885. *Non-aqueous Solutions of Phosphorus Pentabromide.*

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Solutions of phosphorus pentabromide in acetonitrile are electrolytically conducting; the values of molar conductance are reported. The ions present are PBr_4^+ and PBr_6^-. By cryoscopy it has been shown that the system phosphorus tribromide–bromine in nitrobenzene can be described by two equilibria, involving PBr_5 and PBr_7 species.

In continuation of our studies [1, 2] on phosphorus(V) halides, we have investigated non-aqueous solutions of phosphorus pentabromide and the system phosphorus tribromide–bromine, to obtain information about the nature of the solute species. This is of interest since it has been established independently by Powell and Clark [3] and Van Driel and McGillavry [4] that the lattice of crystalline phosphorus pentabromide is built up from [PBr_4] and [Br] units, which are considered as unipositive and uninegative ions respectively. It would be expected therefore that phosphorus pentabromide, in suitable solvents (chemically inert and of high dielectric constant), would behave as a salt and produce electrolytically conducting solutions. This is so for phosphorus pentabromide in arsenic trichloride,[5] sulphur dioxide,[5] bromine,[6] and nitrobenzene.[7] Some data are given in the literature of the molar conductance of these solutions, but the suggested schemes of ionisation are essentially hypothetical and involve a P^{5+} or solvated P^{5+} cation. Bromine solutions of phosphorus pentabromide have been investigated by Finkelstein,[8] who found that electrolysis suggested the presence of a complex positive ion on account of the tendency of phosphorus pentabromide to polymerise in bromine solution.[9]

The molecular dissociation of phosphorus pentabromide, $PBr_5 \rightleftharpoons PBr_3 + Br_2$, as it occurs in solvents of low dielectric constant, has also been studied. Kastle and Beatty [10] estimated by colorimetry that the degree of dissociation of phosphorus pentabromide, in carbon disulphide and carbon tetrachloride, lay between 90 and 100%. Benzene solutions of phosphorus pentabromide were studied cryoscopically by Oddo and Tealdi,[11] who found that the dissociation was complete. More recently, Popov and his co-workers [12, 13] have studied phosphorus pentabromide in carbon tetrachloride cryoscopically and estimated the molar extinction coefficient of phosphorus pentabromide and deduced a value of about 50% for the degree of dissociation.

In the conductance experiments herein described, the solvent used was acetonitrile, which has very favourable dielectric properties; in addition its behaviour as a Lewis base frequently results in ion-stabilisation. It was thought that, in this solvent, phosphorus pentabromide would be dissociated ionically to a considerable degree.

Results and Discussion

The results of conductometric titration for the system phosphorus tribromide–bromine in acetonitrile are shown in the Figure. The conductances of bromine and phosphorus tribromide in acetonitrile have been determined separately; both are virtually non-conductors in this solvent (Br_2, $\Lambda_m = 0{\cdot}22$ ohm^{-1} cm.^{2} mole^{-1}, $c_m = 0{\cdot}033$; PBr_3, $\Lambda_m = 1{\cdot}78$ ohm^{-1} cm.^{2} mole^{-1}, $c_m = 0{\cdot}025$). It is therefore evident that the reaction of bromine and phosphorus tribromide in acetonitrile is accompanied by the production of ions. The form of the

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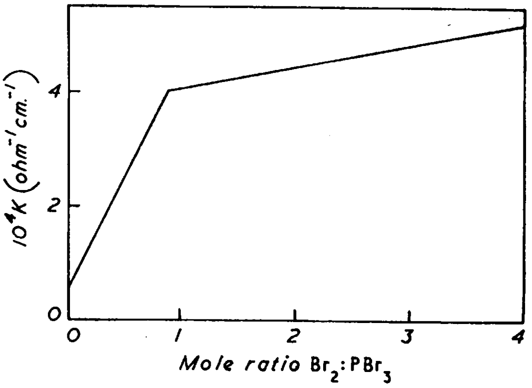
[1] Payne, *J.*, 1953, 1052.
[2] Harris and Payne, *J.*, 1956, 3038.
[3] Powell and Clark, *Nature*, 1940, **145**, 971.
[4] Van Driel and MacGillavry, *Rec. Trav. chim.*, 1943, **62**, 167.
[5] Walden, *Z. phys. Chem.*, 1903, **43**, 434.
[6] Plotnikov, *ibid.*, 1904, **48**, 230.
[7] Finkelstein, *ibid.*, 1925, **115**, 306.
[8] *Idem, ibid.*, 1927, **125**, 229.
[9] *Idem, ibid.*, 1923, **105**, 10.
[10] Kastle and Beatty, *Amer. Chem. J.*, 1899, **21**, 392.
[11] Oddo and Tealdi, *Gazzetta*, 1903, **33**, 435.
[12] Popov and Schmorr, *J. Amer. Chem. Soc.*, 1952, **74**, 4672.
[13] Popov and Skelly, *ibid.*, 1954, **76**, 3916.

graph, with its abrupt change of slope at a mole ratio of 1, indicates the presence of an ionic complex with the composition PBr_3,Br_2 (*i.e.*, phosphorus pentabromide).

