Co. and distilled twice in glass apparatus in an atmosphere of dry air before use. Ethyl fluoride (Air Products and Chemicals, Inc.) and methyl fluoride (Peninsular Chemresearch, Ltd.) were purified by vacuum fractionation. Sulfuryl chlorofluoride, SO_2ClF, was prepared by the method of Seel and Riehl[18] and purified as previously described.[3] Sulfur dioxide was obtained from Matheson of Canada, Ltd. Both solvents were stored as a gas over anhydrous phosphorus pentoxide before use.

Nmr samples were prepared on a vacuum line using a small flask with a detachable tap and nmr tubes sealed to the flask. A small weighed quantity of SbF_5 (about 0.01 mol) was distilled into the flask. Enough solvent (SO_2 or SO_2ClF) to dissolve the SbF_5 was then distilled into the flask. The resulting solution was approximately 1.5 *M* in SbF_5 in the case of SbF_5–SO_2 and 7.5 *M* in the case of SbF_5–SO_2ClF. The solution was held at Dry Ice temperature and stirred while a known volume of alkyl fluoride was allowed to evaporate into the reaction flask, giving a solution of known alkyl fluoride–SbF_5 ratio. The flask was then removed from the vacuum line and tilted so that a suitable amount of solution entered the nmr tube and the tube sealed off, all at low temperature.

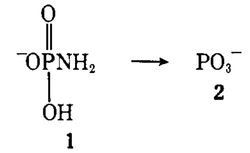
Reactions of Phosphinates in Sulfuric Acid and Oleum[1,2]

Paul Haake*[3] **and Paul S. Ossip**

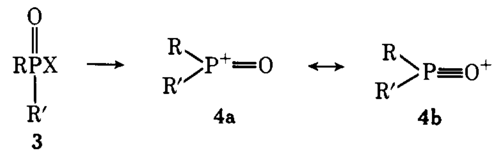
Contribution from the Department of Chemistry,
University of California, Los Angeles, California 90024,
and the Department of Chemistry, Wesleyan University,
Middletown, Connecticut 06457. *Received October 26, 1970*

Abstract: In order to understand the fundamental tendency of pentavalent, tetracoordinate phosphorus to react by dissociative mechanisms and the nature of transformations in strong acids, phosphinic acids, R_2PO_2H, and derivatives, $R_2P(O)X$, have been studied by nmr and cryoscopy in sulfuric acid and oleum. Phosphinylium ions, R_2PO^+, do not appear to be formed. Instead, sulfonation occurs after protonation: $R_2PO_2H + 50\%\ H_2SO_4 \rightarrow R_2P^+(OH)_2$; $R_2P^+(OH)_2 + 10\%\ \text{oleum} \rightarrow R_2P^+(OH)OSO_3H$; $R_2P^+(OH)OSO_3H + 55\%\ \text{oleum} \rightarrow R_2P^+(OSO_3H)_2$. This is a distinct contrast to carboxylic acids which have been shown to protonate and then form acylium ions in about 10% oleum. An amide, $(C_6H_5)_2P(O)N(CH_3)_2$, forms three–four species on solution in 100% H_2SO_4 but all other phosphinates act as simple bases giving two species—protonated substrate and bisulfate ion.

There have been a number of proposals for the occurrence of dissociative mechanisms of displacement at phosphorus.[4–6] These have mainly concerned the reactions of phosphate derivatives, such as phosphoramidate (**1**), where the substituents might participate in the stabilization of the intermediate with reduced coordination number (*e.g.*, **2**). It is therefore important to establish the fundamental facts on the tendency of phosphorus to react by dissociative mechanisms. In this paper we examine the reactions of phosphinic acid derivatives (**3**) in the spectrum of acidities provided by the water–sulfuric acid–oleum system. Spectroscopy of solutions in this system and cryoscopy in 100% sulfuric acid have provided some of the clearest evidence for the existence of carbonium ions.[7] The first studies of acylium ions involved the abnormal freezing point depression of mesitoic acid in sulfuric acid.[8] In this paper, we examine spectral and cryoscopic data on solutions of **3** for evidence of formation of phosphinylium ions, **4** (orbital considerations may make **4b** a minor contributor unlike acylium ions). We have previously observed phosphinylium ions as important fragments in the mass spectra of phosphinates.[9,10] This and the subsequent paper evaluate their stability and occurrence in solution chemistry.



(1)



(2)

Results

Cryoscopy. Cryoscopic measurements on solutions of phosphinates were carried out using the apparatus devised by Gillespie, *et al.*[11] The average number, ν, of dissolved species produced from a given substrate was calculated by eq 3, where θ is the freezing point depression from 10.625°, m^s is the molality of added

$$\nu = \frac{\theta(1 - 0.098m^s s)}{6.12m^s} - \frac{m^d}{m^s} \qquad (3)$$

substrate, *s* is the number of H_2SO_4 molecules reacting

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(1) This research was supported by Grants GP-8142 and GP-13453 from the National Science Foundation and by Grant AM-12743 from the National Institute of Arthritis and Metabolic Diseases.

