Reactions of Some Phosphorus(III) Halides with Strongly Acidic Solvents

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The reactions of PX_3 (X = Cl, Br, or I) with the strongly acidic solvents 100% H_2SO_4, 25 and 65 oleum, $HSClO_3$, and $HSFO_3$ have been investigated by means of [31]P n.m.r. spectroscopy. The usual initial reaction is oxidation to $[PX_3(OH)]^+$, although $HSClO_3$ also forms $[PX_3Cl]^+$. The reduction in acid strength which necessarily accompanies the redox reaction promotes solvolysis of P–X bonds, and halogen exchange in $HSClO_3$ and $HSFO_3$. Formation of $[PBr_4]^+$ from PBr_3 has also been observed in several solvents. Some interesting new species, notably phosphorus(V) cations containing P–I bonds, have been identified in solution, but not in 25 oleum. Condensation reactions involving elimination of HBr or HI may occur in 65 oleum. Possible mechanisms for the various reactions observed are proposed.

THE reactions between phosphorus(III) halides (except PI_3) and strongly acidic solvents have been investigated by a number of workers in recent years, the results depending on both the solvent and the reaction conditions.[1-4] The compounds PCl_3 and PBr_3 yield highly conducting solutions in disulphuric acid,[1] and this behaviour was ascribed to oxidation and protonation to give $[PX_3(OH)]^+$. More surprisingly, perhaps, the same solutes were reported to be non-electrolytes in $HSFO_3$; the suggested explanation was solvolysis to undissociated $P(SFO_3)_3$.[2] Fluorine-19 and [31]P n.m.r. spectra of solutions of PF_3 in $HSFO_3$ indicated that the main species present was the unprotonated starting material (or a rapidly exchanging system), whereas in a 1 : 1 mixture of SbF_5 and $HSFO_3$ (' magic acid ') PF_3 was oxidised to PF_3O, which may be partially protonated in this solvent.[3] More recently, an elegant [31]P n.m.r. investigation of the reaction of PF_3, PCl_3, PBr_3, and the mixed phosphorus-(III) chloride fluorides and bromide chlorides with SbF_5·$HSFO_3$ in liquid SO_2 at 203 K has shown[4] that under these conditions the compounds are protonated at phosphorus with formation of $[HPX_rY_{3-n}]^+$ (X = Cl; Y = F or Br; $0 \leqslant n \leqslant 3$). These species were unstable at higher temperatures, decomposing at ca. 223 K.[4]

We recently reported the results from a systematic study of the reactions of some phosphorus(V) halides and halide oxides with 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.[5] This work has now been extended to the behaviour of PCl_3, PBr_3, and PI_3 in these solvents. Again the solutions have been monitored over a long time when necessary to elucidate the course of reaction.

EXPERIMENTAL

All 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 except for PI_3 which was recrystallised from CH_2Cl_2. Phosphorus-31 n.m.r. spectra were recorded at 307.2 K as described previously,[5] using sample tubes having an outside diameter of 5 mm. The plastic tube caps were further protected by a layer of Parafilm to prevent access to air or moisture. Although many of the caps darkened in time, particularly with more concentrated oleum solvents, no difficulties due to hydrolysis

† Oleum containing 25% free SO_3.

were encountered, even over long periods. Reacting samples were generally kept at ca. 307 K for some hours in the pre-heater of the spectrometer, but were subsequently stored at room temperature and re-examined periodically. No particular precautions were taken to exclude light at this stage, since the course of reaction was usually well established. Chemical shifts were measured from external P_4O_6 (continuous-wave spectrometer) or H_3PO_4 (Fourier-transform spectrometer), but are expressed relative to 85% H_3PO_4, with the upfield direction taken as positive.

RESULTS AND DISCUSSION

The results for the individual phosphorus(III) halides are discussed separately.

(i) *Phosphorus Trichloride.*—This compound was initially immiscible with 100% H_2SO_4, even on shaking, but when the mixture was allowed to stand a vigorous exothermic reaction occurred after 8 h, giving a colourless solution. Its [31]P n.m.r. spectrum showed a single peak at −19 p.p.m., readily assigned to (partially) protonated PCl_3O.[5] After 2 d a second signal had appeared at −15 p.p.m., and 2 d later a third peak was present at −1 p.p.m., ascribed to protonated phosphoric acid, $[P(OH)_4]^+$.[5-7] Solvolysis of $[PCl_3(OH)]^+$ thus takes place, and the signal at −15 p.p.m. must represent one of the species intermediate between $[PCl_3(OH)]^+$ and $[P(OH)_4]^+$. Data from other solvents discussed below indicate that it is due to $[PCl_2(OH)_2]^+$; the second intermediate $[PCl(OH)_3]^+$ remained below the detection limit in this system. Solvolysis to $[P(OH)_4]^+$ was complete after 23 d. This behaviour contrasts with that of PCl_3O itself,[5] where the partially protonated form was stable in 100% H_2SO_4, and arises because the acid strength is reduced initially in the oxidation [equation (1)]. [As in the previous paper,[5] phosphorus(V) species

$$PCl_3 + 2H_2SO_4 \longrightarrow [PCl_3(OH)]^+ + [HSO_4]^- + SO_2 + H_2O \quad (1)$$
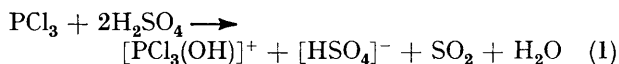
other than H_3PO_4 are unlikely to be completely protonated, but are represented in the protonated form for clarity in equation (1) and subsequently.] The only other change detected in this system was the appearance of a weak peak at 15 p.p.m. after 66 d, the spectrum then remaining unchanged for another 8 months. This resonance probably arises from a protonated trimetaphosphate species,[6] and although not expected in H_2SO_4

as solvent, could be due to formation of the stronger acid $HSClO_3$ during solvolysis of P–Cl bonds [equation (2)].

