Reactions of Some Phosphorus(v) Halides and Halide Oxides with Strongly Acidic Solvents

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The reactions of PCl_3O, PBr_3O, $[PCl_4][PCl_6]$, $[NEt_4][PCl_6]$, and $[PBr_4]Br$ with the highly acidic solvents 100% H_2SO_4, $HSClO_3$, $HSFO_3$, 25 oleum, and 65 oleum have been investigated by means of ^{31}P n.m.r. spectroscopy. The halide oxides undergo protonation at the phosphoryl oxygen, the extent of which depends on the acid strength of the solvent and the solute concentration. Solutions of PCl_3O are stable, as are PBr_3O solutions in the halogenosulphuric acids, but solvolysis of PBr_3O occurs in 100% H_2SO_4 and 25 oleum and condensation in 65 oleum, probably *via* HBr elimination. The initial products from PCl_5 are $[PCl_4]^+$, $[PCl_3(OH)]^+$, or both of these, depending on the solvent; further solvolysis is then observed, together with halogen exchange in $HSFO_3$. Phosphorus(v) bromide forms $[PBr_4]^+$ initially, which may similarly undergo further reaction, but is stable in 65 oleum. The difference in behaviour between PCl_5 and PBr_5 is mainly due to the instability of the $[PCl_6]^-$ ion in these solvents. Possible mechanisms for the observed reactions are proposed.

THE behaviour of phosphorus(v) halides and halide oxides in strongly acidic solvents has been studied by various techniques in recent years,[1-10] but only the fluoro-systems have been followed by n.m.r. spectroscopy.[7] Olah and McFarland [7] deduced from changes in ^{19}F and ^{31}P chemical shifts, and P–F coupling constants, that PF_3O is protonated to a very limited extent, if at all, in fluorosulphuric acid, but is more extensively protonated in fluorosulphuric acid–antimony(v) fluoride. Earlier, Gillespie *et al.*[1] found PCl_3O to be a non-electrolyte in 100% H_2SO_4, while Paul and his co-workers,[3-6] using mainly cryoscopy and conductance techniques, concluded that PCl_3O and PBr_3O are incompletely protonated in $HSFO_3$, but completely protonated by $H_2S_2O_7$ to $[PX_3(OH)]^+$. They found no evidence for protonation of PF_3O. Very recently, partial protonation of PCl_3O by chlorosulphuric acid has been reported.[8] Phosphorus(v) chloride acts as a chloride-ion donor in $H_2S_2O_7$, yielding the $[PCl_4]^+$ ion and $HSClO_3$,[4] while PBr_5 has been suggested to dissociate to PBr_3 and bromine in this solvent. Disulphuric acid was then thought to oxidise PBr_3 to PBr_3O, which in turn became protonated.[4] The formation of the $[PCl_4]^+$ ion from PCl_5 in both $HSFO_3$ [5,6] and liquid hydrogen chloride [9] has also been deduced.

We report the results of a systematic investigation of the behaviour of PCl_3O, PBr_3O, PCl_5, $[NEt_4][PCl_6]$, and PBr_5 in the strongly acidic solvents 100% H_2SO_4, $HSClO_3$, $HSFO_3$, 25 oleum, and 65 oleum, carried out by means of ^{31}P n.m.r. spectroscopy. In several instances the reactions continued over a long time, and the systems have been monitored accordingly. Unlike cryoscopy and conductance work which give information on the bulk properties of the system, this approach enables individual phosphorus species to be identified, thus providing a more complete understanding of the processes which occur.

EXPERIMENTAL

All the manipulations, including sample preparation, were carried out under an inert atmosphere of dry nitrogen. Chemicals of the best available commercial grade were used, generally without further purification. The compound $[PCl_4][BCl_4]$ was prepared from phosphorus(v) chloride and a slight excess of boron trichloride in carbon tetrachloride solution; the white solid which separated was isolated, washed with pentane, and dried *in vacuo*. The preparation of $[NEt_4][PCl_6]$ has been given previously.[11] Samples of $K[PF_6]$ and $[PBr_4][BBr_4]$ were donated by Drs. C. J. Ludman and P. N. Gates respectively. Phosphorus-31 n.m.r. spectra were recorded at 307.2 K, either on a Perkin-Elmer R10 spectrometer operating at 24.29 MHz with a Digiac signal-averaging accessory, or on a Fourier-transform spectrometer constructed in this department by Dr. A. Royston, which utilises the 1.4-T magnet from a Perkin-Elmer R10 instrument and a Varian 620L computer. Samples were contained in tubes of 5-mm outsider diameter. Chemical shifts were measured from external P_4O_6 or 85% H_3PO_4, but are expressed relative to phosphoric acid, with the upfield direction taken as positive.

