884. *The Reaction between Phosphorus Trichloride and Bromine. Part I.*

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A cryoscopic study of the system phosphorus trichloride–bromine in nitrobenzene has shown the existence of two equilibria involving PX_5 and PX_7 species. Results of the conductometric titration of nitrobenzene and phosphoryl chloride solutions of phosphorus trichloride and bromine are given and discussed. The compositions of two solids obtained from carbon tetrachloride solution of the components are reported.

The recent publication by Popov and his co-workers [1] on the phosphorus trichloride–bromine system prompts us to publish the following account of our work on this system. Further studies are intended.

Studies of the reaction between bromine and phosphorus trichloride can be grouped in three historical periods. During the first two (1847—1886 and 1928—1934) the aim was primarily the synthesis of definite bromide-chlorides of phosphorus(V), but despite numerous investigations, the reaction was far from being understood or the products clearly identified, and this was the position at the commencement of the third period in 1951. Since then, three groups, including ourselves, have sought to clarify the position, for it appeared that the evidence for the many individual compounds which had been reported was scanty and often contradictory. Various compositions of the solid phases, including PCl_3Br_2, have been reported, but, in general, the analytical data are poor and there is much confusion concerning the properties.

More recently, Fialkov and Kuz'menko [2a] have examined the phosphorus trichloride–bromine system by thermal analysis and have recognised in the phase diagram two maxima corresponding to the compositions PCl_3Br_4 and PCl_3Br_{18}. They have also reported the isolation of compounds corresponding to these compositions. It appears that the liquid phases corresponding to these compositions are good conductors of electricity ($\kappa_{35^\circ} = 1{\cdot}82 \times 10^{-4}$ and $\kappa_{25^\circ} = 8{\cdot}01 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$ respectively). However, in the solid state only the phase with composition PCl_3Br_{18} has an appreciable conductance ($\kappa_{20^\circ} = 1{\cdot}53 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$). Further work [2b] on the viscosity–composition relationships in this system showed the possible existence of another compound, PCl_3Br_8.

Conductance and transport experiments were carried out on the system in nitrobenzene, and on the basis of the results the compounds are assigned quasi-phosphonium structures, $[PCl_3Br]^+[Br(Br_2)_n]^-$, where n has values of 1, 2, and 8 in the compounds described. A series of equilibria between these forms is envisaged in which the higher conductances observed, as the ratio of bromine to phosphorus trichloride is increased, are attributed to the increasing concentration of a species undergoing ready electrolytic dissociation. However, the very high effective concentration employed, *e.g.*, 0·4—50M in nitrobenzene, makes comparison with other workers' results difficult and uncertain. Popov and his co-workers [1] have found that the system does not yield stable solid phases corresponding to simple formulæ. For example, direct reaction of phosphorus trichloride and bromine led to an unstable aggregate of composition $PCl_{3{\cdot}0}Br_{5{\cdot}7}$, which under reduced pressure yielded a stable mixed halide with the empirical formula $PCl_{4{\cdot}67}Br_{0{\cdot}33}$ (shown to have a face-centred cubic cell corresponding to $P_{12}Cl_{56}Br_4$ per unit cell). It is suggested that this unit cell is built up from 8 PCl_4^+, 4 PCl_6^-, and 4 Br^- units. Absorption spectra of phosphorus trichloride–bromine mixtures in carbon tetrachloride and in nitrobenzene have not revealed the presence of complexes in these solvents.

We have examined the system in solvents which, from previous work with phosphorus pentachloride and pentabromide,[3,4] are known to be suitable for this type of compound. However, preliminary experiments showed that acetonitrile, although suitable for the

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[1] Popov, Geske, and Baenziger, *J. Amer. Chem. Soc.*, 1956, **78**, 1793.

[2] Fialkov and Kuz'menko, *Zhur. obshchei Khim.*, (*a*) 1951, **21**, 433; (*b*) 1952, **22**, 1290, 1335.

[3] Payne, *J.*, 1953, 1052.

[4] Harris and Payne, following paper.

simple pentahalides, is not stable with the phosphorus trichloride–bromine system. The course of conductometric titrations of phosphorus trichloride against bromine both in nitrobenzene and in phosphoryl chloride solution showed a definite increase in conductance but no marked inflections. In phosphoryl chloride solutions the molar conductances calculated at definite mole ratios were not substantially greater than those of the phosphorus trichloride and bromine separately. At the concentrations employed (*ca.* 0·015M) it is clear that in neither of these solvents is the stabilisation of an ionic species favoured; however, the slight increase in conductance observed in the course of the titrations is more than would be expected for simple mixing of the component solutions without any interaction.