$$P\text{–}Cl + H_2SO_4 \longrightarrow P\text{–}OH + HSClO_3 \qquad (2)$$
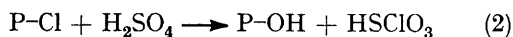
Formation of a peak in this position has been observed for solutions of inorganic phosphates in $HSClO_3$.[6]

Phosphorus trichloride behaved similarly, but initially more rapidly, with 25 oleum. **CAUTION**: The original two-phase system was shaken, and underwent a violent reaction 30 min after preparation, yielding a colourless solution. The [31]P n.m.r. spectrum consisted of one signal at −21 p.p.m., due to $[PCl_3(OH)]^+$.[5] Two days later, a new peak at −14 p.p.m. $\{[PCl_2(OH)_2]^+\}$ was present. After 25 d, three signals at −20, −14, and 2 p.p.m. $\{[P(OH)_4]^+\}$, in the intensity ratio *ca.* 5 : 1 : 3, were found. Solvolysis of $[PCl_3(OH)]^+$ thus occurs more slowly than in 100% H_2SO_4. The ion $[PCl_3(OH)]^+$ when formed directly from PCl_3O was not solvolysed in 25 oleum,[5] the difference again being due to the reduction in acid strength during the redox reaction. The peak at −14 p.p.m. had disappeared after 68 d, and a new resonance at 15 p.p.m. was present, ascribed to protonated trimetaphosphate.[6] Then months after preparation the solution gave three signals at −20, 0, and 15 p.p.m. with relative intensity *ca.* 2 : 5 : 1, showing that solvolysis was still only partial. The initial formation of $[PCl_3(OH)]^+$ is in general agreement with the work of Paul *et al.*[1] on solutions of PCl_3 in disulphuric acid, which is intermediate in SO_3 content between 25 and 65 oleum. Subsequent reaction will clearly depend on the relative concentrations of solute and solvent; a higher solute concentration will give a more marked reduction in acid strength during the redox reaction, and hence accelerate the solvolysis of $[PCl_3(OH)]^+$. It is worth noting that solvolysis of a P–Cl bond in either 25 or 65 oleum will decrease the acid strength, unlike H_2SO_4 where it causes an increase, since $HSClO_3$ is a stronger acid than H_2SO_4 but weaker than the oleums. This is shown by the extent of protonation of weak bases such as PCl_3O.[5]

CAUTION: Addition of 65 oleum to PCl_3 caused an immediate violent reaction, yielding a pale brown solution. The initial [31]P n.m.r. spectrum showed signals at −27 $\{[PCl_3(OH)]^+\}$ and −19 p.p.m., which changed little over 64 d apart from a slight upfield movement of the lower resonance. The second signal is assigned to $[PCl_2(OH)_2]^+$; its appearance in the original spectrum is a little surprising at first sight when compared with the results from sulphuric acid and 25 oleum, but the redox reaction probably occurs so quickly that appreciable local reductions in acid strength cause some solvolysis. The chemical shift seems very reasonable for (partially) protonated $PCl_2O(OH)$ when compared with the value of −9.3 p.p.m. for the pure acid,[8] and the shifts of −15 p.p.m. assigned to this species in H_2SO_4 and 25 oleum, where less extensive protonation is expected. (Protonation of a phosphoryl oxygen causes a downfield shift,[5,7] presumably because of a reduction in electron density in the P–O bond; the extent of this shift

becomes smaller for halogeno-species as the number of oxygen atoms attached to phosphorus increases,[9] reflecting the ability of oxygen to delocalise the positive charge.[7]) After 10 months further reaction had taken place, the spectrum showing resonances at −23 $\{[PCl_3-(OH)]^+\}$, −20 $\{[PCl_2(OH)_2]^+\}$, −10, 12, and 20 p.p.m. The two peaks at highest field are ascribed to equilibria involving protonated cyclic phosphates, as deduced for inorganic phosphates in more concentrated oleum solutions.[6] The signal at −10 p.p.m. is therefore assigned to the intermediate (partially) protonated chlorophosphoric acid, $[PCl(OH)_3]^+$. Very slow solvolysis of the P–Cl bonds thus occurs, unlike PCl_3O solutions in 65 oleum [5] which remain stable since there is no reduction in acid strength due to a redox reaction.
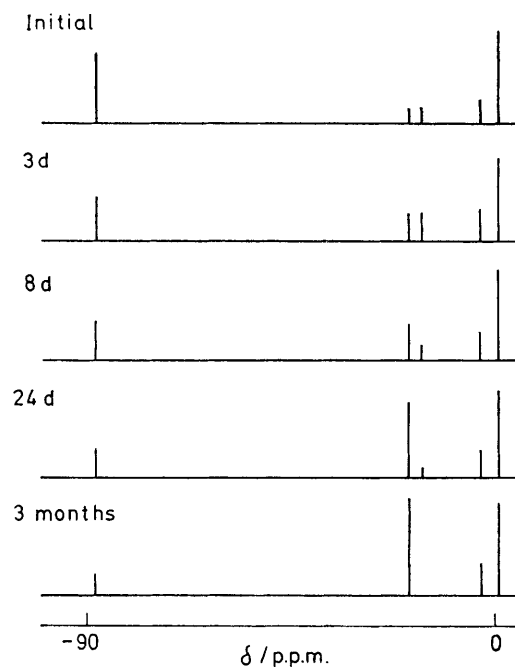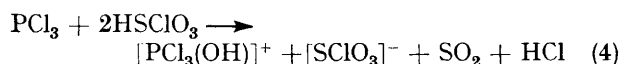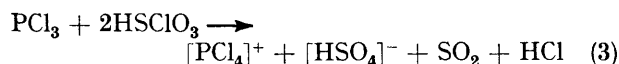

FIGURE 1   Relative peak heights in the [31]P n.m.r. spectrum from the reaction of PCl_3 with $HSClO_3$