RESULTS AND DISCUSSION

The results for individual phosphorus(v) compounds are discussed separately.

TABLE 1

Phosphorus-31 chemical shifts (p.p.m.) for PCl_3O in acid solvents

	Solvent					
	HCl [10]	100% H_2SO_4	$HSClO_3$	$HSFO_3$	25 oleum	65 oleum
$\delta(^{31}P)$	−6.9	−20.0	−25.0	−23.0	−35.3	−55.9

(*i*) *Trichlorophosphine Oxide.*—The compound PCl_3O dissolved in all the acidic solvents to give colourless

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[1] R. J. Gillespie, R. Kapoor, and E. A. Robinson, *Canad. J. Chem.*, 1966, **44**, 1203.

[2] R. J. Gillespie, K. Ouchi, and G. P. Pez, *Inorg. Chem.*, 1969, **8**, 63.

[3] R. C. Paul, V. P. Kapila, and K. C. Malhotra, *J. Chem. Soc.* (*A*), 1970, 2267.

[4] R. C. Paul, V. P. Kapila, J. K. Puri, and K. C. Malhotra, *J. Chem. Soc.* (*A*), 1971, 2132.

[5] K. K. Paul, Ph.D. Thesis, Panjab University, 1970.

[6] R. C. Paul, K. K. Paul, and K. C. Malhotra, *J. Inorg. Nuclear Chem.*, 1972, **34**, 2523.

[7] G. A. Olah and C. W. McFarland, *Inorg. Chem.*, 1972, **11**, 845.

[8] S. A. A. Zaidi and Z. A. Siddiqi, *Acta Chim. Acad. Sci. Hung.*, 1977, **92**, 57.

[9] T. C. Waddington and F. Klanberg, *J. Chem. Soc.*, 1960, 2332.

[10] K. B. Dillon, T. C. Waddington, and D. Younger, unpublished work.

[11] K. B. Dillon, R. J. Lynch, R. N. Reeve, and T. C. Waddington, *J. Inorg. Nuclear Chem.*, 1974, **36**, 815.

solutions, which showed single ^{31}P n.m.r. signals (Table 1). The chemical shift moves to lower field with increasing acid strength, consistent with incomplete protonation of the phosphoryl oxygen in all the solvents except 65 oleum. (Protonation at phosphorus would cause the appearance of a doublet spectrum.) These results may be compared with a shift of -6.9 p.p.m. in the less strongly acidic solvent liquid hydrogen chloride,[10] and are in general agreement with previous work on PCl_3O,[3,5,6,8] except for that of Gillespie *et al.*[1] who concluded that PCl_3O is a non-electrolyte in 100% H_2SO_4. The downfield shift relative to free PCl_3O is quite substantial in this solvent, indicating that partial protonation to $[PCl_3(OH)]^+$ does occur under our conditions. Paul and his co-workers [3,5,6] asserted that PCl_3O is completely protonated in disulphuric acid, which seems unlikely from our results, but the apparent discrepancy may be caused by variation in the concentration of PCl_3O which will affect the extent of protonation. A downfield shift is expected on protonation of the phosphoryl oxygen, probably because of the reduction in electron density in the P=O bond, and is also observed in other systems; [10,12] similar downfield shifts have been reported on formation of PCl_3O complexes co-ordinated *via* the phosphoryl oxygen.[13]

(*ii*) *Tribromophosphine Oxide*.—The compound PBr_3O gave a colourless solution in 100% H_2SO_4 which showed a single ^{31}P n.m.r. signal at 80 p.p.m. This compares with a reported shift of 103.4 p.p.m. for pure liquid PBr_3O,[14] and is consistent with partial protonation of the phosphoryl oxygen. After 10 d three signals were present in the spectrum, two weak ones at -2 and 26 p.p.m. and a stronger one at 80 p.p.m. The intermediate signal had disappeared after 24 d, while the peak at -2 p.p.m. had increased in intensity relative to the upfield resonance. No new signals appeared over the next few months but the peak at -2 p.p.m. continued to increase in intensity, and was in an intensity ratio of *ca.* 3 : 2 relative to the original signal after 8 months. Darkening of the solution, probably due to bromine liberation, was also observed during this period. The value of -2 p.p.m. is very close to the reported shift for protonated phosphoric acid, $[P(OH)_4]^+$, in 100% H_2SO_4,[15] and the results are compatible with slow solvolysis of the P–Br bonds. [With the exception of H_3PO_4,[15] the

