# Behaviour of some Organophosphorus(V) Compounds in Strongly Acidic Solvents. Part 2.† $Ph_2P(O)OH$, $Ph_2P(O)Cl$, $Ph_3PO$, $Ph_3PS$, and $MeP(O)Cl_2$

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The reaction of $Ph_2P(O)OH$, $Ph_2P(O)Cl$, $Ph_3PO$, $Ph_3PS$, and $MeP(O)Cl_2$ with the strongly acidic solvents 100% $H_2SO_4$, $HSClO_3$, 25 and (in most cases) 65 oleum have been investigated by $^{31}P$ n.m.r. spectroscopy. The initial reaction is protonation of the phosphoryl oxygen for phosphoryl compounds, although $Ph_3PS$ appears not to protonate. Further reactions including sulphonation of the aromatic rings, and/or solvolysis of phosphorus–chlorine bonds, have also been observed in many instances. The relative basicities of these and other phosphorus(V) compounds are discussed on the basis of the results.

PREVIOUS work [1-8] on the chemistry of organophosphorus compounds in sulphuric acid and related highly acidic solvents has been summarised in the introduction to the earlier paper in this series,[9] on the behaviour of monophenylphosphorus(V) compounds in 100% $H_2SO_4$, $HSClO_3$, 25 and 65 oleums (oleums containing 25% and 65% free $SO_3$ respectively). We were able to show, by means of $^{31}P$ n.m.r. spectroscopy, the occurrence of protonation, sulphonation, solvolysis, and occasionally chlorination reactions, depending on the solute and solvent. This work has been extended to the reactions of $Ph_2P(O)OH$, $Ph_2P(O)Cl$, $Ph_3PO$, $Ph_3PS$, and $MeP(O)Cl_2$ with the same acidic solvents. The expected initial protonation of the phosphoryl oxygen [1-6,9,10] was indeed observed for the phosphoryl compounds, although $Ph_3PS$ appears not to protonate. Subsequent reactions depend on both solute and solvent; in some instances these took place over a long period of time, and the solutions were monitored periodically by $^{31}P$ n.m.r. spectroscopy, as described previously.[9-11] The relative basicities of these and related phosphorus(V) compounds are discussed on the basis of the results.

## EXPERIMENTAL

All manipulations, including sample preparation, were carried out under an inert atmosphere of dry nitrogen. A sample of diphenylphosphinic acid, $Ph_2P(O)OH$, was available in the laboratory, and $Ph_2P(O)Cl$ was prepared by reaction of $Ph_2PCl_3$, prepared as described previously,[12] with $SO_2$.[13] The more volatile product, $SOCl_2$, was distilled off to leave $Ph_2P(O)Cl$ which gave the expected $^{31}P$ n.m.r. signal at 42.7 p.p.m.[14] Other chemicals were of the best available commercial grade and were used without further purification. Phosphorus-31 n.m.r. spectra were recorded at 307.2 K on the Fourier-transform spectrometer as described in earlier papers,[9-11] using stationary sample tubes of 5 mm outside diameter. Chemical shifts were measured relative to external 85% $H_3PO_4$ and are expressed with the downfield direction taken as positive.

