The Liquid Hydrogen Chloride Solvent System. Part IX.[1] Oxidation of Some Phosphorus(III) Compounds

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The reactions of the halogens and related compounds with phosphorus(III) compounds in liquid hydrogen chloride have been investigated. Where oxidation occurred phosphorus was oxidised from the +3 to the +5 oxidation state. The reactions were followed conductimetrically wherever possible. Evidence was obtained for the existence of the ions PCl_3Br^+ and Ph_3PCl^+ by stabilising them as the tetrachloroborate salts.

THE results of the oxidation reactions studied in this work are given in Table 1, and the conductimetric titration curves are shown in Figures 1—3. Many of the reactions could be followed visually as well as conductimetrically as the colour of the halogen (or polyhalide ion) could be seen after the end-point had been reached. Both types of end-point are included in Table 1.

In the reaction of phosphorus trichloride and bromine the product decomposed on removal of the solvent but could be stabilised by the addition of an excess of boron trichloride. The infrared spectrum of the resulting solid showed the characteristic absorptions of the BCl_4^- ion.[2] Absorptions were also seen corresponding to the PCl_3Br^+ ion, confirming that the compound bromotrichlorophosphonium tetrachloroborate had been formed in the reaction. The PCl_3Br^+ ion is isoelectronic with monobromotrichlorosilane and both will have C_{3v} symmetry. In such molecules as BF_3Cl^-,[2] CF_3Cl,[3] SO_3F^-,[4] and SO_3Cl^-,[1] and those of the XY_4 type with T_d symmetry, a combination mode appears quite strongly in the infrared spectrum; in the latter case the mode is $\nu_1 + \nu_4$ and in $SiCl_4$ appears at 647 cm.$^{-1}$.[5] In PCl_4^+ two absorptions are found, one at 650 and the other at 587 cm.$^{-1}$.[2] The former is probably the PCl asymmetric stretch $\nu_3(F_2)$ and the latter may be the combination band $\nu_1 + \nu_4$. These correspond with bands at 643 cm.$^{-1}$ (E) and 580 cm.$^{-1}$ in the infrared spectrum of PCl_3Br^+. The only other band in this spectrum was at 490 cm.$^{-1}$ and is probably the PCl symmetric stretching frequency (A_1). In the Raman spectrum of $SiCl_3Br$ the SiCl symmetric stretching mode (A_1) has been assigned at 545 cm.$^{-1}$.[6]

TABLE 1

End-point

Reactant	Oxidising agent	Conductimetric Ox : Red	Visual Ox : Red	Product	Remarks
PCl_3	Cl_2	1·0 : 1·0	1·0 : 1·0	PCl_5	
	Br_2	1·0 : 1·0	1·0 : 1·0	PCl_3Br^+	Product stabilised as a tetrachloroborate
	ICl	3·0 : 1·0	—	$PCl_4^+ICl_2^- + I_2$	Conductivity curve sensitive to concentration
PBr_3	Cl_2	1·0 : 1·0	—	PCl_5	Excess of Cl_2 added: probable intermediate PBr_3Cl^+
	Br_2	—	1·0 : 1·0	PBr_5	Solubility difficulties with reactants and products
	ICl	2·0 : 1·0	—	$PCl_4^+ICl_2^-$? + I_2	Excess of ICl added; anion not identified because of I_2
PF_3	Cl_2	No end-point as	1·0 : 1·0	PF_3Cl_2	
	Br_2	molecular	1·0 : 1·0	PF_3Cl_2	PF_3Br_2 solvolysed to PF_3Cl_2
	ICl	species produced	1·0 : 1·0	$PF_3Cl_2 + I_2$	
Ph_3P	Cl_2	1·0 : 1·0	1·0 : 1·0	Ph_3PCl_2	$Ph_3PCl^+BCl_4^-$ also prepared
	Br_2	1·0 : 1·0	1·0 : 1·0	$Ph_3PCl_2 + Ph_3PBr_2$	Solvolysis of Ph_3PBr_2 led to inhomogeneous product

The analytical figures for bromotrichlorophosphonium tetrachloroborate are rather low in halide (especially chloride) as hydrolysis of the product was exceptionally vigorous and some hydrogen halide was invariably lost.

Although the PCl_3Br^+ ion seemed stable to solvolysis in liquid hydrogen chloride neither the product of the reaction of phosphorus tribromide with chlorine nor of triphenylphosphine with bromine appeared stable.