$$[PBr_3(OH)]^+ \longrightarrow [PBr_2(OH)_2]^+ \longrightarrow [PBr(OH)_3]^+ \longrightarrow [P(OH)_4]^+ \quad (1)$$

phosphorus(v) species are unlikely to be completely protonated, but are represented in the protonated form for clarity in equation (1). This also applies to similar species discussed subsequently.] The signal at 26 p.p.m. could arise from either of the intermediate bromophosphorus species, but the results from 25 oleum suggest that it is due to (partially) protonated dibromophosphoric acid, $[PBr_2(OH)_2]^+$. The second intermediate presumably never reaches a high enough concentration to be detected.

Solutions of PBr_3O in chloro- and fluoro-sulphuric acid showed single ^{31}P n.m.r. signals, at 76 and 74 p.p.m. respectively. The solutions remained unchanged over 4 months, showing that $[PBr_3(OH)]^+$ is stable to solvolysis in these solvents. The downfield shift relative to 100% H_2SO_4 confirms that protonation is more extensive, as expected from the PCl_3O data; the results in $HSFO_3$ are in agreement with the conclusions of Paul and his co-workers.[5,6]

A solution of PBr_3O in 25 oleum initially showed a single resonance at 66 p.p.m., as expected for more complete protonation than in the solvents discussed hitherto. The spectrum remained unchanged for more than 1 month, although the solution, previously colourless, took on a faint bromine colouration. After 8 months the solution was darker and weak signals were apparent at -2, 6, and 10 p.p.m. in addition to a very intense peak at 64 p.p.m. Inorganic phosphates show a signal at 6.6 p.p.m. in 25 oleum,[15] ascribed to an equilibrium between $[P(OH)_4]^+$ and a protonated pyrophosphate species, so the probable assignment and solvolysis path is (2). The assignment is supported by the relative

$$\underset{64}{[PBr_3(OH)]^+} \longrightarrow \underset{10}{[PBr_2(OH)_2]^+} \longrightarrow \underset{-2}{[PBr(OH)_3]^+} \longrightarrow \underset{6\ \text{p.p.m.}}{[P(OH)_4]^+\text{–pyrophosphate}} \quad (2)$$

intensities, the weakest signal being at 6 p.p.m., since solvolysis is clearly very slow in this solvent. The downfield shift for the dibromo-species compared with 100% H_2SO_4 is as expected for more extensive protonation, and is indeed comparable with the shift difference for $[PBr_3(OH)]^+$ itself in the two solvents.

Unlike the sulphuric acid and 25 oleum solutions where bromine liberation was slow, the solution of PBr_3O in 65 oleum darkened rapidly, and after 2 d contained a large amount of liquid bromine. The ^{31}P n.m.r. results are represented diagramatically in the Figure. The initial peak at 57 p.p.m. is ascribed to $[PBr_3(OH)]^+$; this signal moves to lower field (55 p.p.m. after 1 d, 47 p.p.m. after 2 d) with decreasing concentration of the species, as expected for increased protonation, and is no longer visible after 3 d. Weak signals at 17 and 26 p.p.m. were apparent in the spectrum after 7 h; the former disappeared with time, while the latter increased in intensity, eventually becoming the strongest resonance. Further peaks at 35 and 42 p.p.m. became visible after 1 d, and were still present after 1 month, the variations in relative peak height being shown in the Figure. It is thus necessary to account for four peaks other than $[PBr_3(OH)]^+$. The relative intensities and chemical shifts of the species are not consistent with the formation

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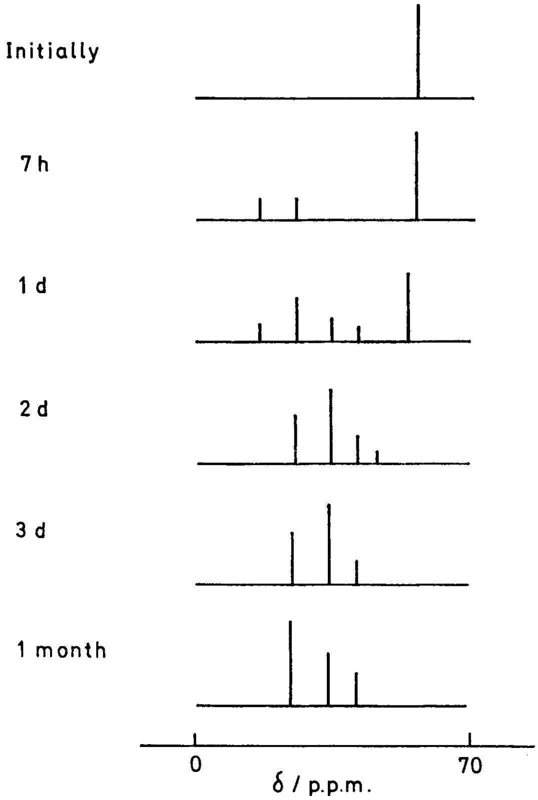
[12] K. B. Dillon, M. P. Nisbet, and T. C. Waddington, manuscript in preparation.

