Reactions of some Phosphorus(III) Halides with Halogens in strongly Acidic Solvents

By **Keith B. Dillon,* Martin P. Nisbet,** and **Thomas C. Waddington,** Chemistry Department, University of Durham, South Road, Durham DH1 3LE

The reactions of some phosphorus(III) halides with halogens in the strongly acidic solvents 25 oleum, $HSFO_3$, and 100% H_2SO_4 have been investigated by means of ^{31}P n.m.r. spectroscopy. The compound PCl_3 and Br_2, and PBr_3 and Cl_2, react to give complex mixtures of products containing tetrahalogenophosphonium ions $[PBr_{4-n}Cl_n]^+$, together with solvolysed species $[PBr_{3-n}Cl_n(OH)]^+$ (25 oleum) or $PF_3O(HSFO_3)$. No evidence has been found for halogenophosphonium ions $[PX_nY_{4-n}]^+$ derived from PI_3, although the partially solvolysed species $[PI_nX_{3-n}(OH)]^+$ (X = Cl or Br) have been identified in solution.

THE only previous investigation of the reactions of halogens with phosphorus(III) halides in strongly acidic solvents was carried out by Paul *et al.*,[1] who deduced from conductivity measurements that PCl_3 is oxidised by Cl_2 or Br_2 in $HSFO_3$ to give $[PCl_4]X$ and $[PBrCl_3]X$ respectively, and that PBr_3 reacts similarly with Cl_2 and Br_2 in this solvent to yield $[PBr_3Cl]X$ and $[PBr_4]X$ respectively, where $X = [SFO_3]^-$. They were able to isolate solid products from the PCl_3 reactions, which were analysed for chlorine and fluorosulphate, but only obtained highly viscous liquids from the PBr_3 reactions.[1] Extensive studies of the PCl_3–Br_2 reaction with Lewis acids such as BCl_3 present in the more weakly acidic solvent HCl and in the inert solvent CH_2Cl_2 have shown, however,[2-6] that single mixed halogenophosphonium ions are not usually formed, but mixtures in varying proportions of the ions $[PBr_{4-n}Cl_n]^+$, which can be isolated as their tetrachloroborate salts. The i.r. data reported for 'PCl_3BrSFO_3'[1] do not extend to a sufficiently low frequency for detailed comparison to be made with more recent vibrational spectroscopic results, in which the fundamental frequencies for all the mixed species have been assigned.[3,5] Our work on the direct reactions of phosphorus-(V)[7] and -(III)[8] halides with strongly acidic solvents, and on the PCl_3–Br_2–BCl_3 reaction in liquid HCl,[6] had shown that various interesting ions could be stabilised, given a suitable choice of solvent, and that these could be readily identified by ^{31}P n.m.r. spectroscopy. It was therefore of interest to look at some reactions between phosphorus(III) halides and halogens in strongly acidic solvents by means of this technique, both to try to identify new species in solution and to establish whether the reactions are simple or complex.

EXPERIMENTAL

All manipulations, including sample preparation, were carried out under an inert atmosphere of dry nitrogen. A special all-glass apparatus was constructed to allow the reactions to take place outside a dry-box.[9] This was baked in an oven overnight to remove any moisture, evacuated on a vacuum line, and opened under a nitrogen atmosphere. Addition of reagents was then carried out under a back-flow of dry nitrogen, to minimise hydrolysis risks and provide a route for the dissipation of any excess of pressure arising from the reaction. After completion of the reaction, the apparatus was transferred to the dry-box for removal of the sample for n.m.r. spectroscopy. Chemicals of the best available commercial grade were used, generally without further purification except for PI_3 which was recrystallised from CH_2Cl_2.

