{\cdot}0$ at molar concentration 0·20 [9]).

EXPERIMENTAL

The trifluoromethylphosphorus compounds were prepared from the autoclave reaction of red phosphorus and trifluoroiodomethane.[5,14] This yielded, after separation by fractionation *in vacuo* and fractional distillation, tristrifluoromethylphosphine, iodobistrifluoromethylphosphine, and di-iodotrifluoromethylphosphine. The last two compounds were converted into the more stable chloro-derivatives by reaction with silver chloride. The compounds were handled in a vacuum system and a nitrogen-filled dry-box.

Dichlorotristrifluoromethylphosphorane and trichlorobistrifluoromethylphosphorane were prepared by addition of 1 mole of chlorine to 1 mole of tristrifluoromethylphosphine and 1 mole of chlorobistrifluoromethylphosphine, respectively.[5,6] A modified method of purification was here employed to yield analytically pure materials. This involved fractionation *in vacuo*, through suitably cooled traps. Since both of the phosphoranes have an appreciable vapour pressure at room temperature they may be handled conveniently in a vacuum system. The m. p.s were measured *in vacuo* in a Stock-type plunger apparatus: $P(CF_3)_3Cl_2$, m. p. 24·0—25·5° (previous value, 20·5° [5]); $P(CF_3)_2Cl_3$, m. p. −26·0° to −25·0° Extrapolation of the vapour-pressure curve for dichlorotristrifluoromethylphosphorane gave b. p. 107°, compared with the earlier value of 94°. Pure anhydrous acetonitrile suitable for the conductance experiments

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[11] Kennedy and Payne, *J.*, in the press.

[12] Siebert, *Z. anorg. Chem.*, 1951, **265**, 303.

[13] Kolditz, *ibid.*, 1957, **293**, 147.

[14] Bennett, Brandt, Emeléus, and Haszeldine, *Nature*, 1950, **166**, 225.

was prepared by Smith and Witten's method.[15] The purified product had κ 10^{-7} ohm^{-1} cm.$^{-1}$ at 25°.

Conductance Experiments.—For these measurements, use was made of a small dipping-electrode type of cell which was adapted to enable the introduction of solute and solvent by distillation *in vacuo.* The electrodes were of smooth platinum and the cell constant was 0·8233 cm.$^{-1}$ (electrodes *ca.* 1 cm. apart; minimum capacity, 2 ml. of solution). Values of conductance were measured by using the Wheatstone bridge apparatus described by Haszeldine and Woolf,[16] or, in cases where a portable bridge was more suitable, a Mullard Conductance Bridge Type E7566. The conductance cell was placed in a thermostat below room temperature, since throughout the experiment the cell was kept evacuated.

Conductometric Titration.—The same conductance cell was used for this experiment and contained the acetonitrile solution of tristrifluoromethylphosphine to be titrated. Successive additions of known weights of the titrant (bromine) were added to the cell by distillation *in vacuo*, and the conductance was measured when equilibrium had been attained following each addition of bromine. This experiment was performed at room temperature.

Infrared Spectra.—The spectra were studied in the region 4000—400 cm.$^{-1}$ by use of a Perkin-Elmer Model 21 double-beam spectrometer fitted with sodium chloride and potassium bromide prisms. The compounds were examined as vapours in a 10 cm. cell with sodium chloride or potassium bromide windows. Values of frequencies of absorption and a qualitative estimate of their intensity are as follows:

$P(CF_3)_3Cl_2$, 2285w, 2250w, 1327m, 1280m, 1227vs, 1201vs, 1186vs, 1148vs, 1133vs, 1096vs, 756m, 596s, 527s, 502s.

$P(CF_3)_2Cl_3$, 2280w, 1326w, 1273m, 1262m, 1226m, 1182vs, 1147vs, 1017w, 790w, 741w, 690w, 613w, 585vs, 529vs.

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[15] Smith and Witten, *Trans. Faraday Soc.*, 1951, **47**, 1304.

[16] Haszeldine and Woolf, *Chem. and Ind.*, 1950, 544.