589. *The Reaction of Triphenyl Phosphite with the Halogens.*

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Conductometric studies in acetonitrile solution have shown that bromine reacts with triphenyl phosphite to yield three successive, distinct ionising systems. The composition corresponding to triphenyl phosphite dibromide produces the ions $[P(OPh)_3Br]^+$ and $[P(OPh)_3Br_3]^-$. Triphenyl phosphite dichloride has been shown to give strongly conducting solutions in acetonitrile. Data on the conductance of these solutions are reported. A study of the triphenyl phosphite–iodine system in acetonitrile has shown the existence of a di-iodide.

The preparation of triphenyl phosphite tetrabromide is described.

ADDITION compounds of trialkyl and triaryl phosphites with halogens, of the type $(RO)_3PX_2$, have been mentioned in the literature from time to time,[1] either as simple compounds or as reaction intermediates. No attempt has previously been made to show directly that any of these compounds exist under certain conditions as essentially ionic species, although this has been postulated in various reaction mechanisms.[2] In particular, the addition compounds of halogens with triphenyl phosphite have been well characterised.[3] The dichloride, dibromide, di-iodide, bromochloride, bromoiodide, and chloroiodide have recently been prepared as crystalline solids.[4] These compounds can be considered as phenoxy-substituted phosphorus pentahalides. Their behaviour in an ionising solvent is important to the understanding of their participation in reactions in synthetic organic chemistry,[4] and also in relation to the known properties of the parent phosphorus pentachloride [5] and pentabromide.[6] It should be made clear that conclusions based on observations of the behaviour of triphenyl phosphite with the halogens are unlikely to be directly applicable to the trialkyl esters.

The electrolytic conductance of triphenyl phosphite dichloride in acetonitrile solution was measured under strictly anhydrous conditions, and the results are shown in the Table.

Conductance at 25° of triphenyl phosphite dichloride in acetonitrile.

c_m (mole l.$^{-1}$)	$10^4\kappa$ (Ω^{-1} cm.$^{-1}$)	Λ_m (Ω^{-1} cm.^{2} mole^{-1})	c_m (mole l.$^{-1}$)	$10^4\kappa$ (Ω^{-1} cm.$^{-1}$)	Λ_m (Ω^{-1} cm.^{2} mole^{-1})
0·0074	7·5	100·8	0·0398	35·5	89·2
0·0211	20·3	95·6	0·0570	42·1	73·8

Pure solvent: $\kappa = 5{\cdot}0 \times 10^{-7}\ \Omega^{-1}$ cm.$^{-1}$.

After a brief initial change whilst the solution reached the temperature of the thermostat bath, the conductance values were constant for 24 hr. The specific conductance had a positive temperature coefficient. In view of the sensitivity of these compounds to moisture, a special study of the conductance of the hydrolysis products, hydrogen chloride and triphenyl phosphate, was undertaken. Both these compounds gave weakly conducting solutions in acetonitrile (at 25° for hydrogen chloride, $\Lambda_m = 0{\cdot}14$, $c_m = 0{\cdot}0349$; for triphenyl phosphate, $\Lambda_m = 0{\cdot}06$, $c_m = 0{\cdot}0986$), and titration of one solution with the other did not increase the conductance. In accordance with these results it was observed that addition of minute traces of water led to a marked fall in conductance of the triphenyl phosphite dichloride solution.

Values of molar conductance bear a linear relationship to the square-root of the concentration down to 0·006M. Below this value the results are unreliable, probably owing to the effect of traces of impurities in the solvent. An extrapolation of the curve obtained by plotting Λ_m against $\sqrt{c_m}$ gives an approximate value of the molar conductance at infinite dilution ($\Lambda_{m,\infty} = 105$).

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[1] Kosolapoff, "Organophosphorus Compounds," Wiley, New York, 1950.

[2] See, *e.g.*, Gerrard, Green, and Phillips, *J.*, 1954, 1148.

[3] Noack, *Annalen*, 1883, **218**, 85; Anschütz and Emery, *ibid.*, 1889, **253**, 105; Autenrieth and Geyer, *Ber.*, 1908, **41**, 146; Anschütz, Boedeker, Broeker, and Wenger, *Annalen*, 1927, **454**, 71.

[4] Coe, Landauer, and Rydon, *J.*, 1954, 2281.

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

[6] Harris and Payne, unpublished work.