[13] K. B. Dillon and T. C. Waddington, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1825.

[14] L. C. D. Groenweghe and J. H. Payne, jun., *J. Amer. Chem. Soc.*, 1959, **81**, 6357.

[15] K. B. Dillon and T. C. Waddington, *J. Chem. Soc.* (*A*), 1970, 1146.

of condensed phosphates containing no bromine, as found for orthophosphates,[15] *via* monomeric $[PBr_2(OH)_2]^+$ and $[PBr(OH)_3]^+$ species. Since solvolysis of P–Br bonds is slow in 100% H_2SO_4 and (particularly) 25 oleum it is unlikely to be fast in 65 oleum. Nevertheless, rapid formation of bromine was observed. A possible mechanism to account for these results is the formation of condensed species *via* HBr elimination, as shown in the Scheme. Hydrobromic acid is oxidised by disulphuric acid according to equation [4] (3) and is not



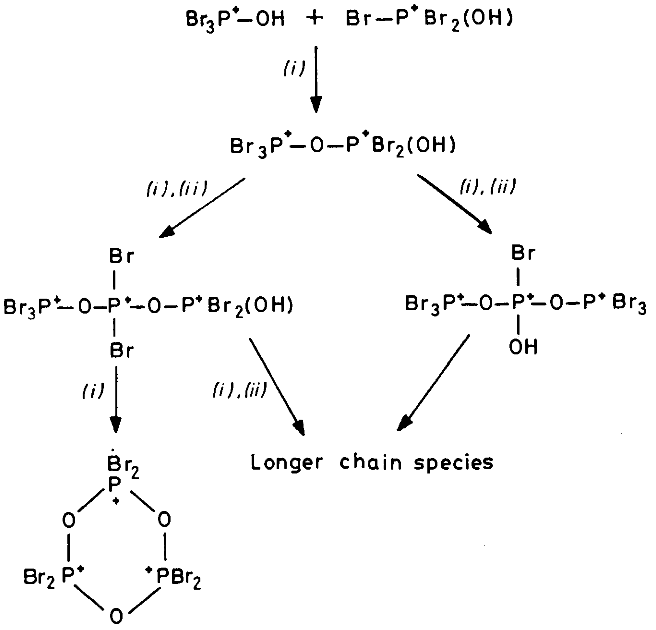
Relative peak heights in the ^{31}P n.m.r. spectrum from the reaction of PBr_3O with 65 oleum

$$2HBr + 2H_2S_2O_7 \longrightarrow Br_2 + SO_2 + 3H_2SO_4 \quad (3)$$

expected to exist as such in 65 oleum, which contains di- and poly-sulphuric acids.[16] Formation of bromine in this way could provide the driving force for condensation, unlike PCl_3O where condensation is not observed since oxidation of HCl to chlorine does not take place. The only possible reaction in chloro-systems is the formation of $HSClO_3$.[17]

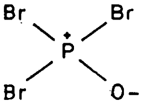
$$HCl + H_2S_2O_7 \longrightarrow HSClO_3 + H_2SO_4 \quad (4)$$

The Scheme shows the possibility of formation of both chain and ring bromophosphonium compounds by HBr elimination. It contains groups of the form (A)—(D). On the assumption that attack is preferential at chain ends rather than middle groups, these are the only species likely to be formed. Any P–P coupling in unsymmetrical compounds will not be visible because of rapid proton exchange between the solvent and P–OH

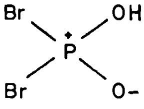


SCHEME (*i*) −HBr; (*ii*) $+[PBr_3(OH)]^+$

groups. Assignment of the peaks is difficult, but since terminal units usually have lower shifts than ring or chain units,[15,18] and groups containing bromine atoms probably have higher shifts than analogous hydroxo-species, a tentative assignment is (A) 26, (B) 17, (C) 42, and (D) 35 p.p.m.