(2) (a) Preliminary communication: P. Haake and P. S. Ossip, *Tetrahedron Lett.*, 4841 (1970); (b) P. S. Ossip, *Diss. Abstr. B*, **29**, 551 (1969).

(3) Wesleyan University.

(4) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, Amsterdam, 1967, pp 284–301.

(5) R. F. Hudson, "Structure and Mechanism in Organosphosphorus Chemistry," Academic Press, New York, N. Y., 1965, pp 269–281.

(6) T. C. Bruice and S. J. Benkovic, "Bio-organic Mechanisms," Vol. 2, W. A. Benjamin, New York, N. Y., 1966, Chapter 5.

(7) (a) A. Hantszch, *Z. Physik. Chem.*, **61**, 257 (1908); (b) L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc*, **55**, 1900 (1933).

(8) H. P. Treffers and L. P. Hammett, *ibid.*, **59**, 1708 (1937).

(9) P. Haake and P. S. Ossip, *Tetrahedron*, **24**, 565 (1968).

(10) P. Haake, M. J. Frearson, and C. E. Diebert, *J. Org. Chem.*, **34**, 788 (1969).

(11) R. J. Gillespie, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2473 (1950).

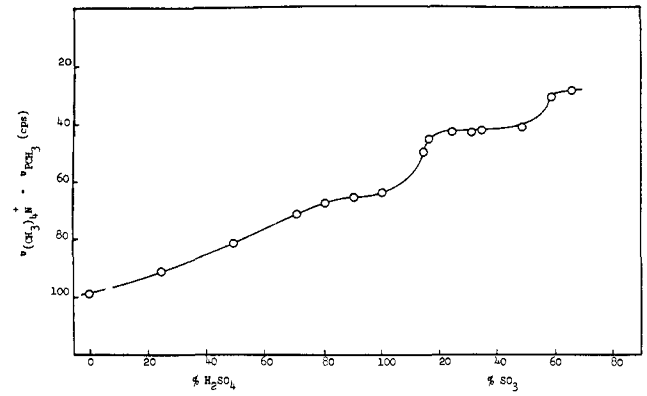

Figure 1. Chemical shift of PCH_3 *vs.* acid concentration for dimethylphosphinic acid.

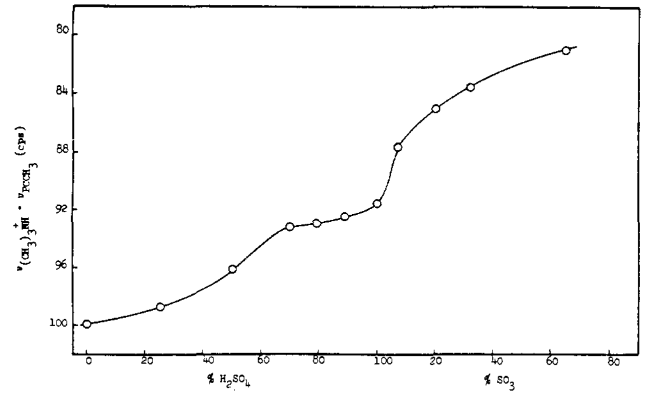

Figure 2. Chemical shift of $PCCH_3$ *vs.* acid concentration for di-*tert*-butylphosphinic acid.

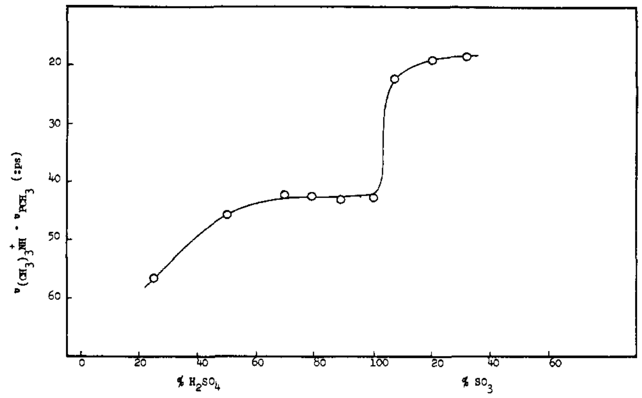

Figure 3. Chemical shift of PCH_3 *vs.* acid concentration for dimethylphenylphosphine oxide.

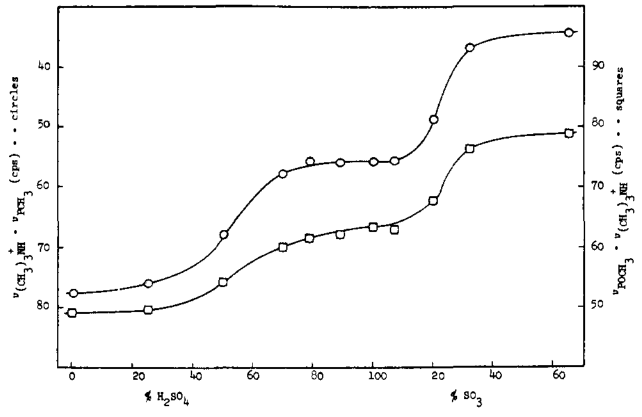

Figure 4. Chemical shift of PCH_3 and $POCH_3$ *vs.* acid concentration for methyl dimethylphosphinate.

with one molecule of substrate, and m^d is the concentration of species produced by autodissociation of H_2SO_4.[12] It was not necessary to use any of the approximate methods[12] for calculating m^d/m^s, because all the phosphinates behaved as simple bases.

