The Behaviour of Some Organophosphorus(v) Compounds in Strongly Acidic Solvents. Part 1. Monophenyl Derivatives

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The reactions of $PPhO(OH)_2$ and $PPhCl_2O$ with the strongly acidic solvents 100% H_2SO_4, 25 and 65 oleum, and $HSClO_3$ have been investigated by means of ^{31}P n.m.r. spectroscopy. Initial protonation of the phosphoryl oxygen, the extent of which varies with solute and solvent, is followed in most instances by sulphonation of the aromatic group (except in H_2SO_4), and/or condensation [$PPhO(OH)_2$] or solvolysis ($PPhCl_2O$). Slow chlorination of $PPhO(OH)_2$ was also observed in $HSClO_3$. Attempts to prepare the intermediate compound PPhClO(OH) did not yield pure products, but reaction of two of the mixtures thus obtained with 100% H_2SO_4 and $HSClO_3$ confirmed its participation in some of the above systems.

THE chemistry of organophosphorus compounds in sulphuric acid and related solvents has not been extensively investigated. Conductivity measurements on triphenyl phosphate in H_2SO_4 were interpreted in terms of protonation at the phosphoryl oxygen.[1] It was deduced from cryoscopic and conductivity data that triethyl phosphate and triphenylphosphine oxide are protonated by sulphuric acid,[2] and by similar means that PPh_3O, $P(OMe)_3O$, and $P(OEt)_3O$ are protonated in $HSFO_3$.[3] The protonation at phosphorus of several phosphites and phosphines dissolved in 100% H_2SO_4 has been observed by means of ^1H n.m.r. spectroscopy.[4] Protonation of some phosphates $P(OR)_3O$ and phosphites $P(OR)_3$, where R = alkyl or aryl, and of some dialkyl phosphonates, in $HSFO_3$ and $HSFO_3$–SbF_5 (' magic acid ') has been studied using both ^1H and ^{31}P n.m.r.[5] Phosphorus(v) compounds were invariably protonated at the phosphoryl oxygen. Preliminary experiments on the behaviour of some aryl phosphates in the solvents 100% H_2SO_4, 20 and 65 oleum (oleum containing 20 and 65% free SO_3 respectively), and $HSClO_3$ suggested that sulphonation of the aromatic rings as well as protonation was occurring.[6] Slow sulphonation of PPh_3 in H_2SO_4, as well as the initial reaction to form PPh_3H^+, has also been reported.[7] The reactions of some alkyl-substituted phosphinic acids and phosphinates with sulphuric acid and oleums of various strengths have been investigated by cryoscopy and ^1H n.m.r.[8] The initial reaction was deduced to be protonation, followed by sulphonation in oleums of greater than 10% SO_3 content. Unlike the aromatic systems mentioned above,[6,7] sulphonation of P–OH groups to give P–OSO_3H units was postulated.[8]

In a previous paper we have described the reactions of some phosphorus(v) halides and halide oxides with strongly acidic solvents.[9] The phosphorus species present were identified by means of ^{31}P n.m.r. spectroscopy, which showed that in many instances the reactions were considerably more complex than had been thought previously. The use of 25 oleum as a solvent for a variety of phosphonium compounds has also been reported.[10] It was therefore of considerable interest to investigate systematically the reactions of some phosphorus(v) compounds containing aryl substituents with the solvents 100% H_2SO_4, 25 and 65 oleum, and $HSClO_3$. In this paper, the behaviour of species with one phenyl substituent only is described. For compounds with halogens present, such as $PPhCl_2O$, solvolysis reactions are possible in addition to protonation and sulphonation as mentioned earlier, and examples of all these types of reaction have been found. In some instances the reactions took place over a long period of time, and the solutions were monitored periodically by ^{31}P n.m.r. as described previously.[9,11]

EXPERIMENTAL

Chemicals of the best available commercial grade were used, in general without further purification. All manipulations, including sample preparation, were carried out under an inert atmosphere of dry nitrogen. Phosphorus-31 n.m.r. spectra were recorded at 307.2 K, using either the continuous-wave or Fourier-transform spectrometers as described previously,[9–11] and sample tubes of 5-mm outside diameter. Chemical shifts were measured from either external P_4O_6 or 85% H_3PO_4, and are expressed relative to phosphoric acid, with the downfield direction taken as positive.