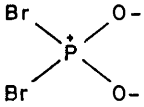


(A)



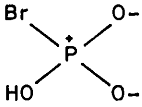
(B)

terminal units



(C)

ring or chain unit



(D)

chain unit

The shift for $[PBr_3(OH)]^+$ in 65 oleum suggests that complete protonation of PBr_3O in $H_2S_2O_7$ is unlikely under our conditions, in contrast with previous deductions.[3] This apparent discrepancy could again arise from a difference in solute concentration, however. The results show that the initial reaction in all the solvents is (partial) protonation, as with PCl_3O, but the product undergoes slow solvolysis in 100% H_2SO_4 and 25 oleum, and possible condensation *via* HBr elimination in 65 oleum.

(*iii*) *Phosphorus*(V) *Chloride*.—Addition of 100% H_2SO_4 to PCl_5 caused a vigorous reaction. The ^{31}P n.m.r. spectrum of the resulting solution showed one

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[16] R. J. Gillespie and E. A. Robinson, *Canad. J. Chem.*, 1962, **40**, 658.

[17] R. J. Gillespie and K. C. Malhotra, *J. Chem. Soc.* (*A*), 1967, 1944.

[18] V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 227.

signal only, at −20 p.p.m., readily assignable to $[PCl_3(OH)]^+$. No change in the spectrum was apparent after 10 weeks, but in 6 months an additional small peak at −1 p.p.m. was present. After 10 months the spectrum showed two peaks at −20 and −2 p.p.m., in the intensity ratio *ca.* 3 : 1. The new peak is due to $[P(OH)_4]^+$,[15] indicating that slow solvolysis of $[PCl_3(OH)]^+$ takes place. The intermediate species $[PCl_2(OH)_2]^+$ and $[PCl(OH)_3]^+$ presumably remain below the limit of detection.

Phosphorus(V) chloride dissolved in $HSClO_3$ with a vigorous reaction to yield a colourless solution, which showed a single peak at −87 p.p.m. This is ascribed to $[PCl_4]^+$, and compares with a shift of −87.3 p.p.m. for $[PCl_4]^+$ in liquid HCl.[19] The spectrum remained constant over 20 d, but after 10 months it contained two peaks of approximately equal intensity, at −88 and −22 p.p.m. The new peak is due to $[PCl_3(OH)]^+$ showing that solvolysis of $[PCl_4]^+$ is extremely slow in this solvent.

The initial reaction with $HSFO_3$ followed a similar course. The pale brown solution gave a single ^{31}P n.m.r. peak at −87 p.p.m., but after 2 d this was greatly reduced in intensity, and a quartet had appeared at 38 p.p.m. [^1J(P–F) 1 070 Hz], due to PF_3O.[7] Only minor changes in intensity were observed after 9 d. The formation of PCl_4^+ is thus followed by solvolysis and halogen exchange, as found for a number of other systems in fluorosulphuric acid.[12] Since no intermediates were detected, the reaction sequence, either *via* $[PCl_3(OH)]^+$, $[PCl_2F(OH)]^+$, and $[PClF_2(OH)]^+$, or *via* $[PCl_3F]^+$, $[PCl_2F_2]^+$, and $[PClF_3]^+$, cannot be established, but the former route appears more likely in view of the results for PBr_5 in $HSFO_3$ [section (*iv*)]. It is noteworthy that $[PCl_3(OH)]^+$ does not exchange directly with $HSFO_3$ [section (*i*)], suggesting that a different source of fluoride for exchange must be generated in the reaction. The most probable source is *via* the hydrogen chloride formed in the initial reaction [equation (5)] which can then equilibrate with the solvent [equation (6)]. This

$$[PCl_4][PCl_6] + 2HSFO_3 \longrightarrow 2[PCl_4]^+ + 2HCl + 2[SFO_3]^- \quad (5)$$

$$HCl + HSFO_3 \rightleftharpoons HF + HSClO_3 \quad (6)$$

equilibrium is expected to lie over to the left, but protonation of HF which is a stronger base than HCl [equation (7)] will pull it further to the right by removing HF.

$$HF + HSFO_3 \rightleftharpoons [H_2F]^+ + [SFO_3]^- \quad (7)$$

$$P\text{–}Cl + HF \longrightarrow P\text{–}F + HCl \quad (8)$$

Exchange of HF with a phosphorus chloro-compound will generate more HCl [equation (8)], thus perpetuating the reaction by affecting the equilibrium in (6). The deduction that chloride can act as a generator of fluoride for exchange is supported by the observation of exchange between $[PBr_3(OH)]^+$ and $HSFO_3$ to give $[PF(OH)_3]^+$,[12] when sodium chloride was added to the solution but not in its absence. Further support is provided by the results for $[NEt_4][PCl_6]$ in this solvent, discussed below.