The freezing point depressions of sodium bisulfate, benzoic acid, and mesitoic acid were first measured to check the reliability of our procedures; we then examined a number of phosphinates and dimethyl sulfoxide. The results are found in Table I.

Table I. Cryoscopic Measurements

Compound	Range of m^s [a]	Average ν[b]
NaO_3SOH	0.00434–0.04191	2.09 ± 0.02
$C_6H_5CO_2H$	0.00418–0.05611	2.04 ± 0.05
Mesitoic acid	0.00394–0.03999	4.28 ± 0.17
5, $(CH_3)_2PO_2H$	0.00664–0.05895	1.99 ± 0.01
6, $CH_3P(O)(C_6H_5)OH$	0.00416–0.05274	2.09 ± 0.02
7, $(CH_3)_2P(O)C_6H_5$	0.00358–0.03594	2.19 ± 0.04
8, $(CH_3)_2P(O)OCH_3$	0.00319–0.05112	2.07 ± 0.02
9, $(C_6H_5)_2P(O)N(CH_3)_2$	0.00336–0.03716	3.71 ± 0.10
10, $(CH_3)_2SO$	0.00366–0.05493	2.16 ± 0.07

[a] See eq 5. [b] Average of five–eight determinations ± standard deviation.

The results fit into a pattern of $\nu = 2$ for all the phosphinates and DMSO except for the amide **9**. Additional data on the nature of the species produced are given at the end of the Results section. Nmr spectra of the amide in 100% H_2SO_4 demonstrated loss of P–N–C–H coupling. Therefore, the P–N bond is cleaved in order to give $\nu = 3.7$.

Detection of Transformations by Nmr Chemical Shifts. In our study of the basicity of $\gt P{=}O$ compounds, we were able to measure protonation by evaluation of chemical shifts of PCH_3 groups as a function of acidity.[13] We have been able to extend those measurements to higher acidities and have detected additional changes.

The nmr spectra of solutions of substrates were observed over a range of acid concentrations from infinite dilution to 65% SO_3. The solutions were generally about 1% substrate by weight. This dilution should minimize any spurious effects due to the presence of substrate in the medium—a common problem due to high concentrations required for nmr. Chemical shifts were measured relative to $(CH_3)_4N^+$ as internal standard. The changes in chemical shifts which were observed were shown to be reversible by lowering the acidity and thereby reproducing the spectra of the substrate.

The primary concern is the qualitative changes in chemical shifts with variation in acidity. The chemical shifts (ν) in hertz have been plotted in each case *vs.* per cent H_2SO_4 and per cent SO_3 (Figures 1–4). In addition to the compounds shown, similar data were collected for diethylphosphinic acid, $(CH_3CH_2)_2PO_2H$, and

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(12) S. J. Bass, R. J. Gillespie, and E. A. Robinson, *J. Chem. Soc.*, 821 (1960).

(13) P. Haake, R. D. Cook, and G. H. Hurst, *J. Amer. Chem. Soc.*, **89**, 2650 (1967); P. Haake and R. D. Cook, *Tetrahedron Lett.*, 427 (1968).

Table II. Changes in Chemical Shift with Changes in Acidity of the Medium

Compound	H's obsd	Acidity at half total change (Δ) in chemical shift		
		Δ_1	Δ_2	Δ_3
$(CH_3)_2PO_2H$	CH_3	49% H_2SO_4	13% SO_3	~55% SO_3
$(CH_3CH_2)_2PO_2H$	CH_3	59% H_2SO_4	10% SO_3	*a*
$C_6H_5P(CH_3)O_2H$	CH_3	46% H_2SO_4	~10% SO_3	>50% SO_3
(*tert*-butyl)$_2PO_2H$	CH_3	48% H_2SO_4	6% SO_3	>50% SO_3
$(CH_3)_2P(O)C_6H_5$	CH_3	~30% H_2SO_4	5% SO_3	*b*
$(CH_3)_2P(O)OCH_3$	PCH_3	52% H_2SO_4	24% SO_3	0– 65% SO_3
$(CH_3)_2P(O)OCH_3$	OCH_3	56% H_2SO_4	25% SO_3	

[a] Not observed. [b] Sulfonation of phenyl ring prevented observation.