Attempted Preparation of Phenylphosphonic Monochloride, PPhClO(OH).—Since this compound or its derivatives had been postulated as taking part in some of the reactions of $PPhCl_2O$ or $PPhO(OH)_2$, synthesis was attempted so that its behaviour in acid solvents could be directly investigated. The compound PPhClO(OH) may be regarded as a derivative of dichlorophosphoric acid, $PCl_2O(OH)$, with one chlorine replaced by a phenyl group, so preparation by similar means was tried initially. Anhydrous $PCl_2O(OH)$ has been prepared by partial hydrolysis of PCl_3O in an ethereal medium at room temperature, and by reaction of PCl_3O and water at temperatures between 253 and 263 K.[12] Further attempts were made by treating a chlorinating agent, thionyl chloride, with phenylphosphonic acid, in the

$$PPhO(OH)_2 + SCl_2O \longrightarrow PPhClO(OH) + SO_2 + HCl \quad (1)$$

hope that reaction (1) would take place. Four separate preparations were used, as described below.

Sample A. An equimolar quantity of water was added to liquid $PPhCl_2O$ at 253 K under a nitrogen atmosphere. No immediate reaction was apparent, and the liquids appeared to be immiscible. The mixture was stirred for 1 h at 253 K, producing a homogeneous liquid, and the temperature then allowed to rise to room temperature. After standing for a further 1 h, the liquid was observed to be evolving a gas, presumably HCl. The mixture was stirred overnight, and yielded a colourless glue-like substance as product.

Sample B. A similar procedure was used as for A, but with diethyl ether as solvent. Addition of an equimolar quantity of water to $PPhCl_2O$ dissolved in diethyl ether at 233 K caused no reaction, except that the water turned to ice. The mixture was stirred for 30 min, and then allowed to warm up to 253 K, during which time the water dissolved. The mixture was allowed to warm further to room temperature and left to stir overnight. The product was a sticky white solid which precipitated from the ethereal solution.

Sample C. Solid $PPhO(OH)_2$ was mixed under an atmosphere of nitrogen with an equimolar amount of liquid SCl_2O. There was no apparent reaction at room temperature so the mixture was heated to 323 K. After 20 min a gas was evolved, and $PPhO(OH)_2$ dissolved in the liquid to give a yellow solution. The reaction vessel was maintained at this temperature overnight, by which time gaseous evolution had ceased. A brown sticky substance was obtained on cooling to room temperature.

Sample D. A similar procedure was followed as for C, but using less forcing conditions. The mixture was warmed to 313 K, and after the initial brisk evolution of gas had subsided the resultant pale yellow liquid was cooled to room temperature.

Phosphorus-31 n.m.r. investigations of these samples, described in the following section, showed that none of them consisted of a single product, although the desired compound was present in each case. Nevertheless, they proved very valuable in elucidating the course of reaction of monophenyl-substituted phosphorus(V) compounds with strongly acidic solvents.

RESULTS AND DISCUSSION

(*i*) *Phenylphosphonic acid*, $PPhO(OH)_2$. The white solid dissolved in all the solvents on shaking, without obvious reaction. The solution in 100% H_2SO_4 showed a single strong ^{31}P n.m.r. signal at 32 p.p.m.; the downfield shift of 14 p.p.m. relative to the parent acid [13] is entirely consistent with protonation of the phosphoryl oxygen.[5,14] The spectrum was unchanged after 8 days. The solution in 25 oleum showed two ^{31}P resonances 15 min after preparation, at 27 and 23 p.p.m., with the peak at lower field of higher intensity. The upfield signal increased rapidly at the expense of the other, being of higher relative intensity after 45 min, and the only peak present after 9 h. No further changes were subsequently observed. The lower-field signal is assigned to the protonated form of the acid, $PPh(OH)_3^+$, and the second one to the (mono)sulphonated form, $P(C_6H_4SO_3H)(OH)_3^+$. These assignments were confirmed by the results from the other solvents. The half-life of the sulphonation reaction at 307 K was estimated as 35 ± 5 min from the spectra. The formation of a sulphonated derivative is in accordance with the properties of 25 oleum, which is a good sulphonating agent for aromatic hydrocarbons.[15] In general monosulphonation only takes place, since the strong electron-withdrawing influence of the $-SO_3H$ group deactivates the ring, and disulphonation requires very forcing conditions. Benzene, for example, is converted to benzenesulphonic acid by 100% H_2SO_4 at room temperature, whereas substitution of a second $-SO_3H$ group requires a temperature of 518 K and fuming sulphuric acid (oleum).[15] Furthermore, the $-PH_2O_3$ or $-P(OH)_3^+$ group will also be electron-withdrawing, so that the phenyl group in $PPh(OH)_3^+$ should be less active than benzene towards sulphonation.