The reaction of triphenyl phosphite with bromine is conveniently studied by conductometric titration, since solutions of triphenyl phosphite and bromine in acetonitrile of known concentration are readily prepared. The apparatus used was designed so that the titration could be carried out on a small scale without the solutions' coming into contact with tap-grease or atmospheric moisture. The result of a typical experiment is shown in the graph (Fig. 1).

The shape of the curve can be interpreted in terms of three ionisation schemes involving different triphenyl phosphite-bromine ratios. The section *AB* shows a steep rise in the conductance up to *B* which corresponds to $P(OPh)_3 : Br_2 = 2 : 1$. The solution during this stage of the titration remained colourless. We are indebted to Professor H. N. Rydon for the suggestion that at this mole ratio the system may be described in terms of the following equilibria:

$$2P(OPh)_3 + Br_2 \rightleftharpoons P(OPh)_2Br + P(OPh)_4Br$$

$$P(OPh)_4Br \rightleftharpoons P(OPh)_4^+ + Br^-$$

Thus two molecules of triphenyl phosphite are required to give rise to a pair of ions, and the conductance of the system would accordingly rise continuously until the composition $2P(OPh)_3 + 1Br_2$ is attained. Additional evidence has been obtained from ion-migration experiments, which, although not completely unambiguous, tend to support the above scheme, and also by the isolation[7] of $P(OPh)_2Br$ and crystalline $P(OPh)_4Br$ from a chlorobenzene solution of triphenyl phosphite and bromine in the mole ratio 2 : 1.

Further addition of bromine (*BC*) led to yellow coloration of the solution but to no change in conductance, a lack which can be attributed to the absence of a net change in the number of ions in the solution and can be interpreted in terms of the following equations which lead to the formation of triphenyl phosphite dibromide at the composition corresponding to *C*:

$$\{[P(OPh)_3]_2Br_2\} + Br_2 \longrightarrow 2P(OPh)_3Br_2 \rightleftharpoons [P(OPh)_3Br]^+ + [P(OPh)_3Br_3]^-$$

In terms of the equilibria discussed for the 2 : 1 ratio, we must regard the formation of these ions as occurring through a series of stages which leads ultimately to a cation and an anion each possessing three phenoxy-groups attached directly to a central phosphorus atom. A further increase in the bromine-triphenyl phosphite ratio leads to the change *CD*, together with an intensification of the colour of the solution. These results are accounted for by the formation of a polybromide ion as shown by the scheme:

$$\begin{tikzcd}
2P(OPh)_3Br_2 + 2Br_2 \arrow[r] \arrow[d, shift left, harpoon] & 2P(OPh)_3Br_4 \arrow[d, shift left, harpoon] \\
\begin{array}{c} P(OPh)_3Br^+ \\ + \\ P(OPh)_3Br_3^- + 2Br_2 \end{array} \arrow[u, shift left, harpoon] \arrow[r] & \begin{array}{c} P(OPh)_3Br^+ \\ + \\ P(OPh)_3Br^+ + 2Br_3^- \end{array} \arrow[u, shift left, harpoon]
\end{tikzcd}$$

Popov and Skelly[8] have drawn attention to the strong tendency of halides to form polyhalide ions in acetonitrile and to the conductance of the resulting solutions.

It has proved possible to isolate this tetrabromide as a yellow crystalline material, m. p. 105—106°, readily hydrolysed to bromine, hydrogen bromide, and triphenyl phosphate. Other polyhalides of general formula PX_3Y_4 have been reported. In the phosphorus trichloride-bromine system Fialkov and Kuz'menko[9] have isolated PCl_3Br_4, and Forsman and Lipkin[10] have obtained triphenyl phosphite tetraiodide, $P(OPh)_3I_4$, from the triphenyl phosphite-iodine system.

The molar conductance of the triphenyl phosphite dibromide is, as might be expected,

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[7] Rydon and Tonge, following paper.

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

[9] Fialkov and Kuz'menko, *Zhur. obshchei Khim.*, 1951, **21**, 433.

[10] Forsman and Lipkin, *J. Amer. Chem. Soc.*, 1953, **75**, 3145.

lower than that of the dichloride for the same concentration (*e.g.*, $\Lambda_m = 35{\cdot}4$, $c_m = 0{\cdot}0110$). The tetrabromide has a molar conductance of 99·5 at $c_m = 0{\cdot}00904$.