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Both oxidations gave good 1 : 1 end-points in conductimetric titrations but in the former case phosphorus pentachloride was formed whilst in the latter a mixture

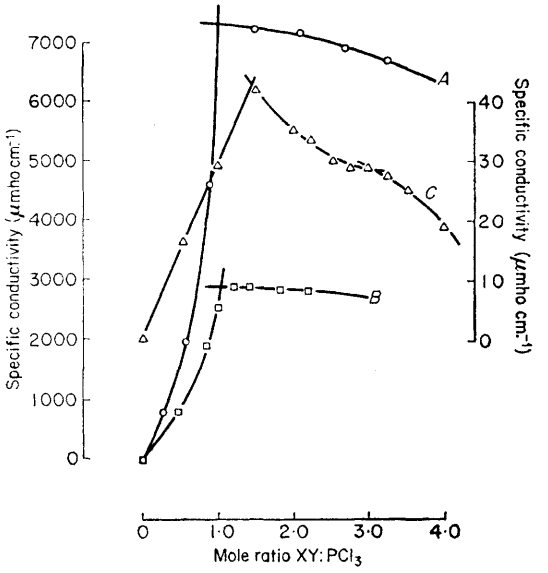

FIGURE 1 Reactions of the halogens with PCl_3 in liquid hydrogen chloride

A, Cl_2 against PCl_3 (scale 0—7000), 0·26M-PCl_3 in HCl.
B, Br_2 against PCl_3 (scale 0—7000), 0·15M-PCl_3 in HCl.
C, ICl against PCl_3 (scale 0—40), 0·023M-PCl_3 in HCl.

of triphenylphosphine dichloride and triphenylphosphine dibromide resulted on evaporation of the solvent.

In the titrations of phosphorus trichloride and of phosphorus tribromide with iodine monochloride, iodine was precipitated throughout the reaction and the end-points were very dependent upon the concentrations of the reacting species in solution. The $PCl_4^+ICl_2^-$ isolated in both reactions was contaminated with iodine and could not be analysed. The infrared spectrum showed the presence of PCl_4^+ only and the product had identical

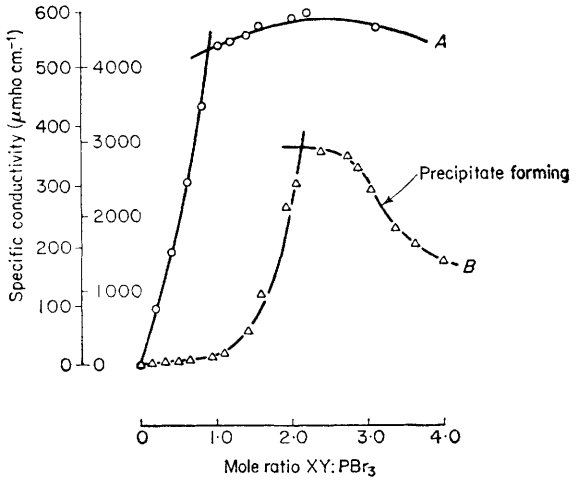

FIGURE 2 Reactions of the halogens with PB_3 in liquid hydrogen chloride

A, Cl_2 against PBr_3 (scale 0—600), saturated in PBr_3.
B, ICl against PBr_3 (scale 0—4000), saturated in PBr_3.

properties with tetrachlorophosphonium dichloroiodide prepared under standard conditions.[7] The end-points in the two titrations were different because they were obtained with different concentrations of reactants. Iodine was liberated immediately in each case showing that it was not possible to observe the various reaction stages separately.

In the titrations of phosphorus trifluoride with the halogens no conductimetric end-points were observed as molecular species were produced. The reactions could, however, be followed visually as the colour of the halogen only became apparent after the end-point had been reached. In the reaction between phosphorus trifluoride and bromine, solvolysis always occurred to form dichlorotrifluorophosphorane; a solution of dibromotrifluorophosphorane in liquid hydrogen chloride gave dichlorotrifluorophosphorane after a short equilibration period. A slow change from the molecular to the ionic form $PCl_4^+PF_6^-$ was observed for solutions of dichlorotrifluorophosphorane in the solvent. The slight

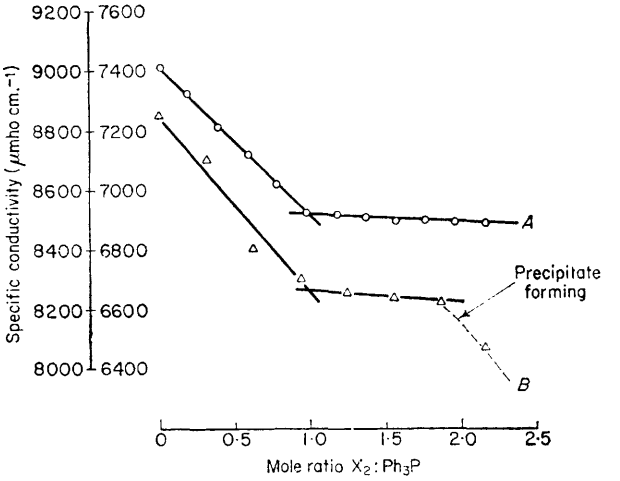

FIGURE 3 Reactions of the halogens with Ph_3P in liquid hydrogen chloride

A, Cl_2 against Ph_3P (scale 8000—9200), 0·34M-Ph_3P in HCl.
B, Br_2 against Ph_3P (scale 6400—7600), 0·15M-Ph_3P in HCl.