Table III. Coupling Constants

Compound	Coupling	State of Molecule			
		Unprotonated	Protonated	Sulfonated	Disulfonated
$(CH_3)_2PO_2H$	P-C-H	14.2	14.6	14.3	13.3
$(CH_3CH_2)_2PO_2H$	P-C-C-H	18.3	21.1	22.6	
$C_6H_5P(CH_3)O_2H$	P-C-H	14.2	15.6	15.0	12.8
(*tert*-butyl)$_2PO_2H$	P-C-C-H	14.5	17.2	18.8	19.0
$(CH_3)_2P(O)C_6H_5$	P-C-H	13.4	13.6	12.9	
$(CH_3)_2P(O)OCH_3$	P-C-H	14.4	14.7	13.6	
	P-O-C-H	11.5	12.0	12.5	

methylphenylphosphinic acid (**6**). The CH_3 hydrogens of $(CH_3CH_2)_2PO_2H$ displayed a similar dependence to that shown in Figure 1 although the magnitude of changes in chemical shifts was smaller due to the observation of β-hydrogens rather than α-hydrogens. Methylphenylphosphinic acid exhibited a very similar curve to that shown in Figure 1. It was impossible to get data for Figure 3 (compound **7**) below 25% H_2SO_4 because this phosphine oxide was highly insoluble at low acidities. Above 40% SO_3, sulfonation of the phenyl ring prevented measurements. Note that the same dependence is found for the ester, $(CH_3)_2P(O)OCH_3$, regardless of whether PCH_3 or OCH_3 groups are observed (Figure 4).

Attempts were made to include dibenzylphosphinic acid, methyl dibenzylphosphinate, and dimesitylphosphinic acid in this study, but it was found that these compounds apparently undergo sulfonation of the aromatic rings in concentrated sulfuric acid, as witnessed by the appearance of new peaks in the aromatic region of the nmr spectra and the failure to return to the original spectra on dilution. An unsuccessful attempt was also made to find a carbonyl compound which could be studied in this fashion. Acetophenone apparently undergoes acid-catalyzed condensation quite readily under these conditions, 4-methylbenzophenone sulfonates readily, and highly branched ketones with no α-hydrogens have been shown to be unstable in sulfuric acid solutions.[14]

The data on all compounds studied are summarized in Table II.

The changes in chemical shifts were in some cases accompanied by changes in coupling constants. The changes in coupling constants are summarized in Table III.[15] There is probably a possible inaccuracy in these couplings of ±0.5 cps since they were obtained by linear measure using as peak center the half-width at half-height.

The amide data in Table I were supplemented by observations on the nmr spectra of the *N,N*-dimethylamide of methylphenylphosphinic acid. The results (Table IV) indicate that the same species is formed from this amide as from methylphenylphosphinic acid.

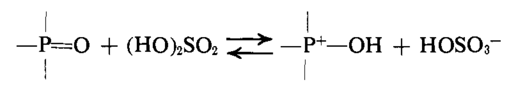
Table IV. Chemical Shifts and PCH Coupling Constants for Oleum Solutions of *N,N*-Dimethylphenylmethylphosphinamide and Phenylmethylphosphinic Acid

% SO_3	*N,N*-Dimethylphenylmethylphosphinamide[a]	Phenylmethylphosphinic acid[a]
0	$\nu = 56.1$; $J = 15.0$	$\nu = 56.5$; $J = 15.4$
5	$\nu = 41.9$; $J = 14.4$	$\nu = 43.0$; $J = 15.0$
17	$\nu = 35.9$; $J = 14.8$	$\nu = 35.3$; $J = 14.4$
25	$\nu = 31.6$; $J = 15.0$	$\nu = 30.5$; $J = 15.0$

[a] Chemical shift given as $\nu(PCH_3) - \nu(Me_4N^+)$. ν and J in hertz.

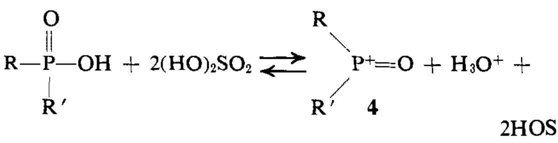
Discussion

Cryoscopy. The phosphinic acids **5** and **6**, the phosphine oxide **7**, the phosphinate ester **8**, and the sulfoxide **10** appear to behave as simple Brønsted bases in sulfuric acid (eq 4, for example). This accounts for



$$-\overset{|}{\underset{|}{P}}{=}O + (HO)_2SO_2 \rightleftharpoons -\overset{|}{\underset{|}{P^+}}-OH + HOSO_3^- \qquad (4)$$

the ν values of 2 found for these compounds (Table I). These ν values of 2 are inconsistent with formation of phosphinylium ions (**4**) from the phosphinic acids for this would require $\nu = 4$ (eq 5) as in the case of mesitoic



$$R-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle R'}{|}}{P}}-OH + 2(HO)_2SO_2 \rightleftharpoons RR'P^+{=}O + H_3O^+ + 2HOSO_3^- \qquad (5)$$

4

acid. Although it is possible that the amide **9** reacts in sulfuric acid analogously to eq 5, we believe this is less likely than alternative possibilities which will be discussed below.

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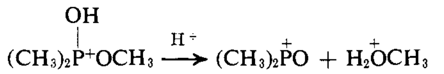
(14) For example: S. Barton, F. Morton, and C. R. Porter, *Nature* (*London*), 169, 373 (1952).