## RESULTS AND DISCUSSION

(*i*) *Diphenylphosphinic Acid*, $Ph_2P(O)OH$.—The white solid dissolved in all the acid solvents on shaking, to give a pale brown solution in 100% $H_2SO_4$ and darker brown solutions in 25 and 65 oleum. The solution in $HSClO_3$ was initially pale brown but darkened slowly over a two-month period. The $^{31}P$ n.m.r. spectrum of the solution in $H_2SO_4$ showed a single peak at 54 p.p.m. and was unchanged after 6 d; the downfield shift relative to the starting material, for which $\delta = 25$ p.p.m.,[14] is entirely consistent with protonation of the phosphoryl oxygen, so the resonance is assigned to $Ph_2P(OH)_2^+$. (As in previous papers,[9-11] the partially protonated form of a phosphoryl compound is represented in the protonated form for clarity. The extent of protonation is discussed in more detail below.) The solution in $HSClO_3$ initially showed a single peak at 55 p.p.m., but after 6 d a smaller resonance was also apparent at 51 p.p.m. The latter gradually increased in intensity at the expense of the former, becoming the dominant peak in the spectrum after two months. The initial peak is again assigned to $Ph_2P(OH)_2^+$, and the higher field signal to the monosulphonated derivative $(HO_3SC_6H_4)(Ph)P(OH)_2^+$, in keeping with the poorer sulphonating properties of $HSClO_3$ compared with oleums.[15,16] The spectrum of the solution in 25 oleum, run as soon as possible after sample preparation, showed resonances at 51 and 48 p.p.m., the former being slightly the more intense. The higher field signal increased rapidly in intensity at the expense of the former, and was the only peak present after 75 min, the spectrum subsequently remaining unchanged. 25 Oleum is a good sulphonating agent,[15,16] and these signals are therefore assigned to the mono- and di-sulphonated species $(HO_3SC_6H_4)(Ph)P(OH)_2^+$ and $(HO_3SC_6H_4)_2P(OH)_2^+$ respectively. The shift for the monosulphonated ion is in excellent agreement with that in $HSClO_3$. In this case sulphonation appeared to occur so rapidly that no signal for $Ph_2P(OH)_2^+$ could be detected. The assignments were strongly supported by the results in 65 oleum, where a single peak was seen at 48 p.p.m. which remained unchanged after 6 d. This powerful sulphonating agent thus converts $Ph_2P(O)OH$ rapidly to the disulphonated derivative $(HO_3SC_6H_4)_2P(OH)_2^+$.

As seen from the data above, the $^{31}P$ n.m.r. shifts for a particular species are virtually independent of solvent,

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† Part 1 is ref. 9.

unlike some of the monophenyl-substituted compounds[9] where the shift depended markedly on the acid strength. The results suggest firstly that $Ph_2P(O)OH$ is completely protonated by all the solvents; the basicity is expected to increase with the number of phenyl groups, since $Ph_3PO$ is quite a strong base. The constancy of shift and lack of further upfield movement with time also suggest that condensation equilibria of the type postulated for $PhP(O)(OH)_2$[9] and derivatives of $H_3PO_4$ itself[17] do not occur in these diphenyl species, which remain monomeric even in 65 oleum.

(*ii*) *Diphenylphosphinic Chloride*, $Ph_2P(O)Cl$.—$Ph_2P(O)Cl$ dissolved immediately in 65 oleum to give a dark brown solution, but formed two layers with the other solvents. It dissolved on shaking, however, with evolution of heat, to yield pale brown solutions. Those in 25 oleum and $HSClO_3$ darkened on standing, the former much more rapidly than the latter. The $H_2SO_4$ solution initially showed a single resonance at 76 p.p.m., consistent with protonation to give $Ph_2P(OH)Cl^+$. A second peak at 54 p.p.m. was apparent 7 h after sample preparation, and grew in intensity with time at the expense of the original signal. After 3 d it was the more intense, and was dominant after 20 d, although the signal at 76 p.p.m. was still present. As in the reaction of $PhP(O)Cl_2$ with $H_2SO_4$,[9] this is entirely compatible with slow solvolysis of the P–Cl bond to give $Ph_2P(OH)_2^+$; the shift of 54 p.p.m. is in excellent agreement with that from the $Ph_2P(O)OH–H_2SO_4$ reaction above. The $HSClO_3$ solution gave a single resonance at 76 p.p.m., which remained unchanged over a period of 1½ months. Hence $Ph_2P(OH)Cl^+$ is formed but the P–Cl bond is stable to solvolysis in $HSClO_3$, in keeping with its reactions with other phosphorus(v) compounds.[9–11,18] There was no evidence of sulphonation in this system.

The reaction of $Ph_2P(O)Cl$ with 25 oleum was more complicated, and is represented schematically as a function of time in Figure 1. The original signal at 76 p.p.m. is readily assigned to $Ph_2P(OH)Cl^+$, and the ultimate reaction product gives a signal at 47 p.p.m., which is commensurate with formation of the solvolysed and fully sulphonated product $(HO_3SC_6H_4)_2P(OH)_2^+$, the shift being in good agreement with resonances assigned to this species in the previous section. The positions of the other two signals at 73 and 70 p.p.m. support the hypothesis that sulphonation occurs before solvolysis, and they are therefore assigned to $(HO_3SC_6H_4)(Ph)P(OH)Cl^+$ and $(HO_3SC_6H_4)_2P(OH)Cl^+$ respectively. This result is not unexpected since 25 oleum is a good sulphonating agent, but solvolysis of phosphorus–halogen bonds usually occurs slowly, if at all, in this medium.[9–11,18–20] These conclusions were strongly supported by the results from the 65 oleum solution, which showed a single $^{31}P$ n.m.r. peak at 70 p.p.m., the spectrum thereafter remaining unchanged for at least 1½ months. This peak is attributed to the completely sulphonated ion $(HO_3SC_6H_4)_2P(OH)Cl^+$, in keeping with the powerful sulphonating properties of 65 oleum, and no solvolysis occurs in this instance.