The order of addition of the reagents depended to some extent on their physical state. All reactions, except where mentioned otherwise, were carried out using a 1 : 1 mol ratio of the reagents. For the PBr_3–Cl_2 reaction, chlorine was condensed as a liquid at 213 K, PBr_3 was added at 233 K, and the acid solvent added after the mixture had warmed to room temperature. For all other reactions in 25 oleum † or $HSFO_3$ as solvents, the phosphorus(III) halide and halogen, whether liquid or solid, were mixed at 233 K and the mixture allowed to warm to room temperature before addition of solvent. For reactions involving PI_3 and 100% H_2SO_4, however, the solid phosphorus halide was immersed under the acid at room temperature and the halogen (or interhalogen) then added. In all cases, vigorous reaction was observed, yielding clear solutions of various shades of brown.

Phosphorus-31 n.m.r. spectra were recorded as described previously,[7,8] using the Fourier-transform spectrometer and sample tubes having an outside diameter of 5 mm. Chemical shifts are expressed relative to 85% H_3PO_4, with the upfield direction taken as positive.

RESULTS AND DISCUSSION

(*a*) PCl_3–Br_2 *and* PBr_3–Cl_2 *Reactions*.—These systems were studied in both $HSFO_3$ solution, for comparison with the conductometric data,[1] and in 25 oleum. The latter was chosen as solvent since there are no complications with halogen exchange, solvolysis of phosphorus(V)–bromine or –chlorine bonds is slower than in 100% H_2SO_4,[7] and no condensation reactions with elimination of HBr from bromo-species take place, as found for 65 oleum.[7,8] In both instances the phosphorus(III) halide and halogen reacted vigorously at 233 K, before addition of solvent, with formation of yellow or yellow-brown solids. After dissolution, these gave rise to quite complex ^{31}P n.m.r. spectra, especially in 25 oleum, as represented diagramatically in Figure 1 for PCl_3–Br_2 and in Figure 2 for PBr_3–Cl_2. Nevertheless, all the resonances may be readily assigned (Table 1). The $HSFO_3$ solutions contain mixtures of bromochlorophosphonium ions, which change proportions in favour of more extensively brominated species as a function

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† Oleum containing 25% free SO_3.

TABLE 1

Phosphorus-31 n.m.r. data for the PCl_3–Br_2 and PBr_3–Cl_2 reactions in some acid solvents

System	PCl_3–Br_2	PCl_3–Br_2	PBr_3–Cl_2	PBr_3–Cl_2	
Solvent	$HSFO_3$	25 oleum	$HSFO_3$	25 oleum	Assignment
$\delta(^{31}P)$/				−86	$[PCl_4]^+$
p.p.m.	−50	−51		−50	$[PBrCl_3]^+$
		−21		−20	$[PCl_3(OH)]^+$
	−9	−10	−10	−9	$[PBr_2Cl_2]^+$
		10		11	$[PBrCl_2(OH)]^+$
	35	35	35	37	$[PBr_3Cl]^+$
	36 *		36 *		PF_3O
		43		44	$[PBr_2Cl(OH)]^+$
				81	$[PBr_3(OH)]^+$
			84	85	$[PBr_4]^+$

* Quartet, ^1J(P–F) 1 080 Hz.

of time, together with PF_3O which is not protonated in this solvent;[10] PF_3O is probably formed *via* an indirect exchange process, as discussed previously.[7,8]

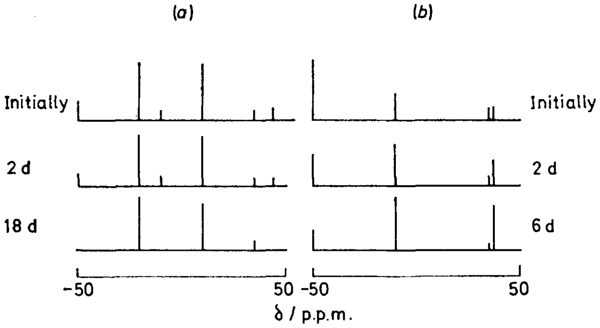

FIGURE 1 Relative peak heights in the ^{31}P n.m.r. spectra from reaction of PCl_3 with Br_2 in 25 oleum (*a*) and $HSFO_3$ (*b*)