At first sight the upfield movement of the signal ascribed to $PPh(OH)_3^+$ relative to its shift in H_2SO_4 (and $HSClO_3$) appears surprising, since a peak in the same position might be expected if the phosphorus compound is completely protonated in all three solvents, and a downfield movement if protonation is more extensive in the stronger acid 25 oleum. A similar pattern was seen for the signal from $P(OH)_4^+$ in these solvents, however, which was attributed to rapid equilibrium between the monomer and condensed species such as (protonated) pyrophosphate in dilute oleum solutions.[16] In view of the similarities between $P(OH)_4^+$ and $PPh(OH)_3^+$, a corresponding process is probably taking place here. This deduction is supported by the results in 65 oleum, where a strong signal at 13 p.p.m. and a weak peak at 6 p.p.m. were observed, the spectrum remaining unchanged after 8 days. 65 Oleum is such a powerful sulphonating agent that the stronger peak is ascribed to a sulphonated form [monomer $P(C_6H_4SO_3H)(OH)_3^+$], but the upfield shift relative to the corresponding species in 25 oleum strongly supports the suggestion that it is involved in condensation equilibria, paralleling the behaviour of $P(OH)_4^+$.[16] The smaller peak at 6 p.p.m. probably represents a different state of aggregation. The two resonances found for $P(OH)_4^+$ in concentrated oleum solutions were ascribed to protonated cyclic species based on tri- and tetra-metaphosphate respectively,[16] but there is no direct evidence in the present system for the state of aggregation. Alternatively the weaker signal could be due to a disulphonated species, but this seems unlikely in view of the conditions normally required.[15]

A more complex spectral pattern was observed in $HSClO_3$ as solvent, as shown in Figure 1. The initial strong resonance is due to $PPh(OH)_3^+$, while the upfield signal which grows with time over a six-month period is readily ascribed to its sulphonated derivative. The slowness of sulphonation in this instance is in agreement with the hypothesis that the reactive electrophile for this process is either SO_3, its H_2SO_4 solvate, or HSO_3^+.[15,17] These species are readily available in oleums, but their production in $HSClO_3$ depends on equilibrium (2).[15]

$$2HSClO_3 \rightleftharpoons HCl + HSO_3^+ + SClO_3^- \quad (2)$$

Since protonation of the phosphoryl group produces $SClO_3^-$, according to equation (3), the equilibrium in (2)

$$P{=}O + HSClO_3 \rightleftharpoons P{-}OH^+ + SClO_3^- \quad (3)$$

is forced more to the left, reducing the concentration of the active sulphonating species. The two signals found at lower field later in the reaction have similar shifts to those observed in the sulphonation and solvolysis reactions of $PPhCl_2O$, and are assigned to the partially chlorinated species $PPhCl(OH)_2^+$ and $P(C_6H_4SO_3H)Cl(OH)_2^+$ respectively. The ability of $HSClO_3$ to act as a chlorinating agent has been observed previously in its reactions with inorganic phosphorus compounds.[9,11]

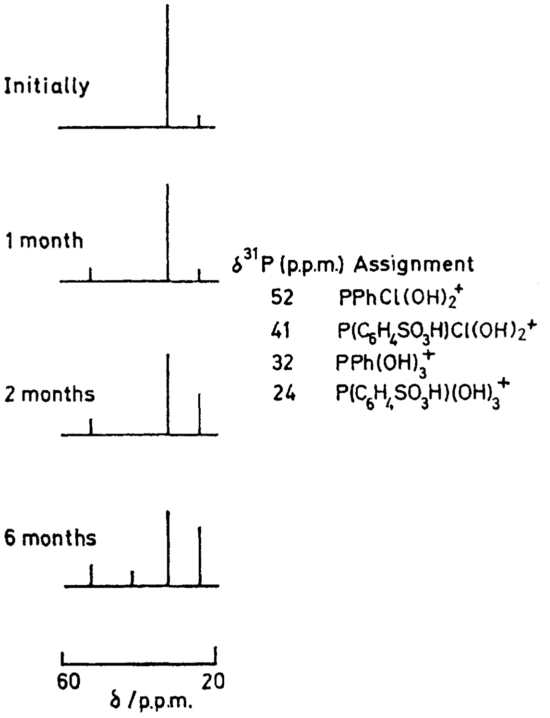


FIGURE 1 Relative peak heights in the ^{31}P n.m.r. spectrum from the reaction of $PPhO(OH)_2$ with $HSClO_3$

