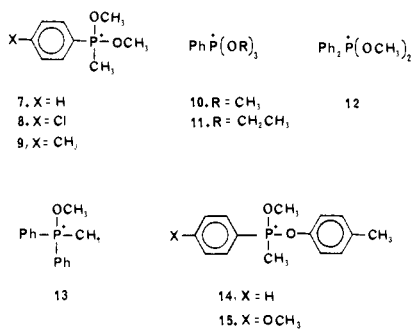


phosphonium ion is an intermediate in this reaction, and our studies have revealed quite pronounced differences in the hydrolytic lability of cyclic and acyclic systems, paralleling those observed in the hydrolysis of cyclic and acyclic phosphate esters.¹ The cyclic phosphonium ion **6**, for example, is not observed during the hydrolysis of **5** and was estimated to have a half-life in water of less than 1 ms.¹⁰ On the other hand, the acyclic ions $\text{PhP}^+(\text{OR})_3$ derived from the phosphoranes $\text{PhP}(\text{OR})_4$ have half-lives of the order of minutes or even hours.¹⁵

In order to obtain a more thorough understanding of phosphonium ion chemistry, we have carried out a study of the hydrolysis as a function of acidity, salt concentration, and buffer concentration of a series of alkoxyphosphonium ions **7–13** and two alkoxyaryloxyphosphonium ions **14** and **15**. These cations



are all of sufficient stability to permit their kinetic study in wholly aqueous solutions. Perhaps the most notable feature is a very pronounced catalysis of the hydrolysis by added buffers. A comparison is also carried out with the hydrolysis or hydration of oxycarbonium ions and other stabilized carbocations.^{16–20}

Experimental Section

Materials. Methyl methylarylphosphinates (aryl = phenyl, 4-chlorophenyl, 4-methylphenyl) were prepared as described by Edwards and co-workers.⁵ (Methoxy-¹⁸O)methyl methylphenylphosphinate containing 11.3% excess ¹⁸O was prepared⁵ from the phosphinic acid chloride²³ and [¹⁸O]-methanol.²⁴ Methyl diphenylphosphinate, dimethyl phenylphosphonate, and diethyl phenylphosphonate were prepared by treatment of diphenylphosphinic acid chloride (Aