initially at −78° and then refluxed for 2 hr. The product gave an expected ^{1}H nmr spectrum (acetone-d_6) for *tert*-butyl (δ 1.12; $^3J_{PCCH}$ = 12.7 Hz) with a measured ratio of phenyl to *tert*-butyl protons of 1.08 (calcd, 1.10).

tert-**Butyldichlorophosphine oxide** was prepared by the method of Kinnear and Perren.[17]

tert-**Butyldichlorophosphine sulfide** was prepared by the method of Crofts and Fox.[18]

Acknowledgment. We are grateful to the National Science Foundation (Grant No. GP-18197) for support. J. A. B. is grateful for an NDEA Title IV Fellowship, 1971–1974.

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Kinetics and Mechanism of the Hydrolysis of Pentaaryloxyphosphoranes

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Abstract: The rates of hydrolysis of pentaphenoxy- and of some substituted pentaphenoxyphosphoranes have been measured in 75% dimethoxyethane–25% water, largely by stopped-flow techniques. The reaction in neutral and alkaline solution is subject to strong electrical and steric effects; these effects are less pronounced in acid. The kinetic data and especially the large steric effect suggest that the reaction takes place by way of a hexacoordinated phosphorus intermediate or transition state.

The hydrolysis of phosphate esters may proceed either through expansion of the coordination number of phosphorus to five (through an hydroxyphosphorane intermediate) or by contraction of the coordination number to three (monomeric metaphosphate intermediate).[1] Much evidence has been accumulated for both mechanisms;[1–3] in particular, the demonstration of pseudorotation[4–6] as a necessary concomitant of the hydrolysis of certain phosphate esters shows that hydroxyphosphoranes are intermediates (as contrasted to transition states) in the hydrolysis of at least some phosphates.

Because of the role that phosphoranes play in the hydrolysis of phosphate esters, the mechanisms of hydrolysis of phosphoranes themselves are of interest. Two general pathways come prominently to mind: ionization to phosphonium salts and expansion of the phosphorus valency shell to form hexacoordinated intermediates. These mechanisms are illustrated below for the hydrolysis of pentaphenoxyphosphorane.

$$(C_6H_5O)_5P \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (C_6H_5O)_4P^+ + C_6H_5O^-$$

$$(C_6H_5O)_4P^+ + H_2O \xrightarrow{k_2} (C_6H_5O)_4POH + H^+$$

$$(C_6H_5O)_4POH \xrightarrow{k_3} (C_6H_5O)_3P{=}O + C_6H_5OH$$

and

$$(C_6H_5O)_5P + H_2O \xrightarrow{k_1} (C_6H_5O)_5POH^- + H^+$$

$$(C_6H_5O)_5POH^- \xrightarrow{k_2} (C_6H_5O)_3P{=}O + C_6H_5OH + C_6H_5O^-$$

Both phosphonium salts[2] and anions of hexacoordinated phosphorus[7] are well known. Ramirez[8] and his collaborators and Denney and his collaborators[9] have reported that the hydrolysis of phosphoranes is rapid, and Ramirez's group has postulated,[10] on the basis of product studies and especially on the basis of observed base catalysis in the hydrolysis of a 1,2-oxaphosphetane,[10] that the reactions take place by way of intermediates or transition states that involve hexacoordinated phosphorus. We have now carried out a kinetic study of the hydrolysis of pentaaryloxyphosphoranes in 75% dimethoxyethane–25% water that strongly reinforces this conclusion for the compounds under study. Pentaaryloxyphosphoranes hydrolyze very rapidly, so