A vigorous reaction took place on addition of 25 oleum to PCl_5, producing a solution which darkened on standing. The initial ^{31}P n.m.r. spectrum showed a weak signal at −89 p.p.m. ($[PCl_4]^+$) and a very strong one at −24 p.p.m. {$[PCl_3(OH)]^+$}. No change was apparent after 16 d, but after 5 weeks the low-field signal had disappeared, showing that $[PCl_4]^+$ is solvolysed slowly. The sample was monitored for another 10 months but no more changes were detected. The difference in shift from $[PCl_3(OH)]^+$ formed directly from PCl_3O [section (*i*)] arises partly from concentration effects, but mainly from a weakening of the acid strength of the solvent in the initial stages of the reaction, since HCl will not be a strong acid in the sulphuric or disulphuric acid solvent

$$[PCl_4][PCl_6] + 2H_2SO_4 + H_2S_2O_7 \longrightarrow [PCl_4]^+ + [PCl_3(OH)]^+ + 3HCl + 2[HS_2O_7]^- \quad (9)$$

systems. This deduction is again supported by the results for $[NEt_4][PCl_6]$ in 25 oleum.

The reaction with 65 oleum followed a very similar course. The ^{31}P n.m.r. spectrum of the freshly prepared solution showed signals at −86 ($[PCl_4]^+$) and −21 p.p.m. {$[PCl_3(OH)]^+$}. The only change after 10 weeks was a decrease in intensity of the signal at lower field, and this had disappeared after 10 months, leaving a single resonance at −22 p.p.m., due to $[PCl_3(OH)]^+$. Again the acid strength of the solvent will have been reduced considerably by the initial reaction, since $[PCl_6]^-$ appears to be unstable in these media.

The most interesting difference in behaviour for the various solvents is that $HSFO_3$ and $HSClO_3$ appear to form $[PCl_4]^+$ exclusively, while 100% H_2SO_4 and the oleums form mainly $[PCl_3(OH)]^+$, accompanied by some $[PCl_4]^+$ in the case of the oleums. Paul and his co-workers deduced previously that in both $HSFO_3$ [5,6] and $H_2S_2O_7$ [4] the only product is the $[PCl_4]^+$ ion, but our results indicate that the reaction is more complex, particularly for $H_2S_2O_7$. Since PCl_5 exists as $[PCl_4][PCl_6]$ in the solid state, the behaviour of $[NEt_4][PCl_6]$ was studied in the various solvents to try to confirm that the anion is unstable. ($[PCl_6]^-$ is readily identifiable by n.m.r. spectroscopy.[11]) The results are summarised in Table 2, and show that the exclusive product in sulphuric acid or the oleums is (partially) protonated PCl_3O; $[PCl_4]^+$ is formed in $HSClO_3$, while $[PCl_4]^+$ and some PF_3O are obtained in $HSFO_3$. Thus $[PCl_6]^-$ is

TABLE 2

Phosphorus-31 chemical shifts (p.p.m.) for $[NEt_4][PCl_6]$ in acid solvents

Solvent	$\delta(^{31}P)$	^1J(P–F)/ Hz	Assignment
100% H_2SO_4	−20		$[PCl_3(OH)]^+$
$HSClO_3$	−90		$[PCl_4]^+$
$HSFO_3$	−88 (s)		$[PCl_4]^+$
	38 (w) quartet	1 070	PF_3O
25 oleum	−26		$[PCl_3(OH)]^+$
65 oleum	−52		$[PCl_3(OH)]^+$

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[19] K. B. Dillon, T. C. Waddington, and D. Younger, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 63.

probably the main source of $[PCl_3(OH)]^+$ observed in the spectra of PCl_5 in oleum solvents; the simultaneous reduction in acid strength causes complete solvolysis of $[PCl_4]^+$ in 100% H_2SO_4, and partial solvolysis in the oleums, the further reduction in acid strength being reflected in less extensive protonation of PCl_3O than observed with PCl_3O as the solute [section (*i*)]. In the halogenosulphuric acids the initial product from both PCl_5 and $[PCl_6]^-$ is $[PCl_4]^+$, further reaction originating from this species.