The 25 oleum solutions contain both $[PBr_{4-n}Cl_n]^+$ and $[PBr_{3-n}Cl_n(OH)]^+$ ions. (As in previous papers,[7,8] the phosphoryl compounds will be partially protonated only, but are represented in the protonated form for clarity.) The latter probably arise initially from reaction of the solvent with phosphorus(III) halides,[8] since the halogenophosphonium ions, both simple [7] and mixed,[11] are stable to solvolysis in 25 oleum. It has been observed previously that the bromine colour of a 1 : 1 PCl_3–Br_2 mixture in liquid HCl disappears on cooling to 195 K, but reappears on warming to room temperature.[6] Halogen exchange, particularly between PBr_3 and Cl_2 since P–Cl bonds are stronger than P–Br bonds, could take place at a lower temperature, however, thus giving rise to a mixture of phosphorus(III) halides together with free halogen before addition of solvent. The subsequent behaviour will depend on the relative strengths of the solvent and halogen as oxidising agents, with the acid providing a large anion such as $[SFO_3]^-$ or $[HS_2O_7]^-$ which can stabilise any cations formed. The results suggest that $HSFO_3$ is a less powerful oxidising agent than a halogen, but that 25 oleum is comparable or even slightly stronger. Interpretation is further complicated for 25 oleum since a redox reaction of a phosphorus(III) halide with the solvent necessarily causes a reduction in acid strength,[8] thus promoting solvolysis and the formation of $[PBr_{3-n}Cl_n(OH)]^+$ ions. Such behaviour probably accounts for the increasing intensities of the signals from the hydroxy-species with time. In the 25 oleum solutions also, it is noteworthy that more extensively brominated species are favoured as reaction proceeds.

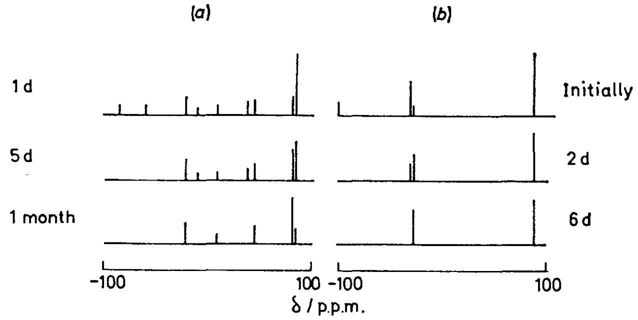

FIGURE 2 Relative peak heights in the ^{31}P n.m.r. spectra from reaction of PBr_3 with Cl_2. Acidic solvents as in Figure 1

It seems most unlikely that reactions of this type can be adapted to prepare pure mixed bromochlorophosphonium species, since mixtures were always observed, although the spectrum of the PBr_3–Cl_2 system in $HSFO_3$ after 6 d suggests that isolation of $[PBr_4][SFO_3]$ might be possible at this stage.

(*b*) *Reactions with* PI_3.—No reactions of PI_3 with halogens in strongly acidic solvents have been reported previously. In an attempt to prepare new phosphorus(V) species containing P–I bonds, the reactions between PI_3 and Br_2 in $HSFO_3$ and between PI_3 and I_2 in 25 oleum were investigated. The results for the PI_3–Br_2 system are represented schematically in Figure 3. With the exception of the single peak at 222 p.p.m., the signals can be readily assigned, as indicated in Table 2. Chemical shifts are in good agreement with literature data in all other instances, as shown. Since $[PI_2(OH)_2]^+$ and $[PI_3(OH)]^+$ give ^{31}P n.m.r. signals at *ca.* 144 and 308 p.p.m. respectively in $HSFO_3$,[8] the peak at 222 p.p.m. is assigned to $[PBrI_2(OH)]^+$, a species very likely to be formed in this reaction. The assignment

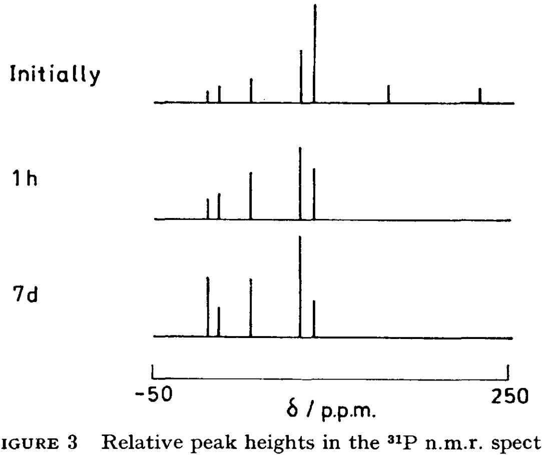

FIGURE 3 Relative peak heights in the ^{31}P n.m.r. spectra from reaction of PI_3 with Br_2 in $HSFO_3$

TABLE 2

Phosphorus-31 n.m.r. data for the PI_3–Br_2 reaction in $HSFO_3$

$\delta(^{31}P)$/p.p.m.	^1J(P–F)/Hz	Assignment	Ref.
−4		$[P(OH)_4]^+$	12 [a]
6 (doublet)	1 000	$[PF(OH)_3]^+$	8, 10
34 (quartet)	1 080	PF_3O	10 [b]
74		$[PBr_3(OH)]^+$	7, 8
84		$[PBr_4]^+$	7, 8
149		$[PI_2(OH)_2]^+$	8
222		$[PBrI_2(OH)]^+$ [c]	

[a] G. A. Olah and C. W. McFarland, *J. Org. Chem.*, 1971, **36**, 1374. [b] V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 227. [c] See text.

was confirmed by subsequent experiments, as described below. The n.m.r. spectrum of the 1 : 1 mixture of PI_3 and iodine in 25 oleum gave no indication of the presence of phosphorus(V) iodo-compounds; the signals at 5(s) and 15(w) p.p.m. are entirely consistent with complete solvolysis to $[P(OH)_4]^+$ and its derivatives, as found both for PI_3 alone [8] and for inorganic phosphates [12] in dilute oleum solutions. 25 Oleum is thus not a suitable solvent for the study of PI_3 reactions, and the use of $HSFO_3$ is complicated by halogen exchange and possibly solvolysis.

As described previously,[8] signals ascribed to $[PI_3(OH)]^+$, $[PI_2(OH)_2]^+$, and $[PI(OH)_3]^+$ were rather unexpectedly found from reaction of PI_3 with 100% H_2SO_4. Some halogen (and interhalogen) oxidations of PI_3 were therefore attempted in this solvent. Phosphorus triiodide was covered with a layer of 100% H_2SO_4 at room temperature, and equimolar amounts of Br_2, I_2, ICl, and IBr were separately added. In all cases the PI_3 did not dissolve completely, even on shaking. Bromine and ICl caused vigorous reactions with liberation of iodine, while IBr reacted more slowly, with formation of some I_2. The ^{31}P n.m.r. spectrum of the PI_3–Br_2 mixture showed signals at 80 and 86 p.p.m., readily ascribed to $[PBr_3(OH)]^+$ and $[PBr_4]^+$, while the PI_3–I_2 mixture gave a single peak at 297 p.p.m. $\{[PI_3(OH)]^+\}$.[8] The ICl reaction produced resonances at −21 $\{[PCl_3(OH)]^+\}$, 54 $\{[PI(OH)_3]^+\}$, and 90 p.p.m. $\{[PCl_2I(OH)]^+\}$, all in good agreement with previous values [7,8] when the shift variation with concentration for partially protonated species is considered. The PI_3–IBr system showed signals at 80 $\{[PBr_3(OH)]^+\}$, 84 $([PBr_4]^+)$, and 169 p.p.m. By comparison with the results for related species such as $[PBr_3(OH)]^+$ and $[PBrI_2(OH)]^+$, the high-field signal at 169 p.p.m. was assigned to $[PBr_2I(OH)]^+$.