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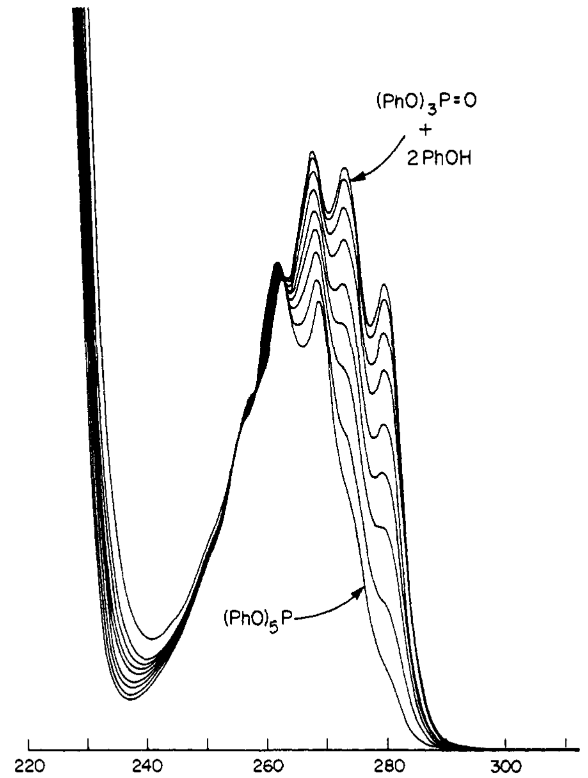

Figure 1. Spectra of pentaphenoxyphosphorane and of its hydrolysis products (triphenyl phosphate and phenol) in dimethoxyethane-water. The spectrum of the phosphorane was determined in dry dimethoxyethane, then about 2% of water was added, and the spectrum was repeatedly "scanned" until it had stabilized to that of the products (about 1 hr).

that the kinetics in mixed solvent were most readily studied by stopped-flow techniques.

Experimental Section

Materials. Dimethoxyethane (DME; Eastman Kodak reagent grade) was passed through a short column of Woelm neutral alumina and then distilled from lithium aluminum hydride prior to use; the purified solvent did not show a positive ferric thiocyanate test for peroxides. Dioxane (for the *Y* value studies) was similarly purified. Other commercial materials were reagent grade.

Phosphoranes were prepared by the general procedure of Ramirez, Bigler, and Smith[11] from PCl_5 and the phenol in the presence of 2,6-lutidine. A cooling bath was not used during the preparations with the less reactive chlorophenols, but the reactions were conducted under an inert atmosphere. The phosphoranes were purified by repeated crystallizations from hexane under an atmosphere of argon in small tubes sealed with serum caps, through which solvent was introduced and mother liquor removed with syringes. The recrystallization of the analytical samples was carried out in a drybox. The properties and analytical data for the phosphoranes are recorded in Table I. Extreme difficulty was encountered in handling penta-*p*-chlorophenoxyphosphorane, since it hydrolyzes with extraordinary rapidity. The analyses for this compound do not fall within the usually accepted limits of error, but, considering the lability of the material, are perhaps satisfactory. The melting point of pentaphenoxyphosphorane (110–111° in a sealed capillary) is higher than that (87–88°) previously[12] reported, but the analytical and spectroscopic data leave little doubt as to its identity.

Products. Phenol and triphenyl phosphate, in the ratio of 1.96:1, were found on hydrolysis of pentaphenoxyphosphorane; the yields of products were determined spectrophotometrically at 267 and 273 nm. The identity of the products was confirmed qualitatively from retention times on a Waters Associates ALC high-pressure liquid chromatograph, using chloroform as solvent and a Carbowax column, with a flow rate of 1.5 ml/min.

Table I. Physical and Analytical Data on Phosphoranes

	Phosphorane				
	Penta-phenoxy	Penta-*o*-cresoxy	Penta-*p*-cresoxy	Penta-*o*-chlorophenoxy	Penta-*p*-chlorophenoxy[a]
Calcd					
% C	72.57	74.18	74.18	53.87	53.87
% H	5.07	6.24	6.24	3.02	3.02
% P	6.23	5.46	5.46	4.63	4.63
% Cl				26.50	26.50
Found					
% C	73.02	74.55	74.29	53.90	52.90
% H	5.09	6.47	6.44	3.00	3.51
% P	6.40	5.28	5.34	4.48	4.78
% Cl				26.48	25.12
^{31}P shift[b] (ppm)	+85.0	+83.0	+83.0	+84.7	+84.6
Uv maxima (nm)[c]	262, 267	267, 273	270, 276	267, 275	272, 277

[a] No satisfactory analysis was obtained for this compound; see text. [b] CH_2Cl_2 solvent; shift relative to 85% H_3PO_4; lit. for the pentaphenyl derivative, +85 ppm. [c] DME solvent.