To confirm the dibromide ionisation scheme, transport experiments were carried out on an acetonitrile solution containing triphenyl phosphite and bromine in the ratio corresponding to triphenyl phosphite dibromide. The apparatus used was a Hittorf type of cell, modified to suit the requirements of the system under examination.

In addition to the mode of ionisation of triphenyl phosphite dibromide postulated above, namely,

$$2P(OPh)_3Br_2 \rightleftharpoons [P(OPh)_3Br]^+ + [P(OPh)_3Br_3]^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

another mode is possible :

$$P(OPh)_3Br_2 \rightleftharpoons [P(OPh)_3Br]^+ + Br^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Provided there is no loss of the products from the solution by deposition on the electrodes or evolution as a gas, it should be possible to distinguish these ionisation schemes by noting the electrolyte concentration changes occurring at the electrodes on electrolysis.

FIG. 1.

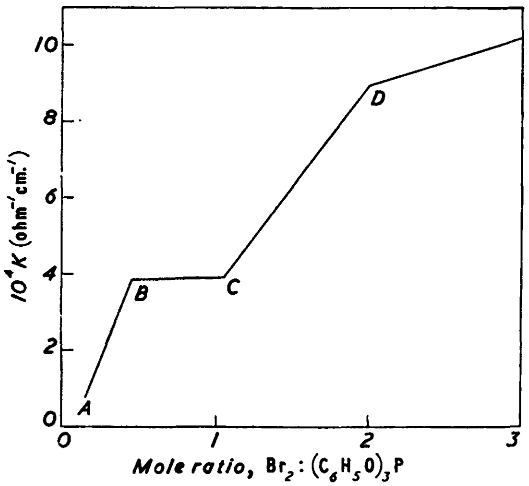
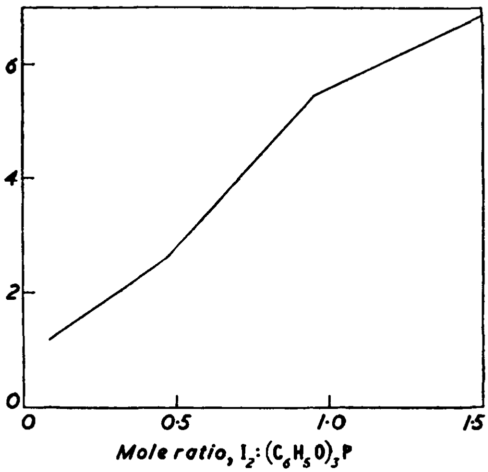


FIG. 2.



If ΔBr and ΔP represent increases in gram-atoms of bromine and phosphorus respectively occurring in the electrode compartments, and t_+ is the transport number of the cation at the concentration used, and x the number of faradays passed, then for ionisation (1),

$$\text{at cathode, } \Delta Br = x(4t_+ - 3)\,; \text{ at anode, } \Delta P = x(1 - 2t_+)$$

and for ionisation (2),

$$\text{at cathode, } \Delta Br = x(2t_+ - 1)\,; \text{ at anode, } \Delta P = -xt_+$$

It was found that ΔBr gave values for t_+ which were more acceptable if ionisation (1) was correct. The values obtained were $t_+ = 0{\cdot}59$, 0·56 (concentration of solution *ca.* 0·05M). During the electrolysis the cathode solution became colourless, whereas bromine was liberated at the anode. The following processes were occurring in the solution at the electrodes :

At cathode :

$$2[P(OPh)_3Br]^+ + 2e \longrightarrow [2P(OPh)_3Br] \longrightarrow \underbrace{[2P(OPh)_3 + Br_2]}_{\text{Colourless mixture}}$$

At anode :

$$2[P(OPh)_3Br_3]^- - 2e \longrightarrow [2P(OPh)_3Br_3] \longrightarrow \underbrace{2P(OPh)_3Br_2 + Br_2}_{\text{Yellow solution}}$$

A notable feature of the triphenyl phosphite–bromine–acetonitrile system is the lability displayed by the phenoxy-groups and the bromine atoms attached to the phosphorus. As a result of this, substantial changes in the concentrations of species present in the solution occur with slight changes of environment.