Considerable interest attaches to the mole ratios 2 and 3 in view of the reported existence of hepta- and ennea-bromides of phosphorus.[14, 15] The absence of inflections in the curve at these ratios suggests that the solution does not contain any new type of ion derived from a hepta- or ennea-bromide, but is simply a solution of phosphorus pentabromide plus excess of bromine.

If phosphorus pentabromide were represented in solution by the same ions as in the solid state, PBr_4^+ and Br^-, then the conditions ('onium type cation [16] in acetonitrile solution [17]) would favour the formation of the tribromide ion on the addition of further amounts of bromine after mole ratio 1, and this would be reflected in the graph by a break at the mole ratio corresponding to PBr_7. However the absence of an inflection on the graph beyond mole ratio 1 seems to indicate that the process



$$PBr_3 \xrightarrow{Br_2} PBr_3,Br_2 \longrightarrow PBr_4^+ + Br^- \xrightarrow{Br_2} PBr_4^+ + Br_3^-$$

is not taking place. It therefore appears reasonable to suggest that phosphorus pentabromide does not ionise in acetonitrile in the manner shown in this scheme. It is possible that the ions present are analogous to those occurring in acetonitrile solutions of phosphorus pentachloride,[1] *viz.*, PCl_4^+ and PCl_6^-, and this point has been pursued by quantitative electrolysis experiments described later.

It is concluded from the result of the conductometric titration that the equilibrium

$$PBr_3 + Br_2 \rightleftharpoons PBr_5 \rightleftharpoons \text{ions}$$

is rapidly established.

The conductances of pure phosphorus pentabromide in acetonitrile, measured at different concentrations, are shown in Table 1. The specific conductance (κ) of the solution increased slightly with time ($2{\cdot}2 \times 10^{-7}$ ohm^{-1} cm.$^{-1}$ hr.$^{-1}$), and the value used to calculate the molar conductance (Λ_m) was obtained by extrapolating a plot of the specific conductance against time to $t = 0$. A conductance drift was observed by Popov and Skelly [18] with acetonitrile solutions of inter-halogen compounds.

TABLE 1. *Conductance of phosphorus pentabromide in acetonitrile at* 25°.

c_m (mole l.$^{-1}$)	0·0152	0·0195	0·0296	0·0729
$10^4\kappa$ (ohm^{-1} cm.$^{-1}$)	2·12	2·78	3·63	5·67
Λ_m (ohm^{-1} cm.^{2} mole^{-1})	13·95	14·25	12·26	7·86

[14] Kastle and Beatty, *Amer. Chem. J.*, 1900, **23**, 505.

[15] Biltz and Jeep, *Z. anorg. Chem.*, 1927, **162**, 32.

[16] Sidgwick, " The Chemical Elements and Their Compounds," Oxford Univ. Press, London, 1950. p. 1194.

[17] Popov and Skelly, *J. Amer. Chem. Soc.*, 1954, **76**, 5309.

[18] *Idem, ibid.*, 1955, **77**, 3724.

The molar conductance of phosphorus pentabromide in acetonitrile varies (approximately) linearly with the square root of the concentration. At values of c_m less than about 0·015M, the values obtained for Λ_m were irregular and unreproducible. This is presumably due to the enhanced influence of traces of impurities at such low concentrations. The molar conductance at a given concentration varied slightly with the batch of acetonitrile, but within the same batch the values formed a consistent series. Solutions of phosphorus pentabromide in acetonitrile had a positive temperature coefficient within the range 0—25°.

It is possible that in acetonitrile phosphorus pentabromide might also undergo molecular dissociation to some extent. These conducting solutions would then also contain molecules of phosphorus tribomide and bromine. That these molecules do not contribute significantly to the conductance of the solutions has already been demonstrated.