Kinetics. Kinetic measurements were carried out with a Model 13701 Durrum-Gibson stopped-flow apparatus, where the photomultiplier detector was powered by a Hewlett-Packard-Harrison Model 6515 A DC power supply. The stopped-flow device was integrated with a Zeiss Model PMQ II spectrophotometer, equipped with a Hewlett-Packard 6281 A power supply. The output from the photomultiplier was fed into a Tektronix Type 564 storage oscilloscope, and photographs of the trace were recorded with a Tektronix-Polaroid camera, Model C 30.

One reservoir syringe of the Durrum-Gibson was filled with DME containing the phosphorane, usually at a concentration designed to yield an absorbance change during the experiment of 0.3–0.5 log unit, and the other syringe was filled with a 1:1 mixture (or other appropriate mixture) of aqueous solution and DME. The syringes and observation chamber were thermostated at 24.9 ± 0.10°. The data were read from the Polaroid photographs, and values of the transmittance and screen coordinates were introduced into a computer program that corrected the transmission readings for the (small) parallax errors at the edges of oscilloscope screen, converted corrected transmission to absorbance, and calculated the rate constants. The formation of phenol was monitored by following the optical transmission at 280 nm, where phenol absorbs much more strongly than either triphenyl phosphate or the phosphorane (Figure 1). A typical oscilloscope trace and the corresponding rate plot are shown in Figure 2. The reliability of the stopped-flow method was checked in 10% aqueous DME (where rates are less), by comparing the rate obtained with the Durrum-Gibson apparatus with that obtained, by conventional spectrophotometry, with a Cary Model 15 recording spectrophotometer. The rate for pentaphenoxyphosphorane at 25° was 4.7×10^{-2} sec^{-1} by stopped flow, and 4.3×10^{-2} sec^{-1} with the Cary. The reasons for the 10% discrepancy have not been resolved.

"pH" Measurements in 25% Aqueous DME. A Radiometer Type TTT1c titrator was calibrated with standard aqueous buffers, and then an apparent pH of 1.89 was determined for 0.0100 *M* HCl in 25% aqueous DME. The deviation of this reading from 2.00 represents both salt effect and the solvent junction potential. For purposes of determining the apparent pH (here written as "pH") for solutions in 25% aqueous DME, the meter was corrected so that 0.0100 *M* HCl showed a "pH" of 2.00. (For some measurements, the meter was then "offset," but the offset obviously included in the calculations.) A solution of 0.00100 *M* KOH in carefully boiled solvent (to remove traces of CO_2) showed a corrected "pH" reading of 13.8 ± 0.1, so that the p*K* of this solvent is 16.8 ± 0.1 log units.

Other Methods. All ^{1}H nmr spectra were recorded on a Varian T-60 or A-60 spectrometer. ^{31}P nmr spectra were recorded on a Varian HA-100 spectrometer, operated in the HR mode at 40.2 mHz. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrometer, and uv with a Cary 15 recording spectrophotometer. Mass spectra were obtained on an AEI MS 9 mass spectrometer.

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[11] F. Ramirez, A. J. Bigler, and C. P. Smith, *J. Amer. Chem. Soc.*, 90, 3507 (1968).

[12] F. Ramirez, G. V. Loewengart, E. A. Tsulis, and K. Tasaka, *ibid.*, 94, 3531 (1972).