In view of the low electrolytic conductances of these solutions we studied them cryoscopically, and ignored ionisation in interpreting the results. Of the solvents carbon tetrachloride, phosphoryl chloride, and nitrobenzene, only the last was suited to such a study. The freezing-point depressions, determined for various ratios of phosphorus trichloride to bromine and plotted against the mole ratio, gave a straight line and thus depressions were obtained for the whole-number ratios of 1 : 1, 1 : 2, and 1 : 3 of phosphorus trichloride to bromine. From these were calculated values of the equilibrium constants of various equilibria considered singly and in combination. The results could be completely described by the two equilibria:

$$PX_3 + X_2 \rightleftharpoons PX_5 \qquad \text{(i)}$$

$$PX_3 + 2X_2 \rightleftharpoons PX_7 \qquad \text{(ii)}$$

where X is chlorine or bromine in this treatment. The corresponding equilibrium constants were, for (i), $K_{5\cdot70^\circ} = 1{\cdot}43$ mole^{-1} l., and, for (ii), $K_{5\cdot70^\circ} = 5{\cdot}45$ mole^{-2} l.^{2}. Table 1 shows the values of α_1 and α_2, the degrees of association corresponding to the equilibria (i) and (ii) at whole-number mole ratios.

TABLE 1.

Mole-ratio $PCl_3 : Br_2$	α_1	α_2	α_1/α_2
1 : 1	0·09036	0·02492	3·625
1 : 2	0·1560	0·08379	1·861
1 : 3	0·1940	0·1552	1·249

Concentration of PCl_3 = 0·0839M.

No other equilibria considered yielded constant values of the equilibrium constants with varying mole ratio. Thus the nitrobenzene solution contains, in addition to phosphorus trichloride and bromine and exceedingly small amounts of ionised species, equilibrium amounts of a PX_5 and a PX_7 species. The failure [1] of the spectrophotometric method to reveal the existence of these complexes is an indication of the close similarity of the spectra of these complexes to that of the free halogen and also an indication of the looseness of the binding in the complexes.

Attempts to repeat the isolation of solid phases in this system were carried out by using solutions of the components in suitable solvents. Only in the system phosphorus trichloride–bromine–carbon tetrachloride was solid material containing phosphorus halide obtained and this contained carbon tetrachloride of crystallisation. The analytical data correspond fairly well to the compositions PCl_3Br_7,CCl_4 and $PCl_3Br_7,2CCl_4$. (Thanks are due to a Referee for drawing attention to this formulation.) However, the analytical figures for chlorine and bromine are not very reliable and the possibility that these compounds are members of the PCl_3,nBr_2 series previously reported by Fialkov and Kuz'menko [2a] cannot be excluded. Attempts to remove the carbon tetrachloride led to loss of bromine. The second compound resulted from an attempt to prepare PCl_3Br_4 by Fialkov's method.[2a]

Little is known of the factors which influence the stability of molecular complexes such as PX_5 and PX_7 in nitrobenzene solution. Craig *et al.* [6] have suggested that the use of 3*d*

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[5] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

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

orbitals by phosphorus will only be likely when the group is effectively strongly electronegative, in keeping with the known stability of the simple phosphorus pentahalides. The formation of the complexes in the phosphorus trichloride–bromine system would not be expected to involve a simple molecule, with bonds involving 3*d* orbitals, in view of the electronegativity of bromine and the well-substantiated instability of mixed halides of both ter- and quinque-valent phosphorus. These mixed halides disproportionate readily as has been observed by Popov in this particular system.[1] The experiments described here cannot distinguish a disproportionation reaction with certainty, but the low electrolytic conductance in the nitrobenzene (Λ_m = *ca.* 0·2; cf. Λ_m for phosphorus pentachloride = *ca.* 3 at comparable concentrations) shows that conversion into phosphorus pentachloride, if it occurs at all, must be to an extent less than about 10%. The possibility that a system involving phosphorus tribromide and chlorine may be set up to any appreciable extent is eliminated by the fact that the colour of the solution did not change appreciably, in the course of the experiment, from that which would be expected of a solution of pure bromine of corresponding concentration. From a general survey of all the compounds reported in the phosphorus trichloride–bromine system under a variety of conditions, it is clear that the ability of bromine, in contrast to chlorine and fluorine, to form polybromides is an important feature. Whether this class of compound contains a polyhalogeno-anion and a phosphorus halogeno-cation, as suggested by Fialkov and his co-workers, or a more complex but less definite formulation as in a loose association of a trichloride molecule and one or more bromine molecules, we hope to decide by further work.