but constant increase in the conductivity with time of solutions of dichlorotrifluorophosphorane in liquid hydrogen chloride was regarded as evidence for the reaction

$$2PF_3Cl_2 \rightleftharpoons PCl_4^+PF_6^-$$

Triphenylphosphine is known to be protonated in liquid hydrogen chloride.[8] On oxidation with chlorine or bromine the conductivity did not decrease to a low value indicating that the resulting species was ionised. On addition of excess of boron trichloride to the products of oxidation of triphenylphosphine with chlorine, triphenylchlorophosphonium tetrachloroborate was isolated. This compound was not perfectly stable at room

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temperature but tended to evolve boron trichloride. Its infrared spectrum showed absorptions characteristic of a tetrachloroborate.[2] The only other absorption not found in the starting material was one at 593 cm.$^{-1}$. A similar absorption, at 587 cm.$^{-1}$, was found for triphenylphosphine dichloride. These absorptions are consistent with that of a P–Cl vibration in a cation of the type Ph_3PCl^+. In PCl_4^+ the absorption is at 584 or 650 cm.$^{-1}$,[2] in PCl_5 vapour at 592 cm.$^{-1}$,[9,10] and in PCl_6^- at 449 cm.$^{-1}$.[11] It is noteworthy that a solution of trimethylamine in liquid hydrogen chloride was not oxidised by chlorine whereas the two compounds reacted violently in the gas phase. The stability to oxidation of the ion $(CH_3)_3NH^+$ against that of the ion Ph_3PH^+ is thus demonstrated.

Neither cyanogen chloride nor nitrosyl chloride showed any oxidising power with phosphorus trichloride. Dinitrogen tetroxide, on the other hand, did oxidise phosphorus trichloride but the products were not ionic. Because the gas-phase reaction is complicated[12] the oxidation was not studied further.

EXPERIMENTAL

The apparatus and techniques have been described.[13] Volatile reactants were distilled into the conductivity cell from a calibrated volume at a known pressure. By use of liquid nitrogen as a refrigerant quantitative transfer was possible. Non-volatile materials were weighed directly into the cell. Phosphorus and halide were analysed as described previously.[14] Two halide ions in the presence of one another were analysed potentiometrically. Gases were characterised by their molecular weights and infrared spectra. Infrared spectra were recorded on a Perkin-Elmer Infracord with sodium chloride or potassium bromide optics. The phosphorus trifluoride was kindly donated by Dr. R. G. Cavell. Other reagents were either commercial or prepared by standard methods. Purification was effected by low-pressure distillation on the vacuum line.

The conductivity cell was of modified design as bromine and iodine monochloride tended to condense on the " legs " of the conventional cell making accurate quantitative transference into liquid HCl difficult. In the new design the cell " legs " were made as short as possible and a flow of air was maintained down the fairly wide central tube supporting the electrodes. Using this device we encountered no trouble in transferring bromine and iodine monochloride. Analyses are in Table 2.

TABLE 2

Analyses

Reaction	Solid product	Analysis (%) Found	Calc.
PCl_3–Cl_2	PCl_5	Cl: 85·0	Cl: 85·1
PCl_3–Br_2–BCl_3	$PCl_3Br^+BCl_4^-$	P: 7·4	P: 7·5
		Br: 21·8	Br: 21·6
		Cl: 62·2	Cl: 67·1
PCl_3–ICl	$PCl_4^+ICl_2^- + I_2$	Analysis impossible owing to liberation of I_2	
PBr_3–Cl_2	PCl_5	Cl: 83·8	Cl: 85·1
PBr–Br_2	PBr_5	Br: 92·2	Br: 92·7
PBr_3–ICl	$PCl_4^+ICl_2^-$? + I_2	Analysis impossible owing to liberation of I_2	
PF_3–Cl_2	PF_3Cl_2	M = 158	M = 159
PF_3–Br_2	PF_3Cl_2	M = 159	M = 159
PF_3–ICl	PF_3Cl_2	M = 159	M = 159
Ph_3P–Cl_2	Ph_3PCl_2	Cl: 21·1	Cl: 21·3
Ph_3P–Cl_2–BCl_3	$Ph_3PCl^+BCl_4^-$	Cl: 38·1	Cl: 39·4
Ph_3P–Br_2	Ph_3PCl_2/Ph_3PBr_2	Inhomogeneous product	

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