(15) Complete data may be found *via* ref 2b.

We have previously published pK_{BH^+} values for phosphinic acids, phosphinate esters, phosphine oxides, and dimethyl sulfoxide.[13] These pK values are in the range -2 to -5 (H_0 scale[16]). Since the H_0 value of 100% sulfuric acid is approximately -12, one would expect complete protonation and $\nu = 2$ as observed (Table I). This should be true even though the phosphine oxides are poor Hammett bases.[13]

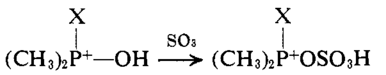
Explanation of Changes in Chemical Shifts. The discovery of three changes in chemical shift of $(CH_3)_2PO_2H$ (Figure 1) is the important observation. The validity of this is corroborated by measurements on other phosphinic acids including di-*tert*-butylphosphinic acid (Figure 2 and Table II). These measurements cover an enormous range of acidity. The first change in chemical shift—in the H_2SO_4 range—is associated with protonation as indicated by previous work[13] and by the ν values in Table I.

The change in chemical shift at approximately 10% oleum is reminiscent of recent nmr measurements[17] on carboxylic acids in which protonation was detected in H_2SO_4 and formation of acylium ions in oleum. Is the change in chemical shift at 10% oleum in Figure 1 due to formation of phosphinylium ion (**3** → **4**)? We believe we can eliminate this hypothesis conclusively. First, if this change in chemical shift were due to generation of phosphinylium ion (**4**), one would not expect further change in chemical shift which is, in fact, observed at approximately 55% oleum. Second, as expected, the nmr spectra of the phosphine oxide **7** in H_2SO_4 and oleum give no evidence of cleavage of a P–C bond. Yet, there is a change in chemical shift at about 10% oleum as in the case of the acid. Cleavage of a P–C bond would be required to generate a phosphinylium ion. Therefore, no phosphinylium ion is generated from **7** and the actual change in 10% oleum for **7** is likely to be valid also for **5**. Third, the ester **8** displays the same change in chemical shift without loss of the OCH_3 doublet in the nmr. This doublet is due to P–O–C–H coupling. Therefore, the P–O bond persists in acidities >10% oleum. Generation of phosphinylium ion would require that the P–O bond be cleaved (eq 6).



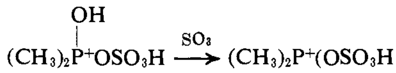
$$(CH_3)_2\overset{OH}{\overset{|}{P^+}}OCH_3 \xrightarrow{H^+} (CH_3)_2\overset{+}{P}O + H_2\overset{+}{O}CH_3 \qquad (6)$$

Therefore, this change in chemical shift at about 10% oleum cannot be due to generation of phosphinylium ions. We suggest, instead, that it is due to sulfonation.



$$\underset{\mathbf{11}}{(CH_3)_2\overset{X}{\overset{|}{P^+}}\text{—}OH} \xrightarrow{SO_3} \underset{\mathbf{12}}{(CH_3)_2\overset{X}{\overset{|}{P^+}}OSO_3H} \qquad (7)$$

This process would accommodate the above observations and would be expected to change the chemical shift of the PCH_3 groups because the OSO_3H group should be considerably more electron withdrawing than the OH group. It also satisfactorily explains the third change in chemical shift (Figure 1, Table II) at approximately 55% oleum because when X = OH, **12** can sulfonate a second time

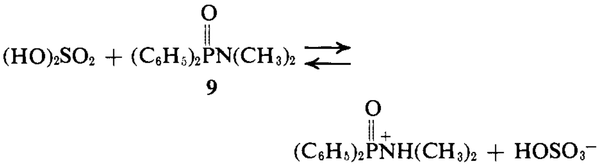


$$(CH_3)_2\overset{OH}{\overset{|}{P^+}}OSO_3H \xrightarrow{SO_3} \underset{\mathbf{13}}{(CH_3)_2P^+(OSO_3H)_2} \qquad (8)$$

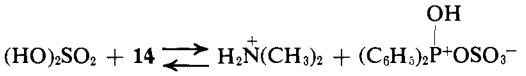
A low number of other hypotheses which might explain our data appear much less likely than sulfonation or appear to violate some of the experimental facts.

Amides in H_2SO_4. The phosphinamide **9** in 100% H_2SO_4 causes an observed $\nu = 3.7$. Many of our ν numbers are slightly high. For example, $\nu = 4.3$ for mesitoic acid. This may be due to some incorporation of atmospheric water during the manipulations required for the measurements, although precautions were taken to exclude moisture. In any case, the other results indicate that $\nu = 3.7$ is a maximum for the amide. We therefore appear to have a ν value between 3 and 4.