Phosphorus trichloride appeared to be immiscible with $HSClO_3$, but dissolved on shaking to give a colourless solution. After *ca.* 10 min the solution began to bubble, and a vigorous reaction took place which was complete after 30 min. The quite complex [31]P n.m.r. spectrum of this solution, and the variation in relative peak heights over 3 months, are represented diagramatically in Figure 1. Assignment of the resonances is reasonably straightforward (Table 1), although there is some shift variation

TABLE 1

Phosphorus-31 n.m.r. data for the reaction of PCl_3 with $HSClO_3$

| $\delta(^{31}P)$/p.p.m.	Assignment
−88	$[PCl_4]^+$
−20 to −18	$[PCl_3(OH)]^+$
−18 to −15	$[PCl_2(OH)_2]^+$
−4 to −2	$[PCl(OH)_3]^+$
0–2	$[P(OH)_4]^+$

with time, presumably because of changes in the acid strength. The shift for $[PCl_4]^+$ is in good agreement with that derived from PCl_5 in $HSClO_3$,[5] and with data for this ion in liquid HCl[10] and organic solvents.[11,12] The other species lie on the solvolytic path between $[PCl_4]^+$ and $[P(OH)_4]^+$, and provide further support for the assignments given above for $[PCl_2(OH)_2]^+$ and $[PCl(OH)_3]^+$ in other solvents. The results suggest that $HSClO_3$ can act as an oxidising agent in two ways, by transferring either Cl or OH to PCl_3 [equations (3) and (4)]. This hypothesis is supported by the results for PBr_3 and PI_3 in $HSClO_3$, discussed below. (The form-

$$PCl_3 + 2HSClO_3 \longrightarrow$$
$$[PCl_4]^+ + [HSO_4]^- + SO_2 + HCl \quad (3)$$

$$PCl_3 + 2HSClO_3 \longrightarrow$$
$$[PCl_3(OH)]^+ + [SClO_3]^- + SO_2 + HCl \quad (4)$$

ation of chlorosulphurous acid, $HSClO_2$, appears unlikely; numerous salts containing the $[SClO_2]^-$ anion are known,[13] but the free acid has not been characterised, though there is spectroscopic evidence for a 1 : 1 complex of SO_2 and HCl in aqueous solution.[14]) The extensive initial solvolysis of both $[PCl_4]^+$ and $[PCl_3(OH)]^+$ apparent from Figure 1 probably arises from marked local reductions in acid strength during the redox reactions. Subsequent solvolysis is much slower once the system has become homogeneous. Solvolysis of $[PCl_4]^+$ derived directly from PCl_5 is extremely slow in $HSClO_3$, progressing only as far as formation of some $[PCl_3(OH)]^+$ after 10 months.[5]

Addition of $HSFO_3$ to PCl_3 gave a two-phase liquid system, with no apparent reaction on shaking. **CAUTION**: The mixture was allowed to stand, and after 1 h a violent exothermic reaction took place, giving a pale brown solution. The first ^{31}P n.m.r. spectrum of this solution showed a strong singlet at -29 p.p.m. $\{[PCl_3(OH)]^+\}$,[5] and a weak doublet at -12 p.p.m. $[^1J(P-F)\ 1\ 200\ Hz]$. Thirty minutes later a weak quartet at 37 p.p.m. $[^1J(P-F)\ 1\ 070\ Hz]$, readily assigned to PF_3O,[3,5] was also present. The doublet and quartet increased in intensity relative to the singlet during the next 3 h. Over 14 d, the same three signals were present, but the quartet increased in intensity and the doublet decreased relative to the single peak. The doublet is ascribed to the intermediate species $[PCl_2F-(OH)]^+$; the unprotonated precursor $PCl_2F(O)$ has a reported shift of 0 p.p.m. and a coupling constant of 1 175—1 190 Hz.[15] The downfield shift and small increase in J are entirely consistent with (partial) protonation of the phosphoryl oxygen.[3,5] The triplet expected for the second intermediate $[PClF_2(OH)]^+$ presumably remained below the detection limit. Since $[PCl_3(OH)]^+$ derived from PCl_3O was stable in $HSFO_3$ over 4 months,[5] a source of fluoride other than the solvent must be present for the observed exchange reactions. The most probable source is HF, which can readily be formed as a by-product of the redox reaction [equation (5)]. (Free fluorosulphurous acid, $HSFO_2$, is
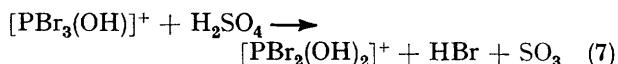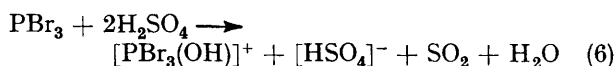
not known.[16]) Fluorine exchange has been reported for other systems in $HSFO_3$ where formation of HF is

$$PCl_3 + 2HSFO_3 \longrightarrow$$
$$[PCl_3(OH)]^+ + [SFO_3]^- + HF + SO_2 \quad (5)$$
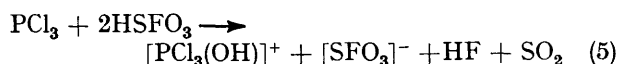
possible.[5] The results for this system do not agree with those of Paul *et al.*,[2] who found PCl_3 to be a non-electrolyte in $HSFO_3$ and tentatively suggested that it may solvolyse to undissociated $P(SFO_3)_3$. Quite clearly this does not happen under our reaction conditions.