EXPERIMENTAL

Materials.—A commercial specimen of phosphorus trichloride was fractionated at a reflux ratio of about 15 to 1 in a two-foot column packed with Fenske rings. The fraction, b. p. 74·4—74·5°, was taken for further purification by repeated fractionation in a vacuum line. The pure compound was stored in sealed ampoules. Bromine ("AnalaR") was carefully fractionated in an all-glass system *in vacuo* and stored in sealed ampoules. Acetonitrile was purified by Smith and Witten's method.[7] Carbon tetrachloride ("AnalaR") was distilled from phosphoric oxide before use. 1 : 4-Dioxan was refluxed for 14 hr. over sodium, then distilled and used directly (b. p. 101·0°). Ethylene dichloride (B.D.H.) was shaken with portions of concentrated sulphuric acid until the acid layer remained colourless. This was followed by washing with water and then with several portions of a sodium hydrogen carbonate solution. After preliminary drying (Na_2SO_4), the material was further dried by azeotropic distillation, and the dry fraction then refluxed with an excess of phosphoric oxide and finally distilled twice from further portions of phosphoric oxide (b. p. 83—83·5°/755 mm.). Nitrobenzene was washed with 5N-sulphuric acid and then with water, followed by repeated washings with saturated aqueous sodium hydroxide solution until the aqueous layer was colourless. The washing was completed by repeated extraction with water until the aqueous layer was neutral to litmus. The nitrobenzene was stored for several days over 14—20-mesh calcium chloride and then after filtration was distilled at atmospheric pressure (b. p. 208—210°). Further purification was achieved by repeated fractional freezing, and the liquid was finally distilled *in vacuo*, and a middle fraction taken (b. p. 64—68°/*ca.* 2 mm.). Phosphoryl chloride was distilled several times through a short column, and the middle fraction of the final distillate was taken for use (b. p. 105·4—105·8°).

Conductometric Titrations.—The experiments were carried out in the apparatus described previously.[7] Solutions were prepared by breaking a bulb containing a known weight of the solute under a known weight of solvent. In each case the bromine solution was the titrant. The conductance rose on addition of the bromine solution and the resulting value was then observed to be constant for at least 1 hr. Such reaction as occurs is thus instantaneous and the resulting products are stable within the time of observation. With nitrobenzene as solvent values for the molar conductance measured at room temperature were, for mole ratio phosphorus trichloride to bromine 1 : 1, $\Lambda_m = 0{\cdot}1088$ ohm^{-1} cm.^{2} mole^{-1}, $c_m = 0{\cdot}01837$; for 1 : 2, $\Lambda_m = 0{\cdot}2132$, $c_m = 0{\cdot}01642$; for 1 : 3, $\Lambda_m = 0{\cdot}3305$, $c_m = 0{\cdot}01483$, and for 1 : 4, $\Lambda_m = 0{\cdot}4362$, $c_m = 0{\cdot}01353$. For phosphorus trichloride alone $\Lambda_m = 0{\cdot}0099$ at $c_m = 0{\cdot}01837$ and for bromine alone $\Lambda_m = 0{\cdot}056$ at $c_m = 0{\cdot}03608$, measured in nitrobenzene solution at room temperature.

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[7] Harris and Payne, *J.*, 1956, 3038.

With phosphoryl chloride as solvent the values for the molar conductance measured at room temperature were for mole ratio phosphorus trichloride to bromine 1 : 1, $\Lambda_m = 0{\cdot}031$, $c_m = 0{\cdot}0137$, and for 1 : 2, $\Lambda_m = 0{\cdot}046$, $c_m = 0{\cdot}0123$. For phosphorus trichloride alone $\Lambda_m = 0{\cdot}023$, $c_m = 0{\cdot}0244$, and for bromine alone $\Lambda_m = 0{\cdot}013$, $c_m = 0{\cdot}0325$ measured in phosphoryl chloride solution at room temperature.