(*ii*) *Phenylphosphonic dichloride,* $PPhCl_2O$. The colourless liquid dissolved immediately in the four solvents, with evolution of some heat. The 65 oleum solution was very dark brown, while the pale brown solution in 25 oleum darkened rapidly on standing, and that in $HSClO_3$ darkened slowly. The solution in 100% H_2SO_4 showed a single ^{31}P n.m.r. signal at 57 p.p.m. after 2 h, assigned to the (partially) protonated species $PPhCl_2(OH)^+$, the downfield shift relative to $PPhCl_2O$ [13] being compatible with protonation of the phosphoryl oxygen. (As in previous papers,[9,11] the compounds with halogens present are unlikely to be completely protonated in any but the most strongly acidic solvents, but are represented in the protonated form for clarity.) Seven hours after preparation of the sample, a second small peak was visible at 51 p.p.m., and a third signal at 33 p.p.m. was apparent after 1 day. The resonance at highest field grew in strength with time, and was the strongest peak in the spectrum after 20 days, although all three signals were still visible. Its shift is in very good agreement with that assigned to $PPh(OH)_3^+$ in 100% H_2SO_4. The signal at 51 p.p.m. is therefore ascribed to the intermediate species $PPhCl(OH)_2^+$. This assignment is supported by the close similarity of its shift to that of the same species formed by reaction of $PPhO(OH)_2$ with $HSClO_3$, showing that the identical ion can be generated *via* two different routes. Protonation and solvolysis, but not sulphonation, thus occur in this system.

The ^{31}P spectra from the solution of $PPhCl_2O$ in 25 oleum are represented diagrammatically as a function of time in Figure 2. The peak at 23 p.p.m. apparent after 5 days is in very good agreement with the one assigned to $P(C_6H_4SO_3H)(OH)_3^+$ from reaction of $PPhO(OH)_2$ with this solvent. A reasonable assignment for the signals at lower field is shown in Figure 2, indicating that sulphonation of $PPhCl_2(OH)^+$ is followed by solvolysis. The lower shift for $PPhCl_2(OH)^+$ compared with that in H_2SO_4 is as expected for more extensive protonation by the stronger acid. A shift of 41.1 p.p.m. for $PPhCl_2O$ in liquid HCl [14] shows that it is a fairly weak base; it is expected to be intermediate in basicity between PPh_3O, which seems to be completely protonated by 100% H_2SO_4,[2,6] and PCl_3O which is a weak base, the shift being both solvent- and concentration-dependent.[9]

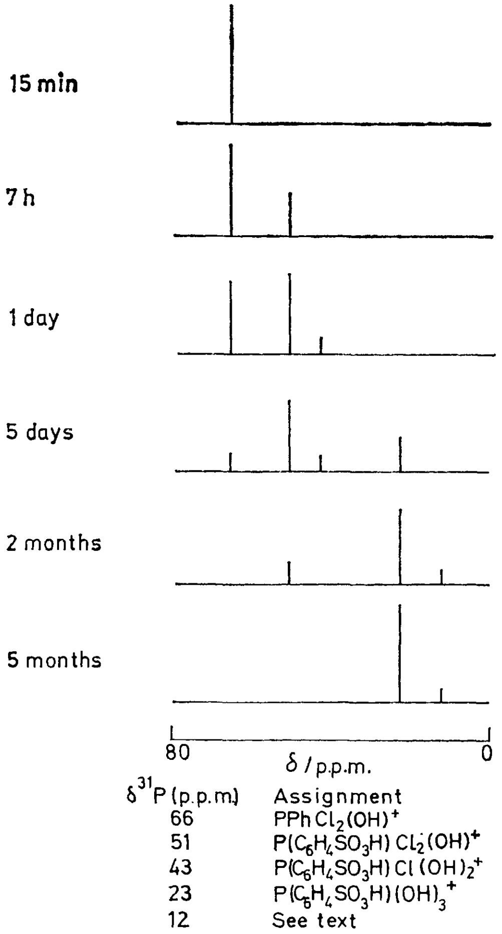


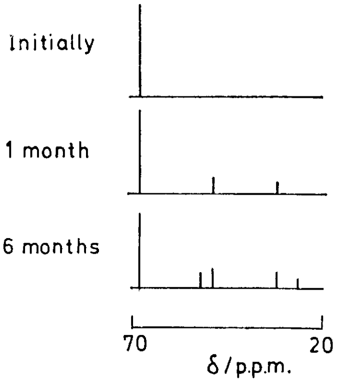
FIGURE 2 Relative peak heights in the ^{31}P n.m.r. spectrum from the reaction of $PPhCl_2O$ with 25 oleum