As in the $Ph_2P(O)OH$ systems, the apparent constancy of shift for a particular species and independence of acid strength indicate that $Ph_2P(O)Cl$ and its sulphonated derivatives are fully protonated, and are thus stronger bases than monophenyl derivatives such as $PhP(O)Cl_2$.[9]

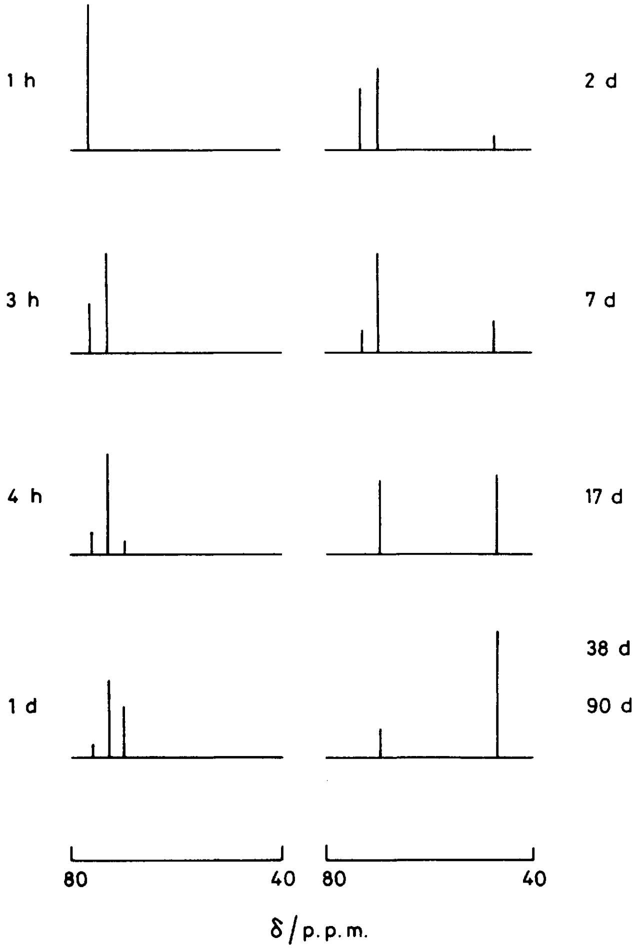

FIGURE 1 Relative peak heights in the $^{31}P$ n.m.r. spectrum of diphenylphosphinic chloride in 25 oleum

There was again no evidence for the occurrence of condensation reactions.

(*iii*) *Triphenylphosphine Oxide*, $Ph_3PO$.—The white solid $Ph_3PO$ dissolved immediately and exothermically in 65 oleum to yield a dark brown solution, but more slowly on shaking to give a pale yellow solution in $H_2SO_4$, and pale brown solutions in 25 oleum and $HSClO_3$ which darkened considerably on standing. The $^{31}P$ n.m.r. spectra of the $H_2SO_4$ and $HSClO_3$ solutions consisted of single peaks only at 58 and 60 p.p.m. respectively, assigned to $Ph_3P(OH)^+$. This deduction is in agreement with the results of cryoscopic and conductimetric work on solutions of $Ph_3PO$ in 100% $H_2SO_4$,[2] and conductimetric work in $HSFO_3$,[3] which indicated that protonation of $Ph_3PO$ occurs in these solvents. The 25 oleum solution showed initially a broad signal at 59 p.p.m., but over a 2-d period this decreased in intensity and was gradually replaced by another broad signal at 56 p.p.m. Similar behaviour was observed in 65 oleum, although the reaction was faster. Two equally intense signals at 64 and 61 p.p.m. were seen 15 min after sample preparation, but the lower field resonance disappeared over the next 2 h, leaving a single peak at 61 p.p.m. No further changes were apparent in any of the spectra over the next 34 d. It is clear from the downfield shift relative to $Ph_3PO$ (δ 25 p.p.m.[14]) that protonation occurs in 25 and 65 oleum also, but the quite rapid replacement of the original signal in each case by an upfield resonance indicates that sulphonation takes place. The speed of reaction to yield a single peak system stable over a long period of time suggests that all the phenyl rings are sulphonated in both instances, and that the final product is $(HO_3SC_6H_4)_3P(OH)^+$. Although the intermediate species were not detected, this is readily explicable in view of the broadness of the signals and close proximity of the chemical shifts. The mono- and di-sulphonated species are expected to give resonances intermediate between those of $Ph_3P(OH)^+$ and the final product, which could therefore be obscured by overlapping of the initial and final peaks. It is also conceivable that the intermediates may be sulphonated more rapidly than the starting material, so that their concentrations remain low throughout. The large downfield shift of the protonated species relative to that of $Ph_3PO$ in all four solvents shows that $Ph_3PO$ is a strong base, and that protonation is essentially complete.