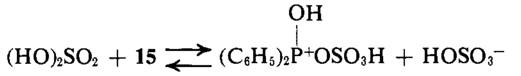
Phosphinamides are highly reactive in acid,[18,19] and the P–N bond would be expected to cleave fairly rapidly even in 100% sulfuric acid unlike carboxylic amides[19,20] which are quite stable in this medium. Our cryoscopic measurements and the accompanying loss of PNCH coupling do indicate that the amide hydrolyzed. Therefore, the following reaction sequence seems likely[21]



$$(HO)_2SO_2 + \underset{\mathbf{9}}{(C_6H_5)_2\overset{O}{\overset{\|}{P}}N(CH_3)_2} \rightleftarrows \underset{\mathbf{14}}{(C_6H_5)_2\overset{O}{\overset{\|}{P}}\overset{+}{N}H(CH_3)_2} + HOSO_3^- \qquad (9)$$



$$(HO)_2SO_2 + \mathbf{14} \rightleftarrows H_2\overset{+}{N}(CH_3)_2 + \underset{\mathbf{15}}{(C_6H_5)_2\overset{OH}{\overset{|}{P^+}}OSO_3^-} \qquad (10)$$



$$(HO)_2SO_2 + \mathbf{15} \rightleftarrows \underset{\mathbf{16}}{(C_6H_5)_2\overset{OH}{\overset{|}{P^+}}OSO_3H} + HOSO_3^- \qquad (11)$$

Tautomerism is possible for **15**, but this structure almost certainly predominates over $(C_6H_5)_2P(O)OSO_3H$ because R_3P^+OH is considerably less acidic than $ROSO_3H$.[13,22] Note that **16** corresponds to the species produced on sulfonation of the protonated acid (eq 7, X = OH). From the nmr data (Table II) we know **16** is formed from acid in low percentage oleum mixtures, so it is not unreasonable that it would be formed from amide in 100% H_2SO_4. As the data in Table IV indicate, the sulfonation process must be reversible

$$\mathbf{16} \rightleftarrows \underset{\mathbf{17}}{(C_6H_5)_2P^+(OH)_2} + SO_3 \qquad (12)$$

In the presence of bisulfate ion, the anion of pyrosulfuric acid should be formed from SO_3, as shown in eq 13.

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[16] M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, **85**, 878 (1963); L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940, Chapter 9.

[17] N. C. Deno, C. U. Pittman, Jr., and M. J. Wisotsky, *J. Amer. Chem. Soc.*, **86**, 4370 (1964).

[18] P. Haake and D. A. Tyssee, *Tetrahedron Lett.*, 3513 (1970).

[19] P. Haake and T. Koizumi, *ibid.*, 4845 (1970), have demonstrated that **9** is 10^6 more reactive to acid-catalyzed hydrolysis than *N*,*N*-dimethylbenzamide.

[20] V. K. Krieble and K. A. Holst, *J. Amer. Chem. Soc.*, 60, 2976 (1938); J. T. Edward and S. C. R. Meacock, *J. Chem. Soc.*, 2000 (1957).

[21] The question of position of protonation in **14** will be discussed in forthcoming publications: P. Haake and T. Koizumi, unpublished results.

[22] E. N. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

$$\mathrm{SO_3 + HO_3SO^- \rightleftarrows HO_3SOSO_3^-} \qquad (13)$$

Summing the equilibria 11–13

$$\mathbf{15} + \mathrm{(HO)_2SO_2} \rightleftarrows \mathbf{17} + \mathrm{HO_3SOSO_3^-} \qquad (14)$$

Since $\mathrm{HOSO_3^-}$ and $\mathrm{H_2N^+(CH_3)_2}$ are generated in eq 9 and 10, ν should be 3 or 4 depending on whether equilibrium 14 lies respectively to the left or right. Our observed $\nu = 3.7$ indicates an intermediate value in accord with desulfonation (eq 12) being partially complete.

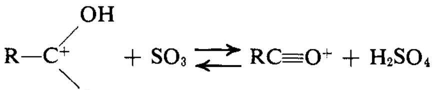
Alternatively, if sulfonation is not reversible, the ν value of 3.7 would indicate that the equilibrium in eq 11 is incomplete. The structure of **16** is in accord with this. Essentially **16** is a substituted sulfuric acid. The $\mathrm{P^+}$ group in **16** should increase the acidity of the $\mathrm{SO_3H}$ proton relative to sulfuric acid, so it is not unreasonable to have partial protonation in $\mathrm{H_2SO_4}$ as solvent.

Acylium *vs.* Phosphinylium Ions. We therefore observe that phosphinylium ions do not form under conditions where acylium ions do form.[23] How do we account for the difference between phosphinic acids and carboxylic acids? Phosphorus reluctantly undergoes reaction by dissociative mechanisms. The data in the following paper elegantly demonstrate that fact. The data in this paper are another indication of the reluctance of tetracoordinate, pentavalent phosphorus to reduce its coordination number.