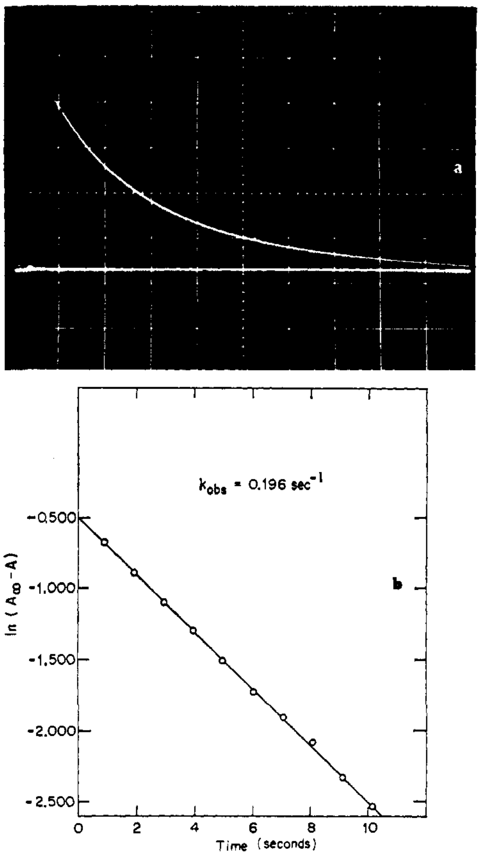

Figure 2. Typical rate determination. Hydrolysis of pentaphenoxyphosphorane in 75% dimethoxyethane–25% water at 25°, with 0.075 M acid. (a) Oscilloscope trace; (b) graphical determination of the rate constant.

Results

The "pH"–rate profile for the hydrolysis of pentaphenoxyphosphorane is shown in Figure 3. The acid and base concentrations for the solution at low and high "pH" were maintained with HCl or KOH, and the ionic strength was held at 0.100 with KCl. The values of "pH" were calculated, for the basic solutions, from the value of pK_w = 16.8. (This value seems quite reasonable when compared with that published for 44% aqueous dioxane.[13]) The data of Figure 3 are correlated with the equation

$$k_{obsd}\ (\text{sec}^{-1}) = 0.202 + 16.4(\text{H}^+) + 12.0(\text{OH}^-)$$

Although only one point is shown for the broad "pH" region of the water rate, numerous experiments in unbuffered solution gave the same rate, so that one may reasonably expect that the profile is smooth in this region. The linearity of the rate in acid and base is shown in the semilog plots of Figure 4.

The effect of water on the reaction rate is shown in Figure 5. Although the other experiments here reported were conducted in aqueous DME, these experiments were carried out in aqueous dioxane, for which Winstein–Grunwald Y values have been determined.[14] The slope of the plot of log k_{obsd} against Y is 0.3.

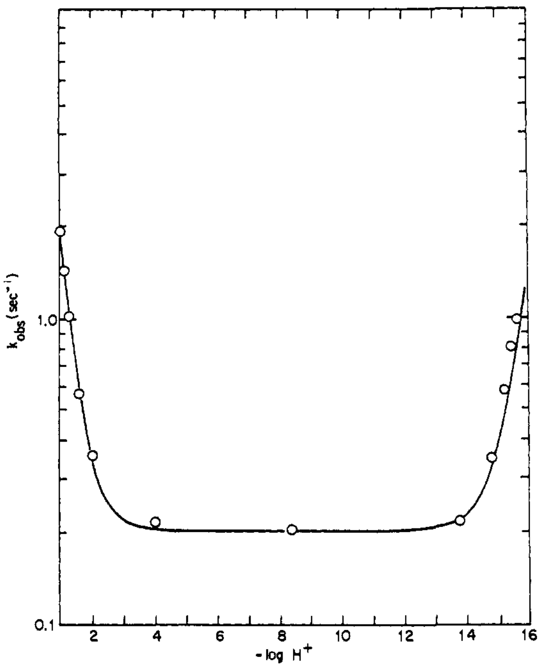

Figure 3. pH-rate profile for the hydrolysis of pentaphenoxyphosphorane in 75% dimethoxyethane–25% water at 25°.