In an attempt to confirm the above assignments for $[PBr_nI_{3-n}(OH)]^+$ ions, and those suggested for $[PCl_nI_{3-n}(OH)]^+$ species formed in the PI_3–$HSClO_3$ reaction,[8] PI_3 was shaken with 100% H_2SO_4 until the liquid was pale yellow, due to $[PI_3(OH)]^+$,[8] and small amounts of ICl, IBr, and Br_2 were added to promote halogen exchange. The resulting ^{31}P n.m.r. spectra are shown diagramatically in Figure 4; those from the IBr and Br_2 reactions were identical. The peaks may be readily assigned to species of the type $[PI_nX_{3-n}(OH)]^+$ (X = Cl or Br), as indicated in Table 3. The shifts for $[PCl_3(OH)]^+$, $[PBr_3(OH)]^+$, and $[PI_3(OH)]^+$ are in good agreement with previous results [7,8] when possible variations with solute concentration and acid strength are considered. The assignments for the intermediate mixed species are thus amply confirmed. A further attempt at oxidation of PI_3 by addition of a solution of bromine in 100% H_2SO_4 led to ^{31}P n.m.r. signals at 75, 150, 222, and 305 p.p.m., in excellent agreement with the results in Table 3 for $[PBr_{3-n}I_n(OH)]^+$ ions.

The above results indicate that, although 100% H_2SO_4 may be a suitable medium for stabilising phosphorus(V) iodo-compounds, at least in the short term, it is less suitable for attempted oxidations of PI_3, since limited solubility of the latter leads to inhomogeneous reactions. No signals assignable to mixed halogenophosphonium ions with P–I bonds were found. The most probable course of reaction between PI_3 and a halogen in 100% H_2SO_4 appears to be initial halogen exchange to give mixed phosphorus(III) halides, followed by oxidation, either by the solvent to yield $[PI_nX_{3-n}(OH)]^+$, or of PBr_3 by unchanged halogen (Br_2 or IBr) to give $[PBr_4]^+$. This hypothesis is supported by the appearance of $[PI_3(OH)]^+$ in the equimolar reactions from the PI_3–I_2 system only. An alternative possibility is the initial formation of mixed halogenophosphonium ions $[PI_nX_{4-n}]^+$, which are then unstable to solvolysis in 100% H_2SO_4 and decompose with replacement of a P–I group by a P–OH group. Ions such as $[PI_3(OH)]^+$, $[PI_2(OH)_2]^+$, and $[PI_2X(OH)]^+$ would then be expected in more of the systems, however. The third possibility is oxidation of PI_3 by the solvent to $[PI_3(OH)]^+$, followed by halogen exchange. While the susceptibility

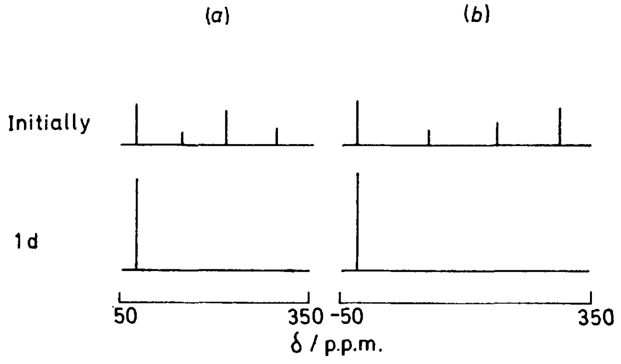

FIGURE 4 Relative peak heights in the ^{31}P n.m.r. spectra from reaction of $[PI_3(OH)]^+$ with (*a*) IBr or Br_2, (*b*) ICl, both in 100% H_2SO_4

TABLE 3

Phosphorus-31 n.m.r. data for the reaction of $[PI_3(OH)]^+$ with some halogens or interhalogens in 100% H_2SO_4

Reagent	ICl	IBr or Br_2	
X	Cl	Br	Assignment
$\delta(^{31}P)$/p.p.m.	−20	78	$[PX_3(OH)]^+$
	91	150	$[PX_2I(OH)]^+$
	198	223	$[PXI_2(OH)]^+$
	305	307	$[PI_3(OH)]^+$

of $[PI_3(OH)]^+$ to halogen exchange is shown by the results in Figure **4** and Table **3** above, such a mechanism would not account for formation of $[PBr_4]^+$ in the PI_3–Br_2 and PI_3–IBr (1 : 1) reactions.