Clearly, then, we must regard the conductance of these acetonitrile solutions as being a consequence of the electrolytic behaviour of phosphorus pentabromide. The general stability of acetonitrile as a solvent for phosphorus pentabromide is supported by the fact that cooling of such a solution yields analytically pure phosphorus pentabromide. There is no evidence for the formation of solid solvates. Phosphorus pentachloride behaves similarly in this respect.[1]

Two modes of ionisation of phosphorus pentabromide appear plausible. First, ionisation might involve the ions present in the solid state, thus :

$$PBr_5 \rightleftharpoons PBr_4^+ + Br^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

On the other hand, as suggested earlier, it may be analogous to that of phosphorus pentachloride in the same solvent : [1]

$$2PBr_5 \rightleftharpoons PBr_4^+ + PBr_6^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

To determine whether one of these schemes is correct, the solution is electrolysed by a known quantity of direct current, and the changes in composition of the solution at each electrode are measured. If ΔBr = increase in g.-atoms of Br at cathode, ΔP = increase in g.-atoms of P at anode, t_+ = transport number of cation, and x = quantity of current passed (in Faradays), then for ionisation (i), provided no phosphorus or bromine is lost from the solution during electrolysis,

$$\Delta Br = x(5t_+ - 1) \qquad \Delta P = -xt_+$$

and for ionisation (ii),

$$\Delta Br = x(10t_+ - 6) \qquad \Delta P = x(1 - 2t_+)$$

Values of t_+ can thus be obtained by substitution of the observed Δ values. This was done, and it was found that a concordant set of results was obtained for t_+ when the experimental data were inserted in the equations for ionisation (ii) ($t_+ = 0{\cdot}55,\ 0{\cdot}54,\ 0{\cdot}44$). Phosphorus pentabromide therefore ionises in acetonitrile to yield a hexabromophosphate anion, whereas in the solid state a simple bromide ion is involved.

Preliminary experiments have shown that phosphorus pentabromide and stannic bromide form two ionic complexes, $PBr_5,SnBr_4$ and $(PBr_5)_2,SnBr_4$, stable in acetonitrile solution. There is no evidence on the nature of the ions present in these solutions, but by analogy with the phosphorus pentachloride–stannic chloride system [19] it seems probable that the 2 : 1-compound ionises to produce the ions PBr_4^+ and $SnBr_6^{2-}$. No attempt has yet been made to isolate these complexes.

Solutions of phosphorus pentabromide in nitrobenzene have been shown by Finkelstein [7] to be very poor conductors of electricity ($\Lambda_m = 0{\cdot}224$ ohm^{-1} cm.^{2} mole^{-1}; $c_m = 0{\cdot}147$); hence it is inferred that electrolytic dissociation of phosphorus pentabromide in this solvent is negligible. A cryoscopic investigation of the phosphorus tribromide–bromine–nitrobenzene system should therefore indicate the extent of molecular dissociation of phosphorus pentabromide in nitrobenzene. Freezing points were determined, first for phosphorus tribromide in nitrobenzene, and then for this solution containing added amounts of bromine.

[19] Payne, unpublished results.

The values bore a linear relationship to the mole ratio $Br_2 : PBr_3$. Thus by graphical interpolation the freezing point of the system could be obtained for integral values of the mole ratio, and thus the number of particles present in the solution at mole ratios 1, 2, and 3 could be calculated. To simplify the calculations these values were used in all subsequent calculations.

Consideration was given to the equilibria

$$PBr_3 + Br_2 \rightleftharpoons PBr_5 \quad \text{. . . . .} \quad (1)$$

$$PBr_3 + 2Br_2 \rightleftharpoons PBr_7 \quad \text{. . . . .} \quad (2)$$

$$PBr_3 + 3Br_2 \rightleftharpoons PBr_9 \quad \text{. . . . .} \quad (3)$$

For each of these, expressions for the association constant at mole ratios 1, 2, and 3 were derived. Substitution of the experimental results in the nine equations so obtained gave the values of association constant shown in Table 2 (the subscript preceding a symbol denotes the mole ratio, and that following the symbol denotes the equilibrium being considered).

TABLE 2. *Association constants in the system* PBr_3–Br_2–$Ph{\cdot}NO_2$

PBr_5	PBr_7	PBr_9
${}_1K_1 = 2{\cdot}208$	${}_1K_2 = 16{\cdot}112$	${}_1K_3 = 164{\cdot}20$
${}_2K_1 = 2{\cdot}246$	${}_2K_2 = 8{\cdot}289$	${}_2K_3 = 41{\cdot}13$
${}_3K_1 = 2{\cdot}731$	${}_3K_2 = 5{\cdot}570$	${}_3K_3 = 17{\cdot}91$

From these results it is clear that the equilibrium $PBr_3 + Br_2 \rightleftharpoons PBr_5$ describes the system more closely than any other single equilibrium.