An additional experiment in which an acetonitrile solution of phosphorus pentabromide was titrated conductometrically with a similar solution of phenol, showed that in acetonitrile solution the replacement of Br by OPh occurs readily. The resulting solutions containing $P(OPh)_nBr_{5-n}$ and hydrogen bromide showed inflections in the specific conductance–mole ratio (*n*) curve at whole-number ratios from 1 to 4. The solution, which was originally yellow, became colourless at a mole ratio between 3 and 4.

The reaction of iodine with triphenyl phosphite in a conductometric titration produced the results shown in Fig. 2. The form of the graph shows that the system is quite different from the bromine–triphenyl phosphite system. As in the latter system, an inflection occurs at the 1 : 2 ratio, and in this case the solution at this stage is yellow-brown. A di-iodide, stable in solution, is also clearly indicated. The shape of the curve and the values of molar conductance (*e.g.*, $\Lambda_m = 46{\cdot}55$, $c_m = 0{\cdot}0011$) can be understood if the di-iodide ionises as follows : $P(OPh)_3I_2 \rightleftharpoons [P(OPh)_3I]^+ + I^-$.

The triphenyl phosphite–iodine system has been investigated by Forsman and Lipkin,[10] who were unable to isolate a di-iodide from benzene solutions of the components, but obtained both a tetra- and an ennea-iodide, which they consider to contain the common ion $[P(OPh)_3I]^+$.

The ionisation of the triphenyl phosphite dichloride has not been studied, but by analogy with phosphorus pentachloride and pentabromide,[5, 6] the ionisation may be considered to parallel that of the triphenyl phosphite dibromide, thus :

$$2P(OPh)_3Cl_2 \rightleftharpoons [P(OPh)_3Cl]^+ + [P(OPh)_3Cl_3]^-$$

EXPERIMENTAL

Materials.—The acetonitrile was purified essentially as by Smith and Witten's method.[11] Immediately before use the material was distilled *in vacuo* from *ca.* 0° to $-183°$. This removed traces of phosphoric oxide which otherwise sublimed over during distillation from the desiccating agent at ordinary pressures. The purified material had a specific conductance of *ca.* $10^{-7}\ \Omega^{-1}\ cm.^{-1}$.

Bromine was fractionated *in vacuo* and filled directly into ampoules. Triphenyl phosphite was purified by fractional distillation under reduced pressure (b. p. 180°/*ca.* 0·5 mm.). The triphenyl phosphite dichloride used (Found : Cl, 18·9, 18·95. Calc. : Cl, 18·6%) was received from Professor H. N. Rydon.

Solutions were prepared in a dry-box containing phosphoric oxide as desiccant.

Conductance Experiments.—These were carried out in a pipette cell adapted in such a way that the solutions could be conveniently handled by a pressure-difference technique. The electrodes were made of smooth platinum, and the cell constant was 0·500 cm.$^{-1}$. The cell and part of the filling system were immersed in a thermostat at 25°, and the conductance measurements made by using a Mullard conductance bridge (Type E7566). The concentrations of the solutions were determined by chemical analysis. Measured samples of the solutions were hydrolysed by sodium hydroxide solution, and the halide ion was estimated by Volhard's method.

Conductometric Titrations.—The apparatus used is shown in Fig. 3. The procedure employed was as follows. Before use the apparatus was baked at 120° for 4 hr. The halogen solution of known concentration was prepared in a separate flask. To this the burette *F* (capacity 25 c.c.) was attached and filled by gentle application of reduced pressure through tap T_4 (tap T_3 was opened to a system of drying tubes). Tap T_4 was then closed, and the burette attached to the main system which was arranged as shown in the diagram. Flask *C* (capacity 50 c.c.) initially contained a known volume (*ca.* 25 c.c.) of the triphenyl phosphite solution of known concentration. During titration tap T_3 was permanently closed and tap T_2 permanently open. Small additions of the titrant were made by opening tap T_4 (the flow of liquid from the burette

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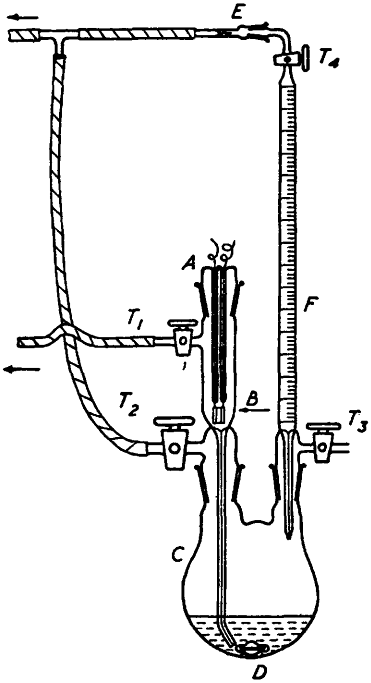
[11] Smith and Witten, *Trans. Faraday Soc.*, 1951, **47**, 1304.