The stability of the $[PCl_4]^+$ ion in 25 oleum was investigated by preparing a solution of $[PCl_4][BCl_4]$ in this solvent. A single peak at −87 p.p.m. ($[PCl_4]^+$) was observed in the ^{31}P n.m.r. spectrum, which remained unchanged over 30 d. The initial spectrum of $[PCl_4]$-$[BCl_4]$ in $HSFO_3$ was identical, but after 2 d a quartet had appeared at 36 p.p.m. [^1J(P–F) 1 070 Hz], due to PF_3O. Nine days later an additional triplet at 22 p.p.m. [^1J(P–F) 1 006 Hz], assigned to $[PF_2(OH)_2]^+$, was present. These results show conclusively that the $[PCl_4]^+$ ion is subject to both fluorination and solvolysis in $HSFO_3$, but is stable in 25 oleum; they are completely in accordance with the deductions from the $[PCl_6]^-$ results.

The reaction of $[PF_6]^-$ (as $K[PF_6]$) with 25 oleum was also studied. The compound dissolved with a vigorous reaction to give a colourless solution, the initial spectrum of which showed a strong quartet at 35 p.p.m. [^1J(P–F) 1 070 Hz], due to PF_3O,[7] and a weak triplet at 21 p.p.m. [^1J(P–F) 1 000 Hz], assigned to $[PF_2(OH)_2]^+$. The intensities of the peaks were approximately reversed after 8 d, indicating that $[PF_6]^-$ is decomposed by 25 oleum to give PF_3O, but the concomitant reduction in acid strength is sufficient to cause slow solvolysis of the latter to $[PF_2(OH)_2]^+$.

(*iv*) *Phosphorus*(V) *Bromide*.—Phosphorus(V) bromide dissolved in 100% H_2SO_4 with a vigorous reaction and much heat evolution. The orange-brown solution contained a small quantity of a dark liquid, presumably elemental bromine. The ^{31}P spectrum showed two signals at 80 and 84 p.p.m. of intensity *ca.* 1 : 4. The intensity ratio was reversed over 5.5 h, and after 1 d only one signal was present, at 80 p.p.m. The spectrum remained unchanged for more than 17 d but after 40 d a weak peak had appeared at 0 p.p.m. After 4 months two signals were present at −3 and 81 p.p.m., in the intensity ratio *ca.* 2 : 3. A large amount of liquid bromine was formed in the tube during the course of the reaction. The original signal at 84 p.p.m. is assigned to $[PBr_4]^+$, and agrees well with the reported shift in liquid HCl.[19] The peak at 80 (or 81) p.p.m. is ascribed to $[PBr_3(OH)]^+$, in agreement with the data for PBr_3O in H_2SO_4, and the resonance between −3 and 0 p.p.m. to $[P(OH)_4]^+$. Tetrabromophosphonium ion is thus formed in the early stages, but is solvolysed in 1 d to $[PBr_3$-$(OH)]^+$, which then undergoes further slow solvolysis. The intermediates between $[PBr_3(OH)]^+$ and $[P(OH)_4]^+$ remained below the detection limit.

The pale orange solution of PBr_5 in $HSClO_3$ showed one signal only, at 85 p.p.m. ($[PBr_4]^+$), over 20 d. The pale colour suggests that the bromide ion is much more stable to oxidation in this solvent than in sulphuric acid or the oleums. After 10 months the solution had darkened slightly, and showed seven peaks in its n.m.r. spectrum, which could be readily assigned to species of the type $[PBr_{4-n}Cl_n]^+$ and $[PBr_{3-x}Cl_x(OH)]^+$ as shown in Table 3. The shifts for the bromochlorophosphonium ions are in excellent agreement with data from liquid HCl,[19] while the intermediates between $[PCl_3(OH)]^+$ and $[PBr_3(OH)]^+$ have been obtained in other reactions.[12] The results show that $HSClO_3$ acts both as a solvolysing agent and as a source of chlorine. Since it does not exchange directly with $[PBr_3(OH)]^+$, however [section (*i*)], an indirect mechanism must be proposed, as suggested in reactions (10)—(12). Reactions (11) and (12)

TABLE 3

Phosphorus-31 chemical shifts (p.p.m.) for species derived from PBr_5 in $HSClO_3$

$\delta(^{31}P)$	Assignment
−22	$[PCl_3(OH)]^+$
−9	$[PBr_2Cl_2]^+$
7	$[PBrCl_2(OH)]^+$
35	$[PBr_3Cl]^+$
40	$[PBr_2Cl(OH)]$
76	$[PBr_3(OH)]^+$
84	$[PBr_4]^+$

$$Br^- + HSClO_3 \longrightarrow HBr + [SClO_3]^- \qquad (10)$$

$$2HBr + HSClO_3 \xrightarrow{\text{slow}} Br_2 + SO_2 + HCl + H_2O \qquad (11)$$

$$HSClO_3 + H_2O \longrightarrow HCl + H_2SO_4 \qquad (12)$$

produce HCl, which may then act as the source of exchanging chlorine. The slowness of the redox reaction (11) would account satisfactorily for the observation of mixed species only after a considerable time.