Solvolysis will be slower in 25 oleum than in 100% H_2SO_4, but the acid strength decreases as sulphonation proceeds, thus favouring solvolysis. The reaction sequence is entirely compatible with this proposition. The weak signal found after 2 months at 12 p.p.m. probably arises from condensation of $P(C_6H_4SO_3H)(OH)_3^+$, similar to the behaviour of $P(OH)_4^+$ in dilute oleums.[16]

The spectrum in 65 oleum showed only a single peak at 70 p.p.m., and was unchanged after 1 month. This signal is ascribed to the sulphonated ion $P(C_6H_4SO_3H)Cl_2(OH)^+$, since the solvent is both a powerful sulphonating agent and a very strong acid. Hence a lower shift than that seen for the corresponding compound in 25 oleum is predicted, compatible with more extensive protonation. Solvolysis is negligibly slow in 65 oleum, as expected.[9]

$PPhCl_2O$ reacted very slowly with $HSClO_3$ after the initial protonation to give $PPhCl_2(OH)^+$; the variation in the spectrum with time is shown schematically in Figure 3. The signal at 32 p.p.m. present after 1 month agrees well in shift with that assigned to $PPh(OH)_3^+$ from reaction of $HSClO_3$ with $PPhO(OH)_2$, so the resonance at 49 p.p.m. is allocated to $PPhCl(OH)_2^+$, in good agreement with the shift for this species in 100% H_2SO_4. The two further signals detected after 6 months are assigned to sulphonated derivatives as shown. Since the protonated starting material is still present in high concentration and sulphonation is very slow in $HSClO_3$, the signal at 52 p.p.m. is ascribed to $P(C_6H_4SO_3H)Cl_2(OH)^+$, rather than to $P(C_6H_4SO_3H)Cl(OH)_2^+$. This deduction is supported by the assignments made previously in 25 oleum, where both these species were found.

The results from solutions of $PPhCl_2O$ in 100% H_2SO_4, 25 oleum, and $HSClO_3$ thus indicate that solvolysis of P–Cl bonds in both sulphonated and non-sulphonated species is possible. The rates of solvolysis for a particular species in different solvents cannot readily be compared, since sulphonation rapidly reduced the acid strength in 25 oleum, whereas sulphonation, and the concomitant reduction in acid strength, occur much more slowly in $HSClO_3$. Nevertheless it is apparent that solvolysis is faster in a more weakly acidic medium, just as for inorganic phosphorus–halogen compounds,[9,11] and is slowest in 65 oleum.



$\delta^{31}P$ (p.p.m.)	Assignment
68	$PPhCl_2(OH)^+$
52	$P(C_6H_4SO_3H)Cl_2(OH)^+$
49	$PPhCl(OH)_2^+$
32	$PPh(OH)_3^+$
27	$P(C_6H_4SO_3H)(OH)_3^+$

FIGURE 3 Relative peak heights in the ^{31}P n.m.r. spectrum from the reaction of $PPhCl_2O$ with $HSClO_3$

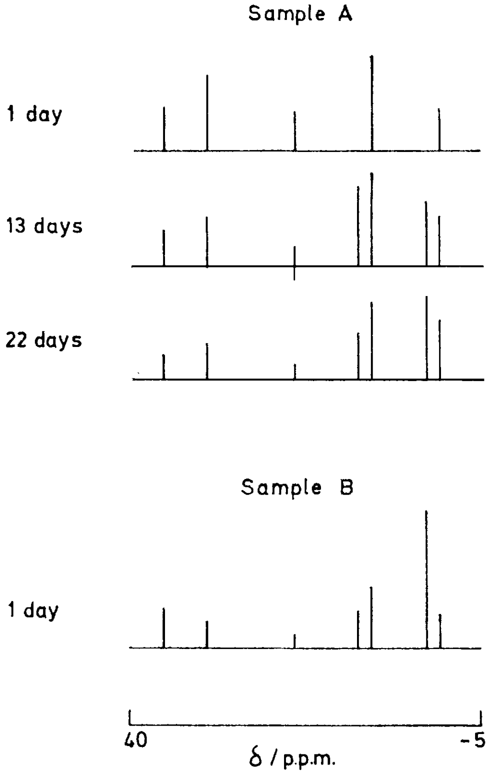
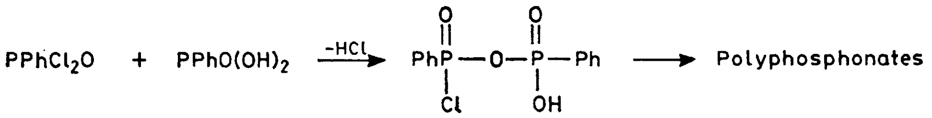