Cryoscopic Experiments.—The cryoscopic cell was an all-glass modification of the Beckmann apparatus, designed to exclude atmospheric moisture. Three attachments pass through the stopper (a B45 cone) of the apparatus; these are a thermometer pocket, a vertical stirrer guide, and a chute *cum* ampoule breaker for the introduction of known amounts of solute. Stirring is accomplished by means of a coil of thin glass surrounding the thermometer pocket. Attached to the upper end of the stirrer and situated within the stirrer guide is a glass-enclosed soft-iron rod which allows of magnetic operation. The cell, containing solvent (*ca.* 80 ml.), was placed in an air jacket, which was in turn placed in the cooling bath. When the freezing point of pure solvent had been found, phosphorus trichloride was introduced, and the freezing point redetermined. Bromine was then added in stages, and the freezing point of the solution determined after each addition. The contributions from the various postulated equilibria were derived by a graphical treatment of the results. The experimental results are shown in Table 2.

TABLE 2.

Mole ratio, $Br_2 : PCl_3$	0·000	0·4568	0·9261	1·4525	1·8729	2·3004	2·7648	3·0186
F. p. (relative)	5·194°	4·981°	4·786°	4·585°	4·409°	4·250°	4·086°	3·993°

F. p. of pure solvent = 5·684° (relative). F. p. of 0·0839M-PCl_3 solution = 5·194° (relative).

Attempts to prepare an Adduct of Phosphorus Trichloride and Bromine.—Solutions containing phosphorus trichloride and bromine in the mole ratio 1 : 1 were prepared in various solvents (the concentration of these solutions was always about 0·5M). In acetonitrile mixing of the reactants was accompanied by evolution of heat, and on standing the colour of the solution diminished to a pale yellow. Examination showed that reaction with the solvent had occurred. In nitrobenzene no heat was evolved on mixing the reactants and the colour remained undiminished after standing for several weeks. Cooling the solution failed to bring about crystallisation of any solid other than solvent. Similar results were obtained with phosphoryl chloride and ethylene dichloride. 1 : 4-Dioxan gave only a precipitate of the crystalline bromine addition compound, $C_4H_8O_2Br_2$, m. p. 66°, mixed m. p. with an authentic specimen 67—68°. In carbon tetrachloride, on mixing of the reactants, there was no liberation of heat but two deep red layers separated, the lower being slightly the darker. Additional solvent was added until the solution was homogeneous, and the solution cooled to 2°. After 24 hr. dark red crystals had formed in the solution and on the walls of the vessel above the level of the liquid. The crystals had m. p. 15—16°, the same as that of the lower layer observed when the original solution was prepared. The solid was carefully separated from solution without allowing it to melt or to come into contact with atmospheric moisture [Found: P, 3·65; Br, 65·30; Cl, 14·02; CCl_4 (by diff.), 17·03. Calc. for PCl_3Br_7,CCl_4: P, 3·64; Br, 65·77; Cl, 12·51; CCl_4, 18·09%. Calc. for $PCl_3Br_6CCl_4$: P, 4·02; Br, 62·22; Cl, 13·80; CCl_4, 19·96%]. The carbon tetrachloride was liberated and identified on hydrolysis of the solid. Fialkov [2a] describes the preparation, by the direct reaction of an excess of phosphorus trichloride with bromine, of a solid of composition PCl_3Br_4, which could be crystallised from carbon tetrachloride. Careful repetition of the method yielded a dark red solid which on hydrolysis and analysis gave a quantity of carbon tetrachloride corresponding to 29·9% of the original solid and a total halide corresponding to 8·10 ml. of N-silver nitrate per g. of solid (Calc. for $PCl_3Br_7,2CCl_4$: CCl_4, 30·63%; N-$AgNO_3$, 9·96 ml. Calc. for $PCl_3Br_6,2CCl_4$: CCl_4, 33·28%; N-$AgNO_3$, 9·73 ml.). Both solids had low m. p. and readily lost carbon tetrachloride and bromine.

Analyses.—Phosphorus was determined by oxidation of the hydrolysate and the subsequent precipitation of the phosphate as magnesium ammonium phosphate, followed by ignition at 900° to magnesium pyrophosphate. Total halogen was determined by Volhard's method. Bromide in the presence of chloride was determined by the method of Kolthoff and Yutzy.[8]

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[8] Kolthoff and Yutzy, *Ind. Eng. Chem. Anal.*, 1937, **9**, 75.