There appear to be several fundamental reasons for this property of phosphorus compounds, but they can be summarized: energy of solvation of the dissociated species plus increase in bond energy in the remaining bonds is less than the bond energy of the bond which breaks in the dissociation

$$\Delta E(\text{solvation}) + \Delta E(\text{bonds remaining}) < E\,(\text{bond dissociated}) \qquad (15)$$

In the generation of acylium ions, there undoubtedly is a large increase in the bond energy of the CO bond which can be summarized by writing the contributor



$$\mathrm{R{-}C^+(OH)_2 + SO_3 \rightleftarrows RC{\equiv}O^+ + H_2SO_4} \qquad (16)$$

18

$$\mathrm{R_2P^+(OH)_2 + SO_3 \rightleftarrows R_2\overset{+}{P}{=}O + H_2SO_4} \qquad (17)$$

19

with a C–O triple bond, **18**. A recent crystal structure demonstrates that this must be an important contributor for r(CO) is only 1.11 Å.[24] Although the P–O bond in **19** would be shorter than a normal P–O bond, valence shell orbitals are not available for a triple bond since three σ bonds are present. In addition the very short C–O bond length in **18** would lead to a large π overlap integral and a large π bond energy, but the P–O bond in **19** will be much longer. Therefore, the π bond energy in **19**, will be much less than in **18** for both reasons: **18** is dicoordinate but **19** is tricoordinate, and r(CO) in **18** is considerably less than r(PO) in **19**.

The stability of the parent ions may also be important. Although $\mathrm{RC(OH)_2^+}$ is a stabilized carbonium ion, it would not be expected to be as stable as the phosphonium ion $\mathrm{R_2P^+(OH)_2}$. This difference is demonstrated by the difference in pK's of these two ions: pK $[\mathrm{RC^+(OH)_2}] \sim -7$;[22] p$K$ $[\mathrm{R_2\overset{+}{P}(OH)_2}] \sim -4$.[13]

The changes in coupling constants in Table III are not large, but the P–X–C–H couplings appear to increase with decreasing chemical shift and, therefore, with increasing electron withdrawal from phosphorus. It is somewhat surprising that there is not a corresponding increase in J (P–C–H) in view of the published values of these couplings.[25] Increased positive charge on the P atom might have been expected to increase both the α and β couplings.

Experimental Section

Nmr spectra were recorded on a Varian A-60 spectrometer. Melting points were observed with a Mel-Temp block and are corrected. Analyses were by Miss Heather King (UCLA).

Nmr Studies. Solutions of $\mathrm{H_2SO_4}$ were prepared by mixing distilled water, reagent grade 96% $\mathrm{H_2SO_4}$, and 30 and 60% oleum. The solutions were analyzed by dilution in $\mathrm{H_2O}$ and titration to phenolphthalein end point with standard NaOH; estimated accuracy is ±0.5% $\mathrm{H_2SO_4}$ or ±2% $\mathrm{SO_3}$.

Chemical shifts and coupling constants were determined by linear measurement using as peak center the half-width and half-height. In oleum, viscosity sometimes caused broadened peaks.

Dilutions to determine the reversibility of the spectral changes were made by cautiously adding small increments of $\mathrm{H_2O}$ to the solution in the nmr tube.

Cryoscopy. The apparatus was built from a ₸ 71/60 joint with two 19/38 openings at the top, one centered for a Beckmann mercury thermometer and one offset for admission of substrate.[11] A glass spiral, soft iron rod, solenoid, and distillation timer were used for stirring.[11] A 4500-ml dewar flask was used as a constant temperature bath, and temperature was found to remain constant within 0.2°. Pure sulfuric acid was prepared as described by Gillespie[11] using 96% $\mathrm{H_2SO_4}$ and 5% $\mathrm{SO_3}$ to adjust composition to maximum freezing point. In the measurements, differences of temperature could be determined accurately to 0.001°; an absolute temperature for calibration was determined by carefully maximizing the freezing point of sulfuric acid and taking that temperature to be 10.371°, the reported maximum freezing point for $\mathrm{H_2SO_4}$.[26]

Freezing points were measured by supercooling the solution to about 1.5° below its freezing point, and the bath temperature was then adjusted to about 1.2° below the freezing point of the solution. Freezing was initiated by touching the outside of the freezing-point cell with a small piece of Dry Ice inserted down the side arm of the air jacket. The steady equilibrium temperature was then read several times from the Beckmann thermometer and recorded as the observed freezing point. The temperature of the solution immediately prior to crystallization was taken as the supercooling temperature, and the observed freezing point was corrected for supercooling by eq 18, where δT is the required correction, S is

$$\delta T = 0.012 S \theta_1 \qquad (18)$$

the amount of supercooling, and θ_1 is the observed freezing point depression.[11] These freezing points were reproducible even after a time lapse of several days.

In the cryoscopic measurements on the amide **9**, ν factors were calculated from.[12]

$$\nu = \frac{2m^s(\mathrm{HSO_4^-})}{m^s} \qquad (19)$$

$$m^s = \frac{m_2 - m_1}{T_1 - T_2}\left[\frac{T_1 - T_2}{m_2 - m_1} m_2 + 12.24 m^s(\mathrm{HOSO_4^-}) + 6.12 m^d - \theta_2\right] \qquad (20)$$

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[23] Our observations on sulfonation cause some concern about the role of sulfonation in the equilibria of carboxylic acids in sulfuric acid and oleum.[17]

[24] J. M. Le Carpentier and R. Weiss, *Chem. Commun.*, 596 (1968).