(*iv*) *Triphenylphosphine Sulphide*, $Ph_3PS$.—The white solid $Ph_3PS$ dissolved exothermically in 65 oleum, giving a dark green solution, but more slowly and on shaking in the other solvents. A yellow-orange solution resulted in 100% $H_2SO_4$ and brown solutions were obtained in 25 oleum and $HSClO_3$ which darkened on standing. The $^{31}P$ n.m.r. spectra of these solutions were quite complex, and are represented schematically as a function of time in Figures 2 (100% $H_2SO_4$ and $HSClO_3$) and 3 (25 and 65 oleum). The spectra were in general very similar to one another, and a common reaction path appeared to be followed, with four main species present: A (42—45 p.p.m.), B (48—49 p.p.m., but not seen in $H_2SO_4$, possibly because of low concentration), C (50—51 p.p.m.), and D (56—60 p.p.m.). In addition to these, two extra signals were detected during the first day of reaction in 65 oleum, at 79 and 47 p.p.m. (Figure 3), which are discussed separately below. The general reaction sequence otherwise seems to be (1), as shown particularly well by the 25 oleum system, with the rate of reaction varying considerably with the solvent.

$$\text{Species A} \longrightarrow \text{Species B} \longrightarrow \text{Species C} \longrightarrow \text{Species D} \quad (1)$$

The chemical shift of $Ph_3PS$ is 43 p.p.m.,[14] so species A is readily assigned as unprotonated $Ph_3PS$. This is in accordance with results from the weaker acid, liquid HCl, where the $Ph_3PO$ resonance moved 30.5 p.p.m. downfield whereas that of $Ph_3PS$ moved 0.5 p.p.m. upfield, indicating little or no protonation of the latter.[21] The other species B, C, and D may then be assigned as the mono-, di-, and tri-sulphonated derivatives $(HO_3SC_6H_4)(Ph)_2PS$, $(HO_3SC_6H_4)_2(Ph)PS$, and $(HO_3SC_6H_4)_3PS$ respectively.