Phosphorus(V) bromide dissolved exothermically in $HSFO_3$, giving a brown solution consistent with bromine liberation, which darkened further on standing. The freshly prepared solution showed an intense resonance at 86 p.p.m. ($[PBr_4]^+$), and a weak quartet at 38 p.p.m. [^1J(P–F) 1 070 Hz (PF_3O)].[7] After 2 d an additional triplet at 22 p.p.m. [^1J(P–F) 997 Hz], assigned to (partially) protonated difluorophosphoric acid,[7] was present. No new signals were apparent after 9 d, but the singlet was much weaker and the multiplets stronger. The intermediates between $[PBr_4]^+$ and PF_3O remained below the limit of detection, but a possible reaction sequence is (13)—(15). The HF formed in reaction (14) can then act as the fluoride source for exchange, as in the PCl_5–$HSFO_3$ reaction discussed earlier. The solvolysis probably proceeds *via* $[PBr_3(OH)]^+$, even though this was not detected directly, since a solution of $[PBr_4]$-$[BBr_4]$ in $HSFO_3$ showed a weak signal at 71 p.p.m. {$[PBr_3(OH)]^+$} in addition to a strong resonance at 85 p.p.m. ($[PBr_4]^+$) after 9 d as discussed below. Further solvolysis of PF_3O to $[PF_2(OH)_2]^+$ presumably takes place because the acid strength is reduced in reactions such as (14) and (15).

$$[PBr_4]Br + HSFO_3 \longrightarrow [PBr_4]^+ + [SFO_3]^- + HBr \quad (13)$$

$$2HBr + HSFO_3 \longrightarrow Br_2 + HF + H_2O + SO_2 \quad (14)$$

$$[PBr_4]^+ \longrightarrow [PBr_3(OH)]^+ \longrightarrow PF_3O \quad (15)$$

25 oleum and 65 oleum reacted in a similar manner with PBr_5. In both instances dissolution was exothermic and bromine was liberated. The initial ^{31}P n.m.r. spectra showed one peak only, at 84 (25 oleum) and 86 p.p.m. (65 oleum), ascribed to $[PBr_4]^+$. A weak peak at 70 p.p.m. appeared very slowly in the 25 oleum solution over 18 weeks, due to $[PBr_3(OH)]^+$, but the 65 oleum solution remained stable for at least 5 months.

Our results and conclusions differ from those of Paul *et al.*,[4] who asserted that PBr_5 dissolved in $H_2S_2O_7$ with dissociation to PBr_3 and Br_2, followed by oxidation of PBr_3 by the solvent to $[PBr_3(OH)]^+$. Since $H_2S_2O_7$ is intermediate in strength between 25 and 65 oleum, and $[PBr_4]^+$ seems to be quite stable in both these solvents, this reaction appears most unlikely. Phosphorus(v) bromide forms $[PBr_4]^+$ initially in all the solvents; this ion is then subject to solvolysis and/or halogen exchange, the rate of solvolysis depending on the acid strength, to the extent that it remains stable in 65 oleum.

The stability of the $[PBr_4]^+$ ion in 25 oleum was further demonstrated by dissolving $[PBr_4][BBr_4]$ in this solvent; the single ^{31}P n.m.r. signal at 85 p.p.m. ($[PBr_4]^+$) remained unchanged over 1 month. The initial spectrum of $[PBr_4][BBr_4]$ in $HSFO_3$ also consisted of a resonance at 85 p.p.m., but a PF_3O quartet at 36 p.p.m. [^1J(P–F) 1 070 Hz] was present 2 d after preparation. Nine days later, additional signals at 22 [t, ^1J(P–F) 1 006 Hz], due to $[PF_2(OH)_2]^+$, and 71 p.p.m. (s), due to $[PBr_3(OH)]^+$, were apparent. This reaction sequence looks to be similar to, but slower than, that of $[PBr_4]Br$ with $HSFO_3$, the difference in reaction rates presumably being due to the greater stability of $[BBr_4]^-$ than Br^- in this solvent.

The main differences in behaviour between phosphorus(v) chloride and bromide thus seems to arise from their different solid-state structures, since $[PCl_6]^-$ is unstable in these media, forming $[PCl_3(OH)]^+$ in H_2SO_4 and the oleums, although the ready oxidation of HBr to Br_2 by all the solvents except $HSClO_3$ must also be taken into account.

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