(ii) Phosphorus Tribromide.—Liquid PBr_3 was immiscible with 100% H_2SO_4; the mixture was shaken for 6 h but two layers were still present, although a yellow colouration had appeared in both. A vigorous exothermic reaction took place after the mixture had been standing for another 5 h, giving a red-brown solution. A brown liquid eventually separated at the bottom of the n.m.r. tube, presumably elemental bromine. The ^{31}P n.m.r. spectrum of the original two-phase sample was recorded, and showed a very intense peak at -228 p.p.m. (PBr_3), with weak signals at 20 $\{[PBr_2(OH)_2]^+\}$, 78 $\{[PBr_3(OH)]^+\}$, and 83 $([PBr_4]^+)$ p.p.m. The shift values for these species agree well with data reported previously[5,15] or discussed below. After formation of the one-phase system, the ^{31}P spectrum contained three signals at -3, 28, and 80 p.p.m. with the highest-field resonance much more intense than the others. These are readily assigned to $[P(OH)_4]^+$,[5,7] $[PBr_2(OH)_2]^+$,[5] and $[PBr_3(OH)]^+$ respectively. (The shifts for partially protonated species are markedly concentration-dependent.) Over 20 d the intermediate signal disappeared while the $[P(OH)_4]^+$ peak increased in intensity relative to $[PBr_3(OH)]^+$, showing that solvolysis takes place. The remaining two signals were of approximately equal intensity after 27 d; further checks after 57 and 80 d confirmed this behaviour, and after 9 months only one signal at -2 p.p.m. was present. No signal for $[PBr-(OH)_3]^+$ was detected at any stage, presumably because it remains at a low concentration level throughout.

The observation of a $[PBr_4]^+$ signal from the two-phase mixture is interesting, and probably arises from a series of reactions at the interface. Some PBr_3 will be oxidised to $[PBr_3(OH)]^+$, equation (6), which causes a local reduction in acid strength leading to solvolysis [equation (7)]. A by-product of the solvolysis reaction is

$$PBr_3 + 2H_2SO_4 \longrightarrow$$
$$[PBr_3(OH)]^+ + [HSO_4]^- + SO_2 + H_2O \quad (6)$$

$$[PBr_3(OH)]^+ + H_2SO_4 \longrightarrow$$
$$[PBr_2(OH)_2]^+ + HBr + SO_3 \quad (7)$$

HBr, which can then be oxidised by the solvent to bromine [equation (8)]. Bromine can then react at the interface

$$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O \quad (8)$$
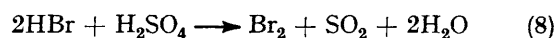
with PBr_3 to form PBr_5, which dissolves in 100% H_2SO_4 yielding $[PBr_4]^+$ ions.[5] Solvolysis of $[PBr_4]^+$ to $[PBr_3-(OH)]^+$ is complete in <1 d,[5] so its disappearance from the spectrum of the single-phase system is as expected.

The behaviour of this system is otherwise similar to that of PCl$_3$ with H$_2$SO$_4$, except for the difference in solvolysis rates. Solvolysis of [PBr$_3$(OH)]$^+$ derived directly from PBr$_3$O in H$_2$SO$_4$ is much slower [5] than observed here, because there is no redox reaction to cause a reduction in acid strength.

25 oleum reacted in a similar manner with PBr$_3$. The liquids, initially immiscible, both changed colour through yellow to brown during continuous shaking, and a vigorous exothermic reaction was observed 4 h after sample preparation. The resulting single phase was dark brown, and liquid bromine separated on standing overnight. N.m.r. spectra could not be obtained immediately following the reaction, but were afterwards successfully recorded. The sample was monitored for 7 months and the results are shown diagramatically in Figure 2. Assignment of the signals (Table 2) presents

TABLE 2

Phosphorus-31 n.m.r. data for the reaction of PBr$_3$ with 25 oleum

$\delta(^{31}P)$/p.p.m.	Assignment
−3	[PBr(OH)$_3$]$^+$
4	[P(OH)$_4$]$^{+}$ [6]
12	[PBr$_2$(OH)$_2$]$^+$
15	Polyphosphate equilibria [6]
72	[PBr$_3$(OH)$^+$]
84	[PBr$_4$]$^+$

few difficulties when compared with previous data for PBr$_3$O, PBr$_5$,[5] and inorganic phosphates [6] in 25 oleum. The peaks ascribed to [PBr$_3$(OH)]$^+$ and [PBr$_4$]$^+$ showed little sign of solvolysis during the period of study, the main changes occurring among lower-field resonances, as shown. The order of appearance of these peaks and their changes in intensity with time are entirely compatible with a stepwise solvolysis of [PBr$_2$(OH)$_2$]$^+$ to [P(OH)$_4$]$^+$ (and cyclic phosphate species [6]) via [PBr-(OH)$_3$]$^+$. As in the case of 100% H$_2$SO$_4$, the formation of [PBr$_4$]$^+$ probably takes place by means of a series of reactions at the interface between the liquid layers, but [PBr$_4$]$^+$ is much more stable in 25 oleum [5] and remains visible in all later spectra. Thus this reaction is more complicated than that of PCl$_3$ with 25 oleum. Previous workers have attempted to explain the highly conducting solutions formed by PBr$_3$ in H$_2$S$_2$O$_7$ as due to formation of [PBr$_3$(OH)]$^+$,[1] but the results show that other competing reactions may occur, certainly under the experimental conditions described.

CAUTION: Addition of 65 oleum to PBr$_3$ caused an immediate, violently exothermic, reaction, with formation of a red solution. After the mixture had stood overnight, a large amount of liquid bromine had collected at the bottom of the tube. Continuous-wave ^{31}P spectra could not be recorded successfully from this sample until 2 d after preparation, when three signals at 25, 33, and 42 p.p.m. were found, in the intensity ratio ca. 3 : 5 : 2. The only change observed over 2 months was in intensity, the ratio being ca. 5 : 4 : 2 at the end of this time. This spectral pattern is very similar to that for solutions of PBr$_3$O in 65 oleum from 3 d to 1 month after sample

preparation; these results were explained in terms of condensation via HBr elimination to give either ring or chain phosphate units with bromine atoms present.[5] To try to elucidate the initial stages of reaction, the system was later reinvestigated by Fourier-transform n.m.r. spectroscopy. The initial ^{31}P spectrum showed a strong signal at 46 p.p.m. {[PBr$_3$(OH)]$^+$}, with weaker ones at 15 {possibly [PBr$_2$(OH)$_2$]$^+$}, 23, 25 (shoulder), and 86 p.p.m. ([PBr$_4$]$^+$). After 14 h the [PBr$_3$(OH)]$^+$ peak had disappeared, and strong signals were present at 24, 32, and 42 p.p.m., similar to those from the continuous-wave spectrum, with weaker peaks at 14, 27 (shoulder), and 86 p.p.m. ([PBr$_4$]$^+$). The spectra are again very similar to those from the early stages of the PBr$_3$O–65