We thus conclude that complex reactions between phosphorus(III) halides and halogens take place in strongly acidic solvents; the solvent itself may well participate in the redox reaction if it is a comparable oxidising agent to a halogen (25 oleum), or if the phosphorus(III) halide is resistant to oxidation (PI_3). Where the halogen (or interhalogen) contains a smaller halogen atom than the phosphorus(III) halide, the most probable initial reaction is halogen exchange [equation (1)]. This

$$PX_3 + Y_2 \longrightarrow PX_2Y + XY, \textit{etc.} \qquad (1)$$

is followed by oxidation either to $[PX_nY_{4-n}]^+$ by free halogen, the solvent providing a large anion for stability, as exemplified for $HSFO_3$ in equation (2), or to $[PX_nY_{3-n}(OH)]^+$ by the solvent, as exemplified for $H_2S_2O_7$ in equation (3). Redox reactions involving the solvent,

$$PX_nY_{3-n} + Y_2 + HSFO_3 \longrightarrow [PX_nY_{4-n}]^+ + [SFO_3]^- + HY \qquad (2)$$

$$PX_nY_{3-n} + H_2S_2O_7 \longrightarrow [PX_nY_{3-n}(OH)]^+ + [HSO_4]^- + SO_2 \qquad (3)$$

such as (3), necessarily cause a reduction in the acid strength, thus promoting solvolysis of phosphorus–halogen bonds.[8]

The favouring of more extensively brominated species from the PCl_3–Br_2 and PBr_3–Cl_2 systems as reaction proceeds in both $HSFO_3$ and 25 oleum has been noted. Since P–Cl are stronger than P–Br bonds, the explanation for this behaviour must lie in the difference in solvation energies of the Cl^- and Br^- ions in these solvents. If reaction (4) is considered, and it is assumed

$$[PBr_nCl_{4-n}]^+ + Br^- \rightleftharpoons [PBr_{1+n}Cl_{3-n}]^+ + Cl^- \qquad (4)$$

that the enthalpies of solvation of the two cations are approximately the same, then we obtain (5) where D is the bond-energy term and H the solvation energy.

$$\Delta H = -D(\text{P–Br}) + D(\text{P–Cl}) + H_{\text{Br}^-} - \text{H}_{\text{Cl}^-} \qquad (5)$$

$$D(\text{P–Br}) + H_{\text{Cl}^-} > D(\text{P–Cl}) + H_{\text{Br}^-} \qquad (6)$$

For ΔH to be negative, relation (6) must apply. This inequality will hold only if the solvation energy terms are dominant. Since solvation energies will be solvent-dependent, a difference in reaction products may result if the dielectric constant of the solvent is changed, with phosphorus(V) chloro-species predominating in less polar solvents. Experimental evidence in favour of this hypothesis is provided by the results for the PCl_3–Br_2–BCl_3 system in liquid HCl,[6] where all the possible phosphorus(V) cations $[PBr_{4-n}Cl_n]^+$ are observed. The ^{31}P n.m.r. spectrum[6] shows that chloro-species are more abundant than their bromo-analogues, with the most intense signal arising from $[PBrCl_3]^+$.

Some interesting new phosphorus(V) species with P–I bonds of the type $[PI_nX_{3-n}(OH)]^+$ (X = Cl or Br) have been prepared from PI_3 and identified in solution, but no simple or mixed halogenoiodophosphonium ions $[PI_nX_{4-n}]^+$ $(1 \leqslant n \leqslant 4)$ were found.

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