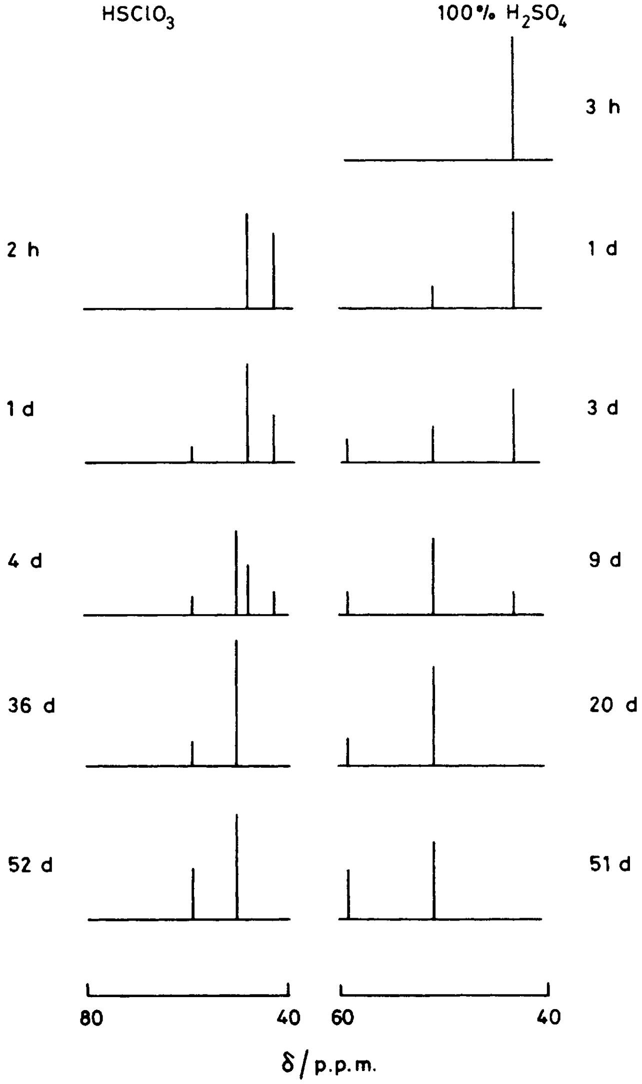

FIGURE 2 Relative peak heights in the $^{31}P$ n.m.r. spectra of $Ph_3PS$ in $H_2SO_4$ and $HSClO_3$

There are two particular points of interest in these systems compared with those described above and previously.[9] Firstly, even 100% $H_2SO_4$ shows sulphonating properties in this instance. This behaviour almost certainly occurs because the thiophosphoryl group is not protonated. Hence the autoprotolysis equilibrium (2) which produces the sulphonating species $HSO_3^+$ [15] is not affected by formation of $HSO_4^-$ ions in reactions such as (3).

$$2\,H_2SO_4 \rightleftharpoons H_2O + HSO_3^+ + HSO_4^- \quad (2)$$

$$R_3PX + H_2SO_4 \rightleftharpoons R_3PXH^+ + HSO_4^- \quad (3)$$

The absence of a positive charge may also make the phosphorus compound more activated towards electrophilic substitution. Secondly, the sulphonated derivatives show downfield shifts relative to the parent compound, unlike previous systems where upfield shifts were observed. This behaviour is less easy to rationalise, but presumably arises from electronic rather than bulk effects. The sulphonic acid groups will be electron-withdrawing and tend to decrease the electron density around the phosphorus atom, thus causing deshielding and a downfield shift, whereas the greater bulk of the $HO_3SC_6H_4$ group compared with $C_6H_5$ would tend to cause increased shielding and an upfield shift. The main difference between $Ph_3PS$ and the other species is that they are at least partially protonated, so the presence of a positive charge on phosphorus may overcome the electron-withdrawing effects of the sulphonate groups sufficiently for bulk effects to predominate.

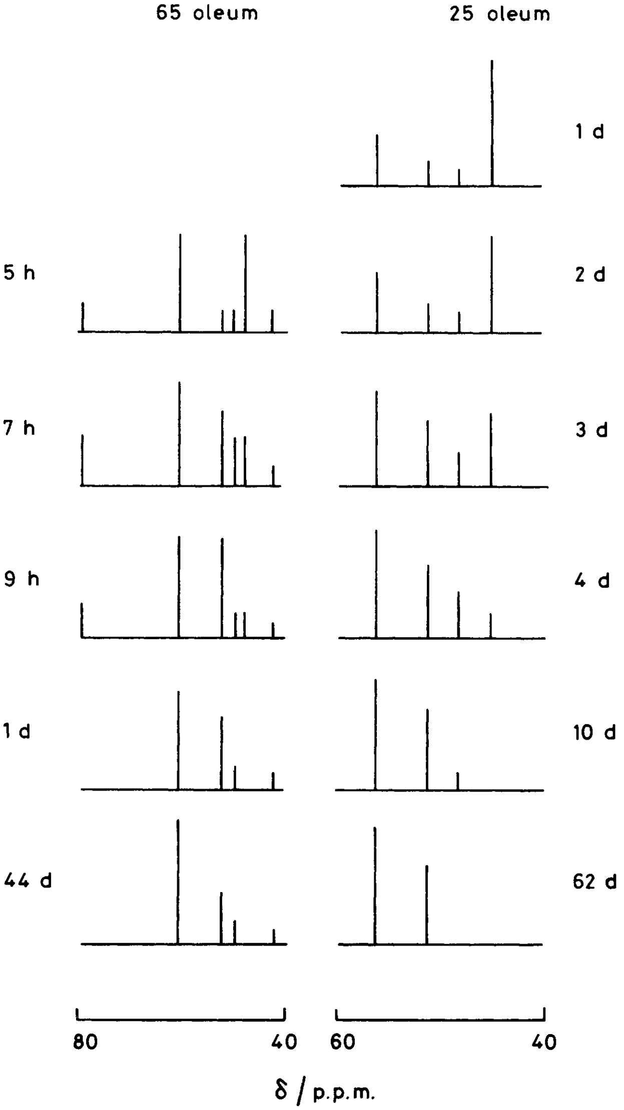

FIGURE 3 Relative peak heights in the $^{31}P$ n.m.r. spectra of $Ph_3PS$ in 25 and 65 oleum

Since the two additional signals at 79 and 47 p.p.m. seen on the first day of reaction of $Ph_3PS$ with 65 oleum subsequently disappeared and the reaction then followed the expected course, they are probably due to transient species formed as a consequence of the high acid strength and oxidising power of the solvent, which then decompose to starting material and/or products as the acid strength is reduced by sulphonation. The lower field signal could arise from a weak Lewis base–Lewis acid adduct of the type $Ph_3PS \rightarrow SO_3$. Sulphur trioxide forms similar adducts with stronger Lewis bases such as pyridine in the absence of a proton donor, and reaction of the Lewis base $P(O)Cl_3$ with $SbCl_5$, $BCl_3$, and $SnCl_4$ has been shown to cause downfield $^{31}P$ n.m.r. shifts of between 33 and 58 p.p.m.[22] Removal of both $Ph_3PS$ and $SO_3$ by sulphonation would then perturb the equilibrium (4) leading to

$$Ph_3PS + SO_3 \rightleftharpoons Ph_3PS{\cdot}SO_3 \qquad (4)$$

re-formation of starting material. The results would then imply that the sulphonated derivatives of $Ph_3PS$ are weaker Lewis bases than $Ph_3PS$ itself, since no further downfield resonances were detected, although the reduction in $SO_3$ concentration following sulphonation could also be a contributing factor. The other signal at 47 p.p.m. could be due to an oxidised derivative of $Ph_3PS$ such as $Ph_3P{=}S{=}O$, but there is no obvious reason for a compound of this type to decompose back to $Ph_3PS$ or its sulphonated derivatives. In any case, these assignments are only tentative since there is no direct evidence for formation of the postulated species.

(*v*) *Methylphosphonic Dichloride*, $MeP(O)Cl_2$.—This compound dissolved readily in 100% $H_2SO_4$, $HSClO_3$, and 25 oleum to yield colourless solutions. Its reaction with 65 oleum was not investigated. In $H_2SO_4$ it originally gave a quartet at 72 p.p.m. [$J$(P–C–H) 15 Hz], downfield from the signal of $MeP(O)Cl_2$ in $CH_2Cl_2$ (δ 44 p.p.m.), and compatible with (partial) protonation to give $MeP(OH)Cl_2^+$. Two further quartets were apparent after 1 d, at 63 p.p.m. [$J$(P–C–H) 17 Hz] and 48 p.p.m. [$J$(P–C–H) 18 Hz], assigned to the solvolysed derivatives $MeP(OH)_2Cl^+$ and $MeP(OH)_3^+$ respectively. These increased in intensity over the next few days at the expense of the original resonance; interestingly, after 16 d the quartet from $MeP(OH)_3^+$ was the most intense, but the intermediate species $MeP(OH)_2Cl^+$ was not apparent in the spectrum, suggesting that it may solvolyse faster than $MeP(OH)Cl_2^+$. The reactions with $HSClO_3$ and 25 oleum followed similar, but predictably slower, courses. The initial quartet in $HSClO_3$ (δ 80 p.p.m., $J$ 15 Hz) was accompanied after 16 d by a second, much smaller quartet (δ 65 p.p.m., $J$ 17 Hz). In 25 oleum the original quartet at 87 p.p.m. ($J$ 15 Hz) was complemented after 7 d by a less intense quartet at 67 p.p.m. ($J$ 17 Hz) and after 16 d by a further quartet at 43 p.p.m. ($J$ 18 Hz), although the initial signal was still the most intense. The shift variations for $MeP(OH)Cl_2^+$ and $MeP(OH)_2Cl^+$ with acid strength show that these solutes are weaker bases than the species with two or more aromatic groups present. The upfield movement of the $MeP(OH)_3^+$ signal on going from 100% $H_2SO_4$ to 25 oleum is not as expected for increased protonation of a monomeric species, however, and suggests that condensation equilibria of the type postulated for $P(OH)_4^+$ [17] and $PhP(OH)_3^+$ (ref. 9) may occur for $MeP(OH)_3^+$ also, giving protonated methyl derivatives of pyrophosphoric acid or higher polymers. No evidence for sulphonation of the OH group was found, although Haake and Ossip [6] deduced from $^1H$ n.m.r. techniques that in compounds of the type $R_2P(O)OH$ and $R_2P(O)X$, where R = alkyl or alkoxy, the initial protonation was followed by sulphonation of the OH group in oleums of greater than 10% $SO_3$ content.