[25] J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, 20, 449 (1964).

[26] S. J. Bass and R. J. Gillespie, *J. Chem. Soc.*, 814 (1960).

where m_1 and m_2 are successive values of molalities, T_1 and T_2 are corrected freezing points at the corresponding molalities, θ_2 is the freezing-point depression (10.625° $- T_2$), pue $m^{s}(HOSO_3^-)$ is the concentration of produced bisulfate assuming 2 moles of $HOSO_3^-$ generated per mole of substrate added. A solution of 20% *N*,*N*-dimethyldiphenylphosphinamide in stock sulfuric acid was used to add the substrate to the cryoscope. The first two measurements were made within 3 hr of preparation of this solution; the remaining five measurements were done between 6 and 8 hr after preparation.

The ν values which we determined for sodium bisulfate, mesitoic acid, and benzoic acid are in good agreement with published values.[11] A sample set of data is in Table V.

The phosphorus compounds were prepared by methods previously published[9,13] except for the following. Methylphenylphosphinic acid was prepared by the method of Harwood and Grisley.[27] Di-*tert*-butylphosphinic acid was prepared by addition of 2 moles of *tert*-butyllithium in pentane to PCl_3 in hexane, using Dry Ice-acetone to cool the reaction mixture. After stirring overnight at room temperature, $CHCl_3$ was added and Cl_2 was bubbled through the solution to oxidize R_2PCl to R_2PCl_3. Water was added to hydrolyze the phosphorane, the layers were separated, and the organic solvents were removed. The resultant yellow oil was refluxed overnight with dilute sodium hydroxide. Acidification with HCl followed by extraction with chloroform gave a small yield of white crystals: mp 201–205° (lit.[28] 208–210°); nmr (CH_2Cl_2) τ 8.80 (doublet), $J_{PCCH} = 17$ Hz; ir (KBr) 2970 m, 2960 m, 2900 m, 2870 m, 1610 broad m, 1470 s, 1390 m, 1365 m, 1350 m, 1240 m, 1140 s, 935 s, 820 m, 810 m, 675 m, 590 m.

Table V. Freezing Point Depression of Solutions of Methyl Dimethylphosphinate

m^{s} [a]	Fp,[a] °C	m^{s} [b]	Fp,[b] °C	θ,[c] °C	ν[d]
0.00000		0.005	10.320	0.295	2.10
0.00319	10.345	0.010	10.288	0.337	2.09
0.00845	10.300	0.015	10.246	0.379	2.05
0.01379	10.257	0.020	10.187	0.428	2.07
0.01883	10.210	0.030	10.089	0.536	2.08
0.02647	10.125	0.040	9.971	0.644	2.06
0.03385	10.050	0.050	9.862	0.763	2.06
0.04300	9.948				
0.05112	9.848				

[a] Experimentally determined molalities and freezing points. Freezing points have been corrected for supercooling. [b] Molalities for which values of m^{d} have been determined. Freezing points obtained by linear interpolation. [c] Freezing point depression (10.625° − fp). [d] Average value for $\nu = 2.07 \pm 0.02$.

N,*N*-Dimethyldiphenylphosphinamide (**9**) was prepared by addition of dimethylamine to diphenylphosphinyl chloride. The amide was extracted with CCl_4, the solution was dried, and solvent was removed by evaporation. Recrystallization from acetone-hexane and sublimation gave white crystals: mp 104–105° (lit.[29] 103–105°).

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SN1 Mechanisms in Displacement at Phosphorus. Solvolysis of Phosphinyl Chlorides[1-3]

Paul Haake*[4] **and P. S. Ossip**[5]

Contribution from the Department of Chemistry, University of California, Los Angeles, California 90024, and the Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457. *Received October 26, 1970*

Abstract: The solvolysis reactions of phosphinyl chlorides have been investigated in order to define the tendency of phosphorus to undergo substitution by dissociative reactions. In the case of di-*tert*-butylphosphinyl chloride, $[(CH_3)_3C]_2P(O)Cl$ there is clear evidence for a dissociative, or SN1(P), reaction. Since this is an exceedingly hindered compound, it is a dramatic indication of the great preference for associative, SN2(P), displacement at phosphorus. This is the mechanism found for diisopropylphosphinyl chloride. Conjugative effects do not lead to SN1(P) mechanisms. Angle strain does not appear to have the inhibitory effect on SN1(P) reactions that it has on SN1(C) reactions. The *m* values from log *k*/*Y* plots are lower for solvolysis of phosphinyl halides than for solvolysis of alkyl halides.

Displacement at tetrahedral carbon by an SN1 dissociative mechanism is one of the most extensively studied fields of chemistry, and the factors which predispose to this mechanism in any particular reaction are well understood.[5,6] Although displacement at tetrahedral phosphorus apparently can proceed by a dissociative pathway, reliably authentic examples are few[7-10] and largely confined to phosphate derivatives[11] where the intermediate of reduced coordination number can be stabilized by delocalization as in the generation of metaphosphate (**2**) from aryl phosphates (eq 1).[12]

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