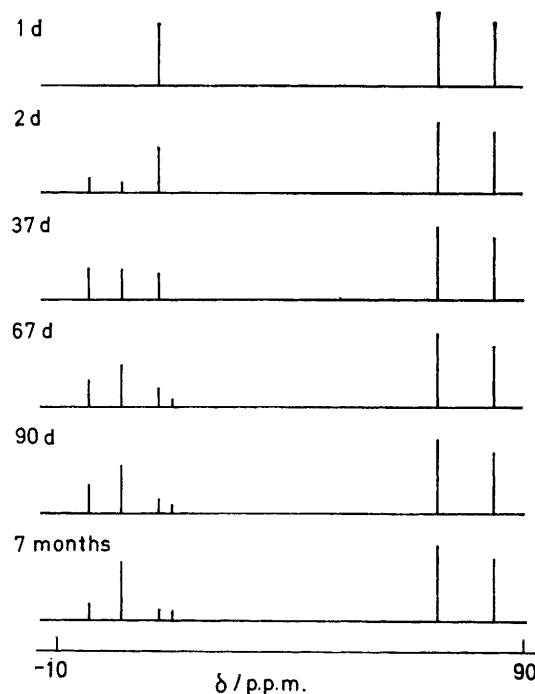
FIGURE 2   Relative peak heights in the ^{31}P n.m.r. spectrum from the reaction of PBr$_3$ with 25 oleum

oleum reaction, apart from the additional [PBr$_4$]$^+$ peak, which presumably arises from a local reaction between PBr$_3$ and liberated bromine, and the shoulder. The overall results indicate that the course of reaction depends markedly on local variations in concentration; the main long-term products are the same as from the PBr$_3$O–65 oleum reaction,[5] via [PBr$_3$(OH)]$^+$ and probably [PBr$_2$(OH)$_2$]$^+$ as intermediates, but [PBr$_4$]$^+$ may be formed as a by-product. Solvolysis of this ion is not expected once the solution is homogeneous, since [PBr$_4$]$^+$ derived from PBr$_5$ is stable to solvolysis in 65 oleum and is solvolysed extremely slowly in 25 oleum,[5] and any reduction in acid strength from the redox reaction will be smaller than the acidity difference between these solvents.

Addition of HSClO$_3$ to PBr$_3$ gave a two-phase system in which reaction was observed at the interface. Shaking of the mixture led to a vigorous exothermic reaction

and the formation of a pale orange solution, which showed a strong ^{31}P n.m.r. signal at 82 p.p.m. and weak signals at 36, 43, and 84 p.p.m. The spectrum remained unchanged for 5 d, but after 23 d a strong peak at 82 p.p.m. was present, together with weaker signals at −19, 11, and 44 p.p.m. Thirty-five days after preparation the sample gave a similar spectrum but with some increase in intensity of the resonance at lowest field. After 7.5 months these same four peaks were present, although the peak at −19 p.p.m. had decreased in intensity and a new signal at −2 p.p.m. was apparent. All of these peaks may be readily assigned, as shown in Table 3, and may

TABLE 3

Phosphorus-31 n.m.r. data for the reaction of PBr$_3$ with HSClO$_3$

$\delta(^{31}P)$/p.p.m.	Assignment
−19	$[PCl_3(OH)]^+$
−2	$[P(OH)_4]^+$
11	$[PBrCl_2(OH)]^+$
36	$[PBr_3Cl]^+$
43—44	$[PBr_2Cl(OH)]^+$
82	$[PBr_3(OH)]^+$
84	$[PBr_4]^+$

be compared with the data from PBr$_5$ in HSClO$_3$ 10 months after preparation of the sample.[5] The formation of $[PBr_4]^+$ ions in the early stages probably arises from a similar sequence of reactions at the interface to that suggested for H$_2$SO$_4$ and 25 oleum solutions. The appearance of mixed bromochloro-species such as $[PBr_3Cl]^+$ and $[PBr_2Cl(OH)]^+$ supports the hypothesis that HSClO$_3$ can act as an oxidising agent in two ways, as discussed for the PCl$_3$ reaction. Subsequent solvolysis appears to be faster for fully halogenated ions such as $[PBr_4]^+$ and $[PBr_3Cl]^+$ than for species with a hydroxyl group present. The presence after 23 d of the more highly chlorinated species $[PBrCl_2(OH)]^+$ and $[PCl_3(OH)]^+$ indicates that halogen exchange as well as solvolysis takes place. Solutions containing $[PBr_3(OH)]^+$ derived directly from PBr$_3$O in HSClO$_3$ did not undergo exchange over 4 months,[5] suggesting that an alternative source of chlorine must be present here. The most probable source is HCl, formed in the redox reaction leading to $[PBr_3(OH)]^+$, equation (9). This parallels the

$$PBr_3 + 2HSClO_3 \longrightarrow$$
$$[PBr_3(OH)]^+ + [SClO_3]^- + HCl + SO_2 \quad (9)$$
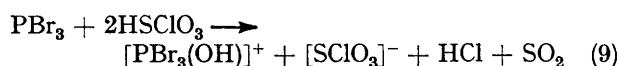
formation of HF in reactions involving HSFO$_3$.