TABLE 1

Phosphorus-31 n.m.r. shift differences (p.p.m.) between the partially protonated and unprotonated forms of $P(O)Cl_3$ and some derivatives in acid solvents

| | δ (protonated species) − δ (parent) | | | |
|---|---|---|---|---|
| Compound | $H_2SO_4$ | $HSClO_3$ | 25 oleum | Ref. |
| $P(O)Cl_3$ | 18 | 20 | 33.5 | 10 |
| $PhP(O)Cl_2$ | 23 | 34 | 32 | 9 |
| $Ph_2P(O)Cl$ | 33.3 | 33.3 | 33.3 | This work |
| $Ph_3PO$ | 33 | 35 | 34 | This work |
| $MeP(O)Cl_2$ | 28 | 36 | 43 | This work |

An interesting comparison may be made of the relative shift differences between the parent compound and its partially protonated derivative in the various solvents, since these should reflect the base strength of the phosphorus(v) compound if protonation is incomplete. This is illustrated in Table 1 for some derivatives of $P(O)Cl_3$, and in Table 2 for some derivatives of $H_3PO_4$, dissolved in 100% $H_2SO_4$, $HSClO_3$, and 25 oleum. (The values for $Ph_3PO$ are included in both Tables for completeness.) The values for the weaker bases are likely to be very concentration-dependent and hence only give an idea of the order of magnitude, since the experiments were not carried out at constant concentration. The low values for $H_3PO_4$ [17] and $PhP(O)(OH)_2$ [9] in 25 oleum have been attributed to condensation equilibria. It seems apparent from the results that $Ph_2P(O)Cl$, $Ph_3PO$, $H_3PO_4$, $PhP(O)(OH)_2$, and $Ph_2P(O)OH$ are essentially completely protonated by all these solvents, and thus behave as strong bases in the sulphuric acid and related solvent systems. $PhP(O)Cl_2$, at the concentrations used, is probably protonated completely by $HSClO_3$ and 25 oleum but not by $H_2SO_4$, while $P(O)Cl_3$ and $MeP(O)Cl_2$ are only protonated completely by 25 oleum, if at all. The order of acid strength is thus confirmed as 25 oleum > $HSClO_3$ > $H_2SO_4$, while $P(O)Cl_3$ appears to be the weakest base from its behaviour in $HSClO_3$. A more weakly acidic solvent such as liquid HCl [21] is required to differentiate further between the bases which are completely protonated by 100% $H_2SO_4$. The value of $^{31}P$ n.m.r. spectroscopy as a means for following reactions in these highly acidic media is again demonstrated by this work, since most of the phosphorus derivatives may be readily identified in solution, in contrast with conductivity or cryoscopy, and isolation of individual species is clearly not feasible in most instances.

TABLE 2

Phosphorus-31 n.m.r. shift differences (p.p.m.) between the partially protonated and unprotonated forms of $H_3PO_4$ and some derivatives in acid solvents

| | δ (protonated species) − δ (parent) | | | |
|---|---|---|---|---|
| Compound | $H_2SO_4$ | $HSClO_3$ | 25 oleum | Ref. |
| $H_3PO_4$ | 2.2 | 1.7 | −6.6 | 17 |
| $PhP(O)(OH)_2$ | 14 | 14 | 9 | 9 |
| $Ph_2P(O)OH$ | 29 | 30 | Not seen | This work |
| $Ph_3PO$ | 33 | 35 | 34 | This work |

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