FIGURE 4 Relative peak heights in the ^{31}P n.m.r. spectra of samples A and B in 1,2-dichloroethane

(*iii*) *Phenylphosphonic monochloride*, $PPhClO(OH)$. Four attempted preparations of this compound, derivatives of which have been postulated as taking part in the reactions of $PPhCl_2O$ and $PPhO(OH)_2$, have been described (see Experimental section). Portions of samples A and B, obtained by partial hydrolysis of $PPhCl_2O$, and of samples C and D, prepared by chlorinating $PPhO(OH)_2$ with SCl_2O, were dissolved separately in 1,2-dichloroethane. Their ^{31}P n.m.r. spectra are represented schematically in Figures 4 (A and B) and 5 (C and D). The spectra from A, B, and C were all quite similar, whereas the spectrum of D was simpler, consisting of three signals only. The resonances at 36 p.p.m. from A, B, and C are due to $PPhCl_2O$, while those at 20 p.p.m. in A and B, and 19 p.p.m. in C, arise from $PPhO(OH)_2$.[13] The intermediate signal at 30 p.p.m. in A and B, and 29 p.p.m. in C, which also corresponds to the lowest-field peak from D is therefore assigned to the desired compound $PPhClO(OH)$.

The higher field resonances between 12 and 0 p.p.m. are understandable in view of the work of Grant *et al.*,[18] who investigated the product formed by volatilisation of HCl from a mixture of $PPhCl_2O$ and $PPhO(OH)_2$ at 338

K. They deduced that elimination of HCl led to the formation of chain and possibly ring polyphosphonates by reactions of the form (4). Condensation was rapid at 338 K,[18] but should be slower under the conditions employed in the present work. This is supported by the changes in the spectrum of sample A with time (Figure 4), where further condensation proceeds slowly at 307 K, as shown by the decrease in relative intensity of signals due to monomers. PPhClO(OH) can likewise take part in condensation reactions, since both of the necessary functional groups are present. Hydrolysis of $PPhCl_2O$ to PPhClO(OH) [and some $PPhO(OH)_2$] is proposed as the initial reaction for A and B, followed by condensation with elimination of HCl. This leads to diphosphonates containing either Ph–PCl(O)–O– or Ph–PO(OH)–O– units, together with chain or ring units Ph–PO(O–)–O– if more than two monomers condense. In the case of C and D, however, where the starting material is PPhO-$(OH)_2$, the formation of PPhClO(OH) by partial chlorination can be followed by HCl elimination to give the condensed species PhPO(OH)–O–PO(OH)Ph or higher polymers, with no Ph–PCl(O)–O– groups. These can be produced once $PPhCl_2O$ is present, but no evidence for its formation was found under the mild conditions used for preparation of sample D. A probable shift assignment for the higher-field peaks is therefore: Ph–PCl(O)–O– end unit, 12 p.p.m. (not present in spectrum of D); Ph–PO(OH)–O– end unit, 10 p.p.m.; Ph–PO(O–)–O– chain unit, 2 p.p.m. (not present in spectrum of D); and Ph–P(O)(O–)–O– ring unit, 0 p.p.m. Although direct evidence, particularly for the final two assignments above, is lacking, the shifts would then follow a similar pattern to those in polyphosphates.[13,16] Spin–spin coupling is expected in compounds containing non-equivalent phosphorus atoms, but this was not observed. Symmetrical compounds may be formed preferentially, but it is more likely that the signals seen are composites, formed by overlap of resonances from similar groups in slightly different chemical environments, caused by attachment to differing neighbouring groups. Further splitting of each signal may also occur from coupling with the phenyl group protons, the overall effect being to mask any P–O–P coupling.



$$PPhCl_2O + PPhO(OH)_2 \xrightarrow{-HCl} PhP(=O)(Cl)-O-P(=O)(OH)-Ph \longrightarrow \text{Polyphosphonates} \qquad (4)$$