Little reaction was apparent when HSFO$_3$ was added to PBr$_3$, even on shaking for 2 h. **CAUTION**: Three hours after mixing, however, a violent exothermic reaction was observed which yielded a dark brown solution, suggesting bromine formation. The ^{31}P n.m.r. spectrum was recorded 15 min after reaction, and showed strong signals at 83 ($[PBr_4]^+$) and 78 p.p.m. $\{[PBr_3(OH)]^+\}$, with a weak quartet at 36 p.p.m. [^1J(P–F) 1 070 Hz], assigned to PF$_3$O,[3,5,15] and a weak triplet at 20 p.p.m. [^1J(P–F) 1 010 Hz], due to (partially) protonated difluorophosphoric acid.[3,5] After 30 min the $[PBr_4]^+$ signal was greatly reduced in intensity, while the $[PBr_3(OH)]^+$

resonance had broadened considerably. One hour after reaction only two signals were present, a broad strong singlet at 80 p.p.m. and a weak triplet at 22 p.p.m. During the next 2 weeks the intensity of the triplet increased, relative to that of the singlet. The mechanism for formation of $[PBr_4]^+$ is expected to be the same as in the other solvents; the faster solvolysis compared with $[PBr_4]^+$ formed from phosphorus(v) bromide in HSFO$_3$ is doubtless because of the reduction of acid strength in the redox reaction, which also promotes solvolysis of PF$_3$O to $[PF_2(OH)_2]^+$. As in the PCl$_3$ reaction, halogen exchange occurs here, but not with $[PBr_3(OH)]^+$ produced by dissolving PBr$_3$O in HSFO$_3$,[5] and the probable fluorine source is again HF, formed by a similar reaction
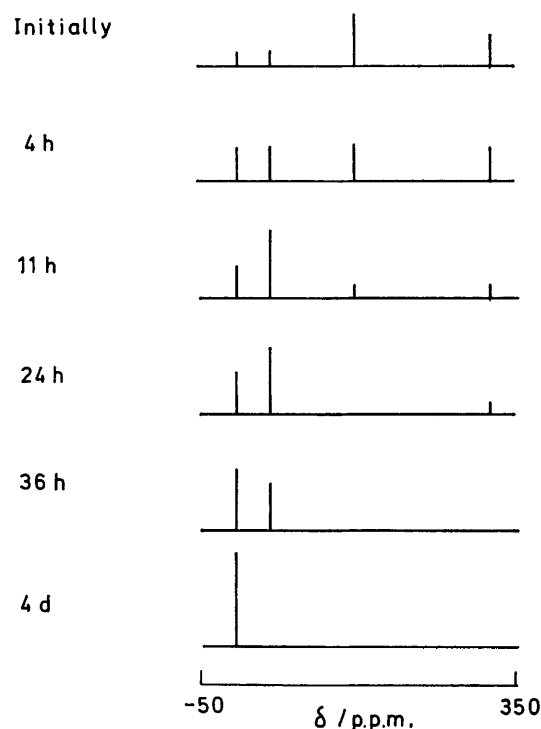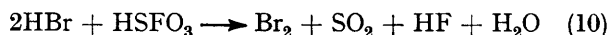

FIGURE 3 Relative peak heights in the ^{31}P n.m.r. spectrum from the reaction of PI$_3$ with 100% H$_2$SO$_4$

to equation (5). Hydrogen fluoride will also be formed when HBr liberated in solvolysis reactions is oxidised to bromine by the solvent [equation (10)]. The water

$$2HBr + HSFO_3 \longrightarrow Br_2 + SO_2 + HF + H_2O \quad (10)$$

produced may also contribute to HF formation by hydrolysing the solvent [equation (11)].[17] The observed

$$HSFO_3 + H_2O \longrightarrow HF + H_2SO_4 \quad (11)$$

reaction products may thus be accounted for satisfactorily. No evidence was found for solvolysis of PBr$_3$, or the presence of undissociated P(SFO$_3$)$_3$, as suggested previously.[2]

(iii) Phosphorus Tri-iodide.—When 100% H$_2$SO$_4$ was added to PI$_3$ and the mixture shaken, slow dissolution of the solid occurred and the solution darkened. As reaction proceeded, iodine in the form of long lustrous

needles was deposited. The initial [31]P n.m.r. spectrum showed four signals (Figure 3), at -4, 41, 149, and 325 p.p.m. The subsequent changes in this spectrum with time are represented schematically in Figure 3, culminating in a single peak at -4 p.p.m. after 4 d. The four original signals are readily assigned to $[P(OH)_4]^+$,[5-7] $[PI(OH)_3]^+$, $[PI_2(OH)_2]^+$, and $[PI_3(OH)]^+$ respectively, in accord with the PCl_3 and PBr_3 reactions. The chemical shifts for all four species were concentration dependent, indicating that they are partially protonated. The value for $[PI_3(OH)]^+$ is higher than expected, since the reported shift for unprotonated PI_3O in iodoethane solution is 273.4 p.p.m.,[18] and protonation of a phosphoryl oxygen usually causes a downfield shift.[5-7] The result was readily reproducible, however, and a value higher than 300 p.p.m. has also been obtained in the stronger acid $HSFO_3$, as discussed below, and in other systems.[19] The high shift is certainly compatible with the presence of iodine in the moiety, and formation of six-co-ordinate anions containing iodine substituents appears most unlikely in view of the instability of $[PF_6]^-$ and $[PCl_6]^-$ in highly acidic solvents.[5] Very high shift values have also been reported for some four-co-ordinate thiophosphoryl compounds containing P–I bonds.[20]