The possibility of two or more equilibria being involved simultaneously was considered, and it became clear that the experimental observations could best be interpreted by taking into account equilibria (1) and (2). The values of equilibrium constants were calculated to be:

for equilibrium (1), $K_{5{\cdot}7^\circ} = 2{\cdot}018$ mole^{-1} litre;

,, ,, (2), $K_{5{\cdot}7^\circ} = 1{\cdot}448$ mole^{-2} litre^2.

The degrees of association at the various mole-ratios are given in Table 3 and it is seen that these are relatively low. Thus it can be concluded that the degree of molecular dissociation of phosphorus pentabromide in nitrobenzene is fairly high (*ca.* 90%).

TABLE 3. *Degrees of association in the system* PBr_3–Br_2–$Ph{\cdot}NO_2$, *consisting of equilibria* (1) *and* (2)

Mole-ratio $PBr_3 : Br_2$	PBr_5 equilibm.	PBr_7 equilibm.	α_1/α_2
1 : 1	${}_1\alpha_1 = 0{\cdot}1134$	${}_1\alpha_2 = 0{\cdot}005208$	${}_1\alpha_1/{}_1\alpha_2 = 21{\cdot}77$
1 : 2	${}_2\alpha_1 = 0{\cdot}2033$	${}_2\alpha_2 = 0{\cdot}01875$	${}_2\alpha_1/{}_2\alpha_2 = 10{\cdot}84$
1 : 3	${}_3\alpha_1 = 0{\cdot}2709$	${}_3\alpha_2 = 0{\cdot}03769$	${}_3\alpha_1/{}_3\alpha_2 = 7{\cdot}24$

Initial PBr_3 concentration = 0·07306M.

This result indicates that solutions of phosphorus pentabromide in nitrobenzene do contain PBr_5 entities and to a smaller extent PBr_7 entities. The question of the structure of these units arises, but cannot yet be answered with certainty. The PBr_5 unit may be either a trigonal bipyramidal structure or an ion-pair. The PBr_7 unit may be regarded as a complex formed between the PBr_5 entity and a bromine molecule through the latter's donating a pair of its unbonded electrons to the phosphorus atom producing a six-co-ordinated phosphorus atom with the same electronic structure as in PBr_6^-. An ion-pair formulation, $[PBr_4^+][Br_3^-]$, is also possible for PBr_7, but it should be noted that PBr_3,Br_4 could not be recognised as an ionic complex in acetonitrile solution.

A cryoscopic investigation of the system phosphorus tribromide–bromine in carbon tetrachloride would have been valuable in view of the spectrophotometric studies of solutions of phosphorus pentabromide in this solvent,[12, 13] but this was not possible because of the low solubility of the pentabromide (or more correctly $PBr_5,2CCl_4$).

EXPERIMENTAL

Purification of Materials.—The purification of acetonitrile for conductance measurements has already been described,[2] and the preparation of pure nitrobenzene is given in the preceding paper. Bromine and phosphorus tribromide were purified by fractionation in a vacuum, and the pure material was stored in sealed ampoules. Phosphorus pentabromide was purified by recrystallisation (cf. Van Driel and Gerding [21]). The crude material (10 g.) was dissolved in pure nitrobenzene (50 c.c.) at 60°. A fine, white, insoluble residue remained and this was removed by filtering the solution through a sintered-glass filtration apparatus (designed to produce anhydrous conditions). The solution was cooled, and the phosphorus pentabromide appeared as fine yellow crystals which were filtered off. The crystals were washed with sodium-dried ether (100 c.c.) and stored in a ground-glass, stoppered tube kept in a desiccator (Found: Br, 92·83, 93·30; P, 7·18. Calc. for PBr_5: Br, 92·81; P, 7·19%).

Analysis.—The solid material and solutions of phosphorus pentabromide were hydrolysed by boiling with 2N-sodium hydroxide solution. Aliquot portions of the resulting solution were then analysed separately for bromide and phosphate ion. The former was determined by Volhard's method, and the latter by precipitation as magnesium ammonium phosphate, which was ignited and weighed as pyrophosphate.

Conductometric Analysis, Conductance Measurements, Quantitative Electrolysis and Cryoscopy.—The apparatus and techniques were similar to those described in previous papers.[1, 2, 20]

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[20] Harris and Payne, *J.*, preceding paper.

[21] Van Driel and Gerding, *Rec. Trav. chim.*, 1941, **60**, 869.