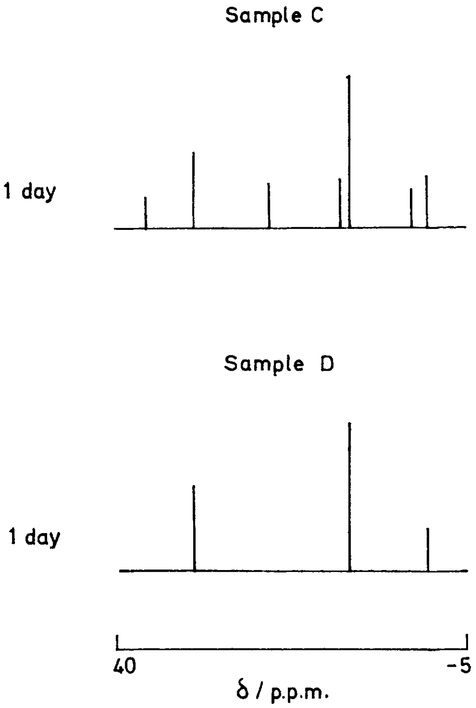


FIGURE 5 Relative peak heights in the ^{31}P n.m.r. spectra of samples C and D in 1,2-dichloroethane

Separate portions of samples A and D were dissolved in both 100% H_2SO_4 and $HSClO_3$, so that the results could be compared with data for $PPhO(OH)_2$ and $PPhCl_2O$ in these solvents. (Their behaviour in 25 or 65 oleum was not investigated, since further condensation would undoubtedly occur, leading to complex n.m.r. spectra.) The resultant spectra are shown diagrammatic-

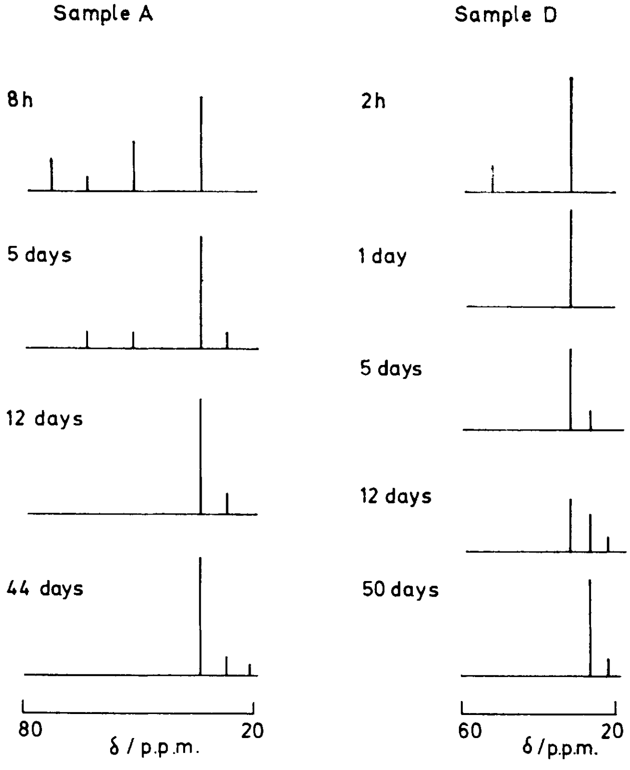


FIGURE 6 Relative peak heights in the ^{31}P n.m.r. spectra from reaction of samples A and D with 100% H_2SO_4

Phosphorus-31 n.m.r. data for samples A and D in H_2SO_4 and $HSClO_3$

Sample	A	D	A	D	Assignment
Solvent	H_2SO_4	H_2SO_4	$HSClO_3$	$HSClO_3$	
δ ^{31}P (p.p.m.)	72		74		$PPhCl_2(OH)^+$
	63				$P(C_6H_4SO_3H)Cl_2(OH)^+$
	51	52	53	52	$PPhCl(OH)_2^+$
			46	44	$P(C_6H_4SO_3H)Cl(OH)_2^+$
	33	32	33	33	$PPh(OH)_3^+$
	27	27	27	27	$P(C_6H_4SO_3H)(OH)_3^+$
	21	22	22	23	See text

ally in Figures 6 (H_2SO_4) and 7 ($HSClO_3$). When compared with the spectra for A and D in 1,2-dichloroethane, the data indicate that dissolution of the polyphosphonates in the acids is accompanied by rupture of the P–O–P linkage to give monophosphorus species, just as found for both linear and cyclic polyphosphates.[16] Protonation of the phosphoryl oxygen then gives signals comparable with those from $PPhO(OH)_2$ and $PPhCl_2O$ in these solvents, and the majority of the peaks can be readily assigned, as shown in the Table. The shift values are mostly slightly lower for A and D than those given previously for H_2SO_4 and $HSClO_3$ solutions; this is entirely compatible with more extensive protonation, since scission of the P–O–P linkage increases the acid strength, equations (5) and (6). Support for this