CAUTION: Dissolution of PI_3 in either 25 or 65 oleum gave rise to immediate violently exothermic reactions, with the production of large amounts of iodine. The dark brown solution in 25 oleum gave a simple [31]P n.m.r. spectrum with a strong peak at 5 p.p.m. and a weak one at 15 p.p.m., which did not change with time. This is comparable with the spectra of inorganic phosphates in fairly dilute (17.5—20) oleum solutions,[6] which have been explained in terms of a protonated orthophosphate–pyrophosphate equilibrium peak together with protonated trimetaphosphate. Thus no ions with P–I bonds survive long enough for their spectra to be recorded. The dark blue solution in 65 oleum, the colour of which is due to the $[I_2]^+$ cation,[21] initially showed strong signals at 20 and 28 p.p.m. and a weak peak at 40 p.p.m. The peak at lowest field grew in intensity relative to the others over 11 d, and after 40 d only two signals were present, a strong one at 23 and a weak one at 31 p.p.m. The resonances at 20—23 and 28—31 p.p.m. are almost certainly due to equilibria involving protonated cyclic phosphates, since inorganic phosphates give very similar spectra in concentrated (>55) oleum solutions. The weak signal at 40 p.p.m. could be due to $[PI(OH)_3]^+$, since solvolysis of phosphorus–halogen bonds is sometimes slower in 65 oleum than in 25 oleum.[5] The possibility of condensation reactions with elimination of HI to give species containing P–I groups, analogous to the bromo-compounds proposed for the PBr_3O [5] and PBr_3 systems in 65 oleum, cannot be discounted, however.

The most surprising feature of the above results is the apparently greater stability of P–I bonds in 100% H_2SO_4 than in 25 or 65 oleum, since P–Cl and P–Br bonds are usually solvolysed much more rapidly in a more weakly acidic medium. This behaviour is probably due to

kinetic factors such as the slow dissolution of PI_3 in H_2SO_4, and the greater oxidising power of the oleums, which liberate iodine immediately from HI formed by solvolysis. Phosphorus tri-iodide itself is kinetically inert in other reactions, such as that with liquid HCl where no halogen exchange was observed, even though PBr_3 exchanges under comparable conditions.[22]

Addition of $HSClO_3$ to solid PI_3 caused a vigorous reaction, yielding a dark brown solution and a black oily material. The oil and solvent then reacted further, giving a brown solution. Precipitation of iodine commenced ca. 15 min after sample preparation, and continued for 2 d. On further standing, however, the iodine
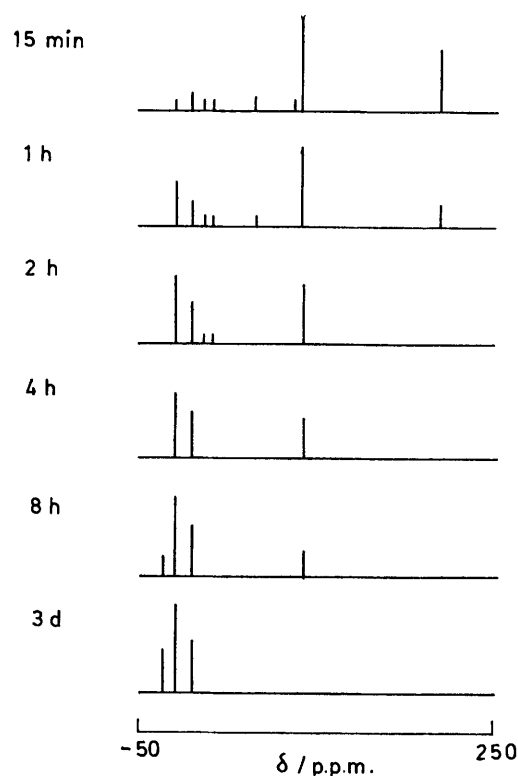

FIGURE 4 Relative peak heights in the [31]P n.m.r. spectrum from the reaction of PI_3 with $HSClO_3$

redissolved to give a clear brown solution, possibly containing the $[I_3]^+$ cation.[21] The solution was monitored by [31]P n.m.r. spectroscopy during the reaction period, and the results are presented diagrammatically in Figure 4. The complexity of the spectra shows that more than a simple oxidation–solvolysis sequence takes place, but the peaks may all be assigned on the basis of species containing I, Cl, or OH groups or mixtures of these (Table 4). Formation of any such ions is possible when the behaviour of $HSClO_3$ towards PCl_3 and PBr_3 is considered. The solvent can oxidise PX_3 to either $[PX_3(OH)]^+$ or $[PX_3Cl]^+$, both of which may then be subject to solvolysis giving ions with more OH groups, or halogen exchange with HCl formed in the redox reaction to yield more highly chlorinated derivatives. The shifts for known species are in good agreement with data

TABLE 4

Phosphorus-31 n.m.r. data for the reaction of PI_3 with $HSClO_3$

$\delta(^{31}P)$/p.p.m.	Assignment
-27	$[PCl_3(OH)]^+$
-16	$[PCl_2(OH)_2]^+$
-2	$[PCl(OH)_3]^+$
6	$[PCl_3I]^+$
14	$[PCl(I)(OH)_2]^+?*$
48	$[PI(OH)_3]^+$
83	$[PCl_2I_2]^+$
89	$[PCl_2(I)(OH)]^+$
207	$[PClI_2(OH)]^+$

* See text.

from the other solvents, and the values assigned to the ions $[PClI_2(OH)]^+$, $[PCl_2I(OH)]^+$, $[PCl_2I_2]^+$, and $[PCl_3I]^+$ all seem reasonable by comparison. The species $[PClI_2(OH)]^+$ and $[PCl_2I(OH)]^+$ have since been found in other systems.[19] The preparation of a compound containing the $[PCl_3I]^+$ cation has been proposed,[23] but no n.m.r. data were given. The resonances assigned to $[PCl_2I_2]^+$ and $[PCl_3I]^+$ were independent of concentration, as expected for ions not containing partially protonated oxygens. The most difficult peak to assign is the small one at 14 p.p.m., present during the first 2 h of reaction. It could be due to $[PCl(I)(OH)_2]^+$, which is the logical intermediate in the solvolytic path between $[PClI_2(OH)]^+$ and $[PCl(OH)_3]^+$, but the shift value looks rather low for this species. Solutions of inorganic phosphates in $HSClO_3$ show a peak in this region, ascribed to protonated trimetaphosphate,[6] but this signal does not disappear with time. The overall picture is nevertheless clear, with P–I bonds being solvolysed preferentially to P–Cl bonds in this medium.

