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Phosphinylium Ions as Intermediates in Solvolysis of Sterically Hindered Phosphinyl Chlorides.[1]

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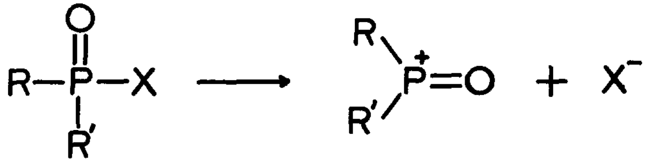
Displacement reactions at phosphorus can be divided into two major classes: associative and dissociative reactions. Although there are many examples of displacement at phosphorus proceeding by associative pathways, there are few authentic examples of dissociative mechanisms.[2,3] Therefore, important fundamental problems in the chemistry of phosphorus concern the factors which predispose toward dissociative or associative pathways for displacement and the extent of the barrier to the dissociative pathway. In phosphinates (1), a dissociative displacement would result in a phosphinylium ion (2). The transformation, 1 → 2, has similarity to the formation of a carbonium ion from an alkyl halide. However, 2 might be stabilized by delocalization of positive charge to oxygen as in acylium ions.[4]

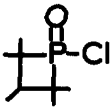


1 2 (1)

We have examined the rates of solvolysis of phosphinyl chlorides (1, X = halide) in HCO_2H and CF_3CO_2H with water-acetone mixtures in which t-butyl chloride reacts at the same rate (Table 1).[2,5] That is, the rate-ratio of 1 for t-butyl chloride indicates that dissociative reactions should proceed at approximately equal rates in 41% acetone and CF_3CO_2H, but the much greater nucleophilicity of aqueous acetone will cause associative reactions to be much faster in that solvent. It is clear from the enormous ratio found for diisopropylphosphinyl chloride (1: X = Cl, R = R' = i-propyl) that, at least in aqueous acetone, reaction does not occur by the dissociative pathway (eq. 1). However, a dissociative reaction does appear to occur in the solvolysis of di-butylphosphinyl chloride (1: X = Cl, R = R' = t-butyl).[6] Either the di-t-butylphosphinylium ion (2: R = R' = t-butyl) is present as a reaction intermediate or the transition state in the solvolysis reaction has considerable phosphinylium ion character.

Table I

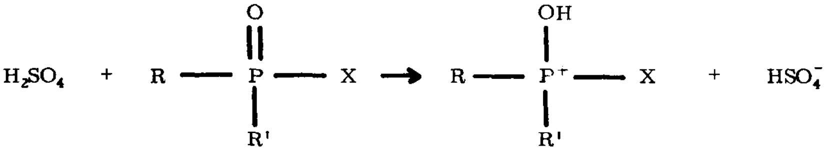
Comparison of Rate Constants in Aqueous Acetone and Formic and Trifluoroacetic Acids for Solvolysis of Phosphinyl Halides.

	$\frac{k(38.5\%\ \text{acetone})}{k(HCO_2H)}$[a]	$\frac{k(41\%\ \text{acetone})}{k(CF_3CO_2H)}$[a]	Relative k in 41% acetone
$(CH_3)_3CCl$	1	1	
i-Pr_2POCl (25.0°)	50	2000	1
 (100°)	---	10	6.5×10^{-4}
t-Bu_2POCl (100.0°)	---	2	3.6×10^{-6}

[a] Ratios of first-order rate constants in the solvents indicated

This result provides considerable clarification of the division between associative and dissociative pathways for displacement at phosphorus. Dissociative reactions can take place, but the fact that it appears in the case of the very sterically hindered di-t-butyl compound is a clear demonstration of the great preference for associative reactions at phosphorus. The inhibition of the associative reaction by the four membered ring appears to be a result of both the angle strain and the steric effect of the α-methyl groups.[7]

We have used freezing point depressions[8] in sulfuric acid and n.m.r. studies in oleum to determine if phosphinylium ions (2) are sufficiently stable to be formed in equilibrium with phosphinic acids (1: X = OH). If the ions, 2, were formed, the freezing point depression would correspond to four ions ($\nu = 4$) formed from one molecule of acid. In each case studied (Table 2), two ions are formed corresponding to equation 2 (X = OH).

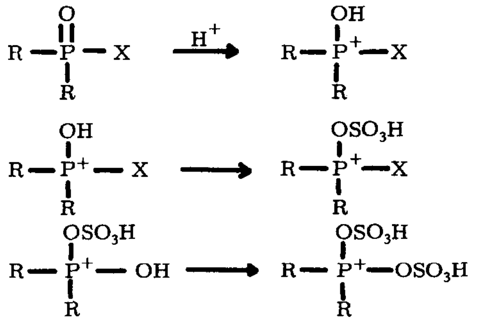


$$H_2SO_4 + R-\overset{\overset{O}{\|}}{\underset{\underset{R'}{|}}{P}}-X \rightarrow R-\overset{\overset{OH}{|}}{\underset{\underset{R'}{|}}{P^+}}-X + HSO_4^- \qquad (2)$$

X = OH, CH_3

3

In the determination of the basicity of dimethylphosphinic acid (**1**: R = R' = CH_3; X = OH), protonation was observed to cause a decrease in chemical shift of the methyl groups.[9] We have extended these studies to higher acidities and find additional changes in chemical shift in oleum. For dimethylphosphinic acid, there are actually three inflections in chemical shift as acidity is increased. The first inflection (at lowest acidity) is due to protonation and formation of **3** (X = OH).[10] If the second inflection (in oleum) were due to formation of **2** by dehydration of **3** (X = OH), it would be difficult to explain the third inflection (also in oleum). This problem appears resolved by examination of dimethylphenylphosphine oxide. It exhibits only two inflections at acidities corresponding to the first two inflections observed for the acid. Formation of a phosphinylium ion is not possible in this case. Our explanation of this data involves the following sequence of reactions:



1) protonation: $R{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle R}{|}}{P}}{-}X \xrightarrow{H^+} R{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle R}{|}}{P^+}}{-}X$ X = C_6H_5,OH

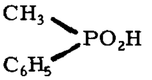
2) sulfonation: $R{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle R}{|}}{P^+}}{-}X \longrightarrow R{-}\overset{\overset{\displaystyle OSO_3H}{|}}{\underset{\underset{\displaystyle R}{|}}{P^+}}{-}X$ X = C_6H_5,OH

3) sulfonation: $R{-}\overset{\overset{\displaystyle OSO_3H}{|}}{\underset{\underset{\displaystyle R}{|}}{P^+}}{-}OH \longrightarrow R{-}\overset{\overset{\displaystyle OSO_3H}{|}}{\underset{\underset{\displaystyle R}{|}}{P^+}}{-}OSO_3H$

The last step is not possible for a phosphine oxide. It therefore appears that even in fuming sulfuric acid phosphinylium ions are not stable enough to exist in appreciable concentrations although they can appear as reaction intermediates.[11]

Table 2

Numbers (ν) of particles formed in 100% H_2SO_4

Compound	Average ν^a
Benzoic Acid	2.04 ± .05
Mesitoic Acid	4.28 ± .17
$(CH_3)_2PO_2H$	1.99 ± .01
 $\overset{CH_3}{\underset{C_6H_5}{}}\!>\!PO_2H$	2.09 ± .02
$(CH_3)_2P(O)C_6H_5$	2.19 ± .04
$(CH_3)_2PO_2CH_3$	2.07 ± .02
$(CH_3)_2SO$	2.16 ± .07

[a] Based on 5-7 determinations in each case.

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(b) I. Oney and M. Caplow, *J. Am. Chem. Soc.*, **89**, 6972 (1967).

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