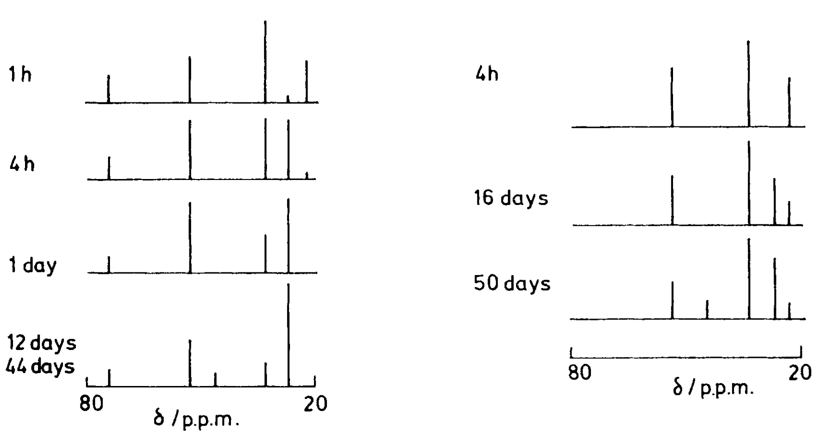


FIGURE 7 Relative peak heights in the ^{31}P n.m.r. spectra from reaction of samples A and D with $HSClO_3$

$$\text{P–O–P} + H_2SO_4 \longrightarrow \text{P–OH} + \text{HO–P} + SO_3 \quad (5)$$

$$\text{P–O–P} + HSClO_3 \longrightarrow \text{P–OH} + \text{Cl–P} + SO_3 \quad (6)$$

mechanism, with formation of SO_3, is provided by the observation of sulphonated species among the reaction products, even in H_2SO_4.

The only signal which cannot be ascribed immediately to a particular monomeric species is that at *ca.* 22 p.p.m., found after some time in the spectra of samples A and D in H_2SO_4, and present initially in quite high concentration in the solutions of A and D in $HSClO_3$, but then declining markedly in intensity with time. This behaviour suggests that it is probably due to a condensed species, and the comparatively simple spectrum of D in *sym*-$C_2H_4Cl_2$ favours a protonated form of the diphosphonate, PhP(OH)(O)–O–(O)(OH)PPh. Mono- or diprotonated forms are possible, but the former is more likely; although protonation of one phosphoryl oxygen leads in principle to non-equivalent phosphorus atoms, rapid proton exchange would make them indistinguishable on the n.m.r. time scale. This species would subsequently cleave in $HSClO_3$ to $PPhCl(OH)_2^+$ and $PPh(OH)_3^+$, in agreement with the spectral changes with time. The presence of the same peak in later stages of the reactions of A and D with 100% H_2SO_4 is probably due to condensation of $PPh(OH)_3^+$ ions with elimination of H_2O, caused by the increase in acid strength discussed above. The results for A in $HSClO_3$ also illustrate well the difference in sulphonation rates for $PPh(OH)_3^+$, $PPhCl(OH)_2^+$, and $PPhCl_2(OH)^+$. In the early stages of reaction there is little sign of sulphonation, but the signal for $P(C_6H_4SO_3H)(OH)_3^+$ is quite intense after 4 h. The sulphonated derivative of $PPhCl(OH)_2^+$ is only apparent after 12 days, and the derivative of $PPhCl_2(OH)^+$ does not appear in the spectra even after 44 days, although the possibility of a small concentration below the detection limit being present cannot be discounted. Replacement of OH by Cl thus decreases the rate of sulphonation.

We therefore conclude that, although pure PPhClO(OH) was not obtained and indeed may well be intrinsically unstable, the reactions of samples A and D with the acid solvents are entirely in keeping with participation of this compound. The results provide valuable support for the assignments made previously in the reactions of $PPhO(OH)_2$ and $PPhCl_2O$ with strongly acidic solvents.

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