Phosphorus tri-iodide dissolved in $HSFO_3$ with effervescence, giving a dark brown solution which started to deposit iodine crystals after *ca.* 30 min. Precipitation continued for 1 d, and the course of reaction was followed by Fourier-transform n.m.r. spectroscopy, as shown schematically in Figure 5. (Multiplets are represented

TABLE 5

Phosphorus-31 n.m.r. data for the reaction of PI_3 with $HSFO_3$

$\delta(^{31}P)$/p.p.m.	Multiplicity	^1J(P–F)/Hz	Assignment
-1			$[P(OH)_4]^+$
7	Doublet	$1\,000$	$[PF(OH)_3]^+$
22	Triplet	$1\,010$	$[PF_2(OH)_2]^+$
37	Quartet	$1\,070$	PFO_3
144			$[PI_2(OH)_2]^+$
167	Doublet	$1\,290$	$[PFI_2(OH)]^+$
308			$[PI_3(OH)]^+$

by a single line at the shift position for clarity.) The n.m.r. data and assignments, which are relatively straightforward, are shown in Table 5. The small downfield shifts of $[PI_3(OH)]^+$ and $[PI_2(OH)_2]^+$ compared with the values in H_2SO_4 are consistent with more extensive protonation in the stronger acid $HSFO_3$, although the signal ascribed to $[PI_3(OH)]^+$ is again upfield from the Russian value for unprotonated PI_3O.[18] The most interesting new resonance is the doublet at 167 p.p.m. [^1J(P–F) $1\,290$ Hz], assigned to $[PFI_2(OH)]^+$. The

coupling constant seems very reasonable for sp^3-hybridised phosphorus, and compares with the value of $1\,296$ Hz reported for $[PCl_3F]^+$.[24] As in previous systems in $HSFO_3$, clear evidence for both solvolysis of phosphorus–halogen bonds and fluorine exchange is found, the exchange again being attributed to reaction with HF, formed as described previously. Unfortunately, the other expected intermediates $[PF_2I(OH)]^+$, $[PFI(OH)_2]^+$, and $[PI(OH)_3]^+$ were not found, presumably because their concentrations remained below the limit of detection throughout.

The reactions of these phosphorus(III) halides PX_3 with strongly acidic oxidising solvents thus involve
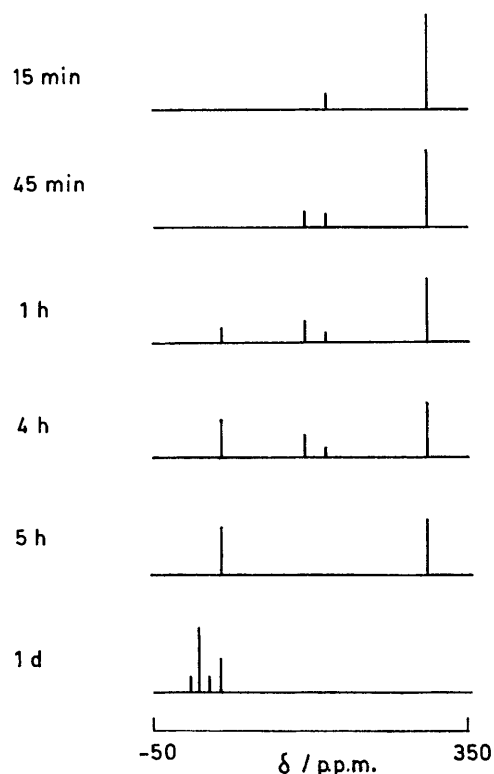

FIGURE 5   Relative peak heights in the ^{31}P n.m.r. spectrum from the reaction PI_3 with $HSFO_3$

initial oxidation to a phosphorus(v) compound. One of the routes in all cases is direct oxidation by the solvent to $[PX_3(OH)]^+$, and $HSClO_3$ may also form $[PX_3Cl]^+$. The redox reaction causes a reduction in acid strength, promoting solvolysis of phosphorus–halogen bonds, the rate of which varies inversely with the acid strength. Sometimes solvolysis products are observed in the initial ^{31}P n.m.r. spectra from more strongly acidic solvents because of inhomogeneity in the sample, particularly for two-phase systems. Once the system is homogeneous, however, subsequent solvolysis is very slow. Reactions involving PBr_3 or PI_3 result in the liberation of free halogen, since HBr or HI formed by solvolysis are unstable to oxidation by the solvent, unlike HCl from PCl_3. The liberation of Br_2 from PBr_3 in this way while two liquid layers are still present leads to reaction at the

interface, with formation of $[PBr_4]^+$, although this ion is solvolysed rapidly by 100% H_2SO_4. No evidence was found for formation of $[PI_4]^+$ by a similar reaction from PI_3, not surprisingly perhaps since very rapid solvolysis is expected for this species.

Halogen exchange is observed in both $HSClO_3$ and $HSFO_3$ solutions; this behaviour can be rationalised in terms of an indirect exchange mechanism involving HX molecules formed as by-products or in side reactions, since both $[PCl_3(OH)]^+$ and $[PBr_3(OH)]^+$ formed by protonation of PX_3O do not undergo direct exchange with these solvents.[5] Phosphorus–iodine bonds appear to be unstable to solvolysis in 25 oleum and, to a lesser extent, in 65 oleum, in which condensation reactions with elimination of HX are possible for both bromo- and iodo-species. Nevertheless, several interesting new phosphorus(v) iodo-derivatives have been identified in 100% H_2SO_4, $HSClO_3$, or $HSFO_3$ solutions.

The long-term behaviour of the samples is entirely explicable when the reactions of phosphorus(v) halides, halide oxides, and inorganic phosphates in strongly acidic solvents are taken into account.[5,6] The differences in solvolysis rates arise from the reduction in acid strength for the phosphorus(iii) systems during the initial redox reaction, while halogen exchange occurs in $HSClO_3$ or $HSFO_3$ when formation of HX molecules is possible, as discussed above.

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