was conveniently " damped " by the very fine constriction *E*). Complete mixing was ensured by use of a magnetic stirrer *D*. To measure the conductance of the solution at each stage in the titration a sample was introduced through the capillary tube into the electrode chamber *B* by applying slightly reduced pressure through tap T_1. The sample was held there by closing T_1. After the conductance had been noted the sample was returned to the titration flask.

A standard pair of smooth platinum dipping electrodes, *A* (area 1 cm.^{2}, cell constant 0·324 cm.$^{-1}$), was used. The conductance was measured (by the Mullard conductance bridge previously mentioned) when equilibrium had been attained after each addition of halogen solution.

Transport Experiments.—Solutions for electrolysis were prepared by the controlled mixing of standard solutions of bromine and triphenyl phosphite in acetonitrile. The electrolysis was carried out in a cell of the Hittorf type containing a middle compartment. The cell was incorporated in a system which permitted manipulation of the solutions by pressure difference in a closed circuit. The electrodes consisted of coiled smooth platinum foil and each had a total surface area of 37·5 cm.^{2} and their distance apart was about 40 cm. The bottom of each compartment terminated in a short thin-walled spindle which was easily broken when the compartments had to be emptied. In this way the halide solutions never came into contact with tap-grease. Before an experiment the apparatus was flamed out *in vacuo*.

FIG. 3.



The cell was immersed in a well-stirred thermostat at room temperature. Current was supplied at 240 v by two high-tension batteries, and the amount of current passed was determined from the increase in weight of the cathode of a silver coulometer incorporated in the circuit. A sensitive milliammeter was also included in the circuit and during electrolysis the current recorded was 7·5 mA. After electrolysis the contents of the middle, cathode, and anode compartments were removed for analysis. Results were considered valid only if the middle solution varied negligibly in concentration from that of the original solution.

Preparation and Analysis of Triphenyl Phosphite Tetrabromide.—An excess of bromine was added to triphenyl phosphite (0·005 mole) in ether solution. This produced a heterogeneous precipitate accompanied by the evolution of heat. The solvent, containing excess of bromine, was decanted off. The precipitate was dissolved in acetonitrile, in which it is very soluble. Ether was then added until a yellow crystalline precipitate was obtained. The solvent was decanted, and the crystals washed by decantation with ether until the ether was almost colourless. After the final decantation the residual solvent was removed under slightly reduced pressure. The product was a very hygroscopic yellow crystalline solid, m. p. (sealed tube) 105—106°. The yield was about 60%.

Analysis was accomplished by hydrolysing the solid with sodium hydroxide solution in a closed system. The resulting solution was yellow and contained an insoluble white solid (triphenyl phosphate). The bromine was reduced to bromide by passing sulphur dioxide through the solution. The solid was then removed by filtration, and the solution acidified with dilute nitric acid. Carbon dioxide was then bubbled through the boiling solution to expel excess of sulphur dioxide. After cooling, the bromide-ion content of the solution was determined by Volhard's method.

Phosphorus was determined after oxidation of the *tetrabromide* with concentrated nitric acid and potassium permanganate.[12] After an initial precipitation as ammonium phosphomolybdate the phosphate was precipitated as magnesium ammonium phosphate and finally ignited to pyrophosphate which was weighed (Found: P, 4·94, 5·01, 5·08; Br, 49·97, 49·57, 50·24. $C_{18}H_{15}O_3PBr_4$ requires P, 4·92; Br, 50·76%).

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[12] Marie, *Compt. rend.*, 1899, **129**, 766.

The authors thank Professor H. N. Rydon for his original suggestion which led to the work described and for his correspondence during the investigation, and also Messrs. Albright and Wilson for a gift of triphenyl phosphite. One of the authors (G. S. H.) gratefully acknowledges the receipt of a Maintenance Allowance from the Department of Scientific and Industrial Research.

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[*Received, December 7th,* 1955.]