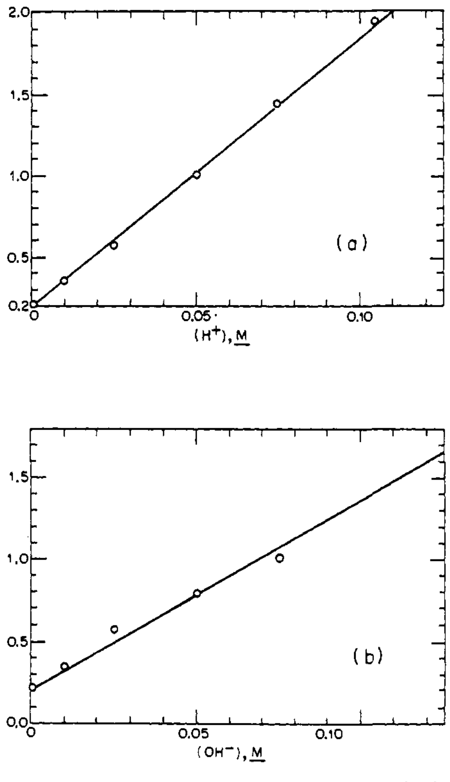

Figure 4. (a) Plot of the observed rate constant for the hydrolysis of pentaphenoxyphosphorane at 25° in 75% dimethoxymethane–25% water, plotted against the concentration of added hydrogen ion (ionic strength, 0.10). (b) Plot of the observed rate constant for the hydrolysis of pentaphenoxyphosphorane at 25° in 75% dimethoxyethane–25% water, plotted against the concentration of added base (ionic strength, 0.10).

The addition of phenol (up to four times the concentration of the phosphorane) did not change the rate within experimental error. The hydrolysis proceeds at the same rate in the absence of salt as in the presence of 0.1 M NaCl. Individual rate experiments show accurate first-order plots. Furthermore, the rate constant for the hydrolysis of penta-p-cresyloxyphosphor-

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(13) E. M. Woolley, D. G. Hurkot, and L. G. Helper, *J. Phys. Chem.*, 74, 3908 (1970).

(14) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 78, 2770 (1956).

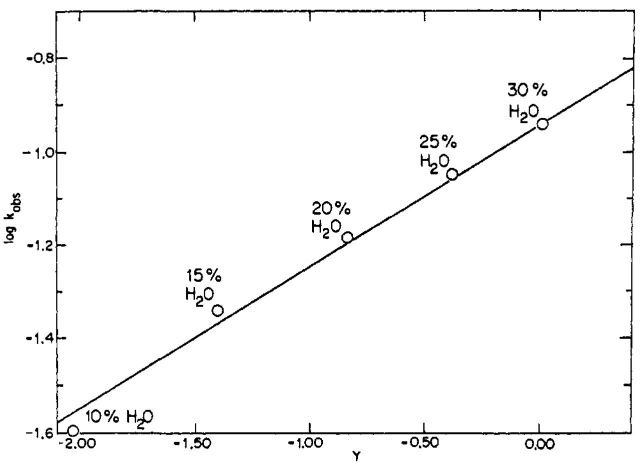

Figure 5. Plot of the observed rate constant for the hydrolysis of pentaphenoxyphosphorane at 25° in aquoeus dioxane plotted against the *Y* value for the solvent.

ane determined with 1×10^{-3} *M* phosphorane (in a 2-mm cell in the Cary spectrophotometer) was found to be 2.00×10^{-2} sec^{-1}; this is essentially identical with the rate constant of 1.97×10^{-2} determined with one-fifth (*i.e.*, 2.0×10^{-4} *M*) the concentration of phosphorane.

The effect of structure on the rates of hydrolysis is shown in Table II.

Table II. Rates of Hydrolysis of Pentaaryloxyphosphoranes at 25° in 25% Aqueous DME

	PPP[a]	P-*o*-MPP	P-*p*-MPP	P-*o*-CPP	P-*p*-CPP
k_w, sec^{-1}	0.202	1.1×10^{-5}	0.0197	0.106	390
k_{H^+}, M^{-1} sec^{-1}	16.4	1.3	79		
k_{OH^-}, M^{-1} sec^{-1}	11.4	7.5×10^{-4}	3.4		

[a] Abbreviations: PPP = pentaphenoxyphosphorane; P-*o*-MPP = penta-*o*-methylphenoxyphosphorane; P-*p*-MPP = penta-*p*-methylphenoxyphosphorane; P-*o*-CPP = penta-*o*-chlorophenoxyphosphorane; P-*p*-CPP = penta-*p*-chlorophenoxyphosphorane.

Discussion

Several features of the kinetics make an ionization mechanism unlikely, at least for the water reaction and the hydroxide ion reaction, and argue for a hexacoordinated intermediate or transition state; nothing in the present data will distinguish between these two latter possibilities. The chemistry of the reaction with water, and those catalyzed by base and by acid, will be considered in turn.

First and foremost, the water reaction is subject to a strong steric effect. The inductive effect of the methyl group in penta-*p*-cresoxyphosphorane decreases the rate of hydrolysis about tenfold. The penta-*o*-cresoxyphosphorane, however, hydrolyzes only 10^{-4} times as fast as the pentaphenoxy derivative, and only 10^{-3} times as fast as its para analog. A similar effect is noted with the chloro-substituted compounds, where the penta-*p*-chlorophenoxyphosphorane hydrolyzes nearly 2000 times as fast as the unsubstituted compound, whereas the corresponding *o*-chloro analog actually hydrolyzes less rapidly than does pentaphenoxyphosphorane. Such a steric effect would be unexpected if the reaction proceeded by rate-limiting ionization, where the coordination number of the phosphorus atom in the transition state would be intermediate between four and five. In fact, the rates of ionization of analogous compounds (methyltetraphenoxyphosphorane and methyltetra-*o*-cresoxyphosphorane) have been measured,[15] and are not greatly different. Further, the hydrolytic reaction is unlikely to proceed by reversible ionization followed by rate-limiting attack of water or of hydroxide ion, since here too the direction of the large steric effect would be unexpected. On the other hand, a steric effect is reasonable for a reaction with octahedral geometry about phosphorus in the transition state; the phenyl groups in such a transition state would be more crowded than in the starting material.

Several other features of the reaction reinforce this conclusion. The reaction shows an *m* value, in a Grunwald–Winstein[14] plot, of only 0.3; such a low value would be highly unusual for an ionization process. The inductive effects are consistent with a displacement mechanism. The *p*-methyl group retards and the *p*-chloro group accelerates hydrolysis. Although three points are too few to establish a reliable Hammett ρ value, the order of magnitude of the polar effects can be indicated by noting that the data would lead to a ρ value of 10–12, corresponding to a ρ value of 2–2.4 for each of the five para substituents, acting additively. A displacement reaction should exhibit these inductive effects, whereas the magnitude, and even the sign, of the inductive effects of polar substituents on rate-limiting ionization are uncertain. Electron-withdrawing substituents would stablize the anion but destabilize the cation formed in an ionization process. Since these opposing effects of polar substituents would tend to cancel, a large value of ρ would not be anticipated for ionization.[16] The water reaction shows a solvent deuterium isotope effect, k_{H_2O}/k_{D_2O}, of 3; this value would be unexpected for an ionization,[17] or a displacement reaction by water; the large value suggests that a proton is actually removed in the rate-limiting step. Further investigation of this suggestion (*e.g.*, measurements of possible buffer catalysis) is needed. A satisfactory process would be possible for a displacement or for a reaction leading to an octahedral, hexacoordinated intermediate. The acid-catalyzed hydrolysis shows a low solvent isotope effect (near unity); this result is typical of reactions where a protonation equilibrium with a large inverse isotope effect precedes a rate process with a comparable normal effect, and so is consistent with the mechanistic picture here advanced.

The solvolysis of pentaphenoxyphosphorane is insensitive to the presence or absence of neutral salt, with the same rate in 25% aqueous DME as in solutions in that solvent containing 0.4 *M* KCl. The absence of a salt effect is consistent with a displacement-type mechanism, whereas a strong salt effect would be expected for an ionization reaction, whether or not the ionization were rate limiting. It must be noted, however, that the hydrolysis of penta-*o*-cresoxyphosphorane (in marked contrast to that of pentaphenoxyphosphorane) is

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[15] D. Phillips, Ph.D. Thesis, Harvard University, 1972; I. Szele, unpublished.

[16] E. Anderson and T. H. Fife, *J. Amer. Chem. Soc.*, 93, 1701 (1971).

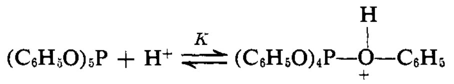
[17] (a) K. Wiberg, *Chem. Rev.*, 55, 713 (1955); (b) R. L. Schowen, *Progr. Phys. Org. Chem.*, 9, 275 (1972).

strongly catalyzed by chloride ion. Although this catalysis has not yet been investigated in detail, it implies some sort of intervention of ions. Perhaps when solvolysis through a hexacoordinated intermediate has been slowed by steric effects, an alternative pathway through ions or ion pairs may become dominant. Possibly the two major mechanisms are nearly balanced, so that changes in structure or experimental conditions can alter the rate-limiting step in the overall process.

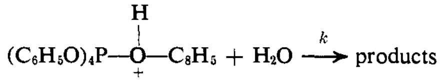
The reactions catalyzed by hydroxide ion show the same large steric effects as those with water. Here again an ionization mechanism appears unreasonable. In order to accommodate a reaction that is first order in hydroxide ion within the framework of an ionization mechanism, it would be necessary to postulate rapid and reversible ionization followed by rate-limiting reaction with hydroxide ion. In other words, phenoxide ions, formed in low concentration in the ionization process, would have to compete successfully with higher concentrations of the more nucleophilic hydroxide ions; this alternative is plainly unreasonable. A mechanism that postulates fast and irreversible ionization, followed by rate-limiting hydrolysis of the phosphonium cation with water or hydroxide ion, must also be discarded, since such a mechanism would rapidly produce a burst of phenoxide ion or phenol, and no such burst is observed in the uv spectra.

Finally, one must consider whether the data could or must be accommodated by a mechanism that involves ion pairs.[18] Although ion-pair phenomena are most important in poorly ionizing solvents such as acetic acid, they cannot be ignored even in solvents with as much water as that here used.[19] Displacement by water on a tight ion pair could produce a crowded transition state of octahedral geometry, in a process that could not easily be distinguished from a direct displacement, or formation of a hexacoordinated intermediate.

The acid-catalyzed reaction presumably proceeds by protonation of the phosphorane, followed by rate-limiting displacement of phenol by water, where again the questions concerning intermediates *vs.* transition states remain unresolved.



$$(C_6H_5O)_5P + H^+ \overset{K}{\rightleftharpoons} (C_6H_5O)_4P\text{—}\overset{\overset{\displaystyle H}{|}}{\underset{+}{O}}\text{—}C_6H_5$$



$$(C_6H_5O)_4P\text{—}\overset{\overset{\displaystyle H}{|}}{\underset{+}{O}}\text{—}C_8H_5 + H_2O \xrightarrow{k} \text{products}$$

This mechanism is in accord with the substituent effects (reversed from those in water or alkali), since the effects of substituents on the ionization step will be dominant. It is in accord with the low solvent deuterium isotope effect, as explained above. Further, although the steric effects for the acid-catalyzed reaction are much smaller than those for the water reaction, or with alkali, they nevertheless at least suggest a crowded transition state, and therefore reaction by way of hexacoordinated species.

Further investigations will undoubtedly circumscribe the area in which the mechanism here adduced may be applied. Gillespie, *et al.*,[20] have ascribed the hydrolysis of methyl ethylene phosphate in strong alkali (the part of the process that is second order in hydroxide ion) to reaction through a hexacoordinated intermediate, and the present work (like previous investigations on hexacovalent phosphorus compounds) enhances that possibility. Nevertheless, specific evidence for hexacovalent intermediates in that example has not yet been advanced.[21]

The hydrolysis of these phosphoranes in 75% aqueous dimethoxyethane contrasts sharply with that of ortho esters, where the reaction has been shown to proceed by an ionization mechanism. The hydrolysis of ortho esters shows a strong positive salt effect[22] (whereas that of the phosphoranes shows none) and a substituent effect that can be and has been interpreted as arising at least in part from steric acceleration caused by decreased crowding in the transition state[22] (in marked contrast to steric retardation in the hydrolysis of the phosphoranes). Further, the inductive effects, if not exactly comparable, are in the opposite direction[23] to those here noted. Of course, phosphorus differs from carbon, among other ways, in that the valence shell of phosphorus is easily expanded, whereas that of carbon is not.

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(18) S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, No. 19, 109 (1965).

(19) R. A. Sneen, *Accounts Chem. Res.*, **6**, 41 (1973).

(20) P. Gillespie. F. Ramirez, I. Ugi, and D. Marquarding, *Angew. Chem., Int. Ed. Engl.*, **12**, 109 (1973).

(21) *Cf.* ref 5, footnote 28.

(22) C. A. Bunton and J. D. Reinheimer, *J. Phys. Chem.*, **74**, 4457 (1970).

(23) H. G. Bull, K. Koehler, T. C. Fletcher, J. J. Ortiz, and E. H. Cordes, *J. Amer. Chem. Soc.*, **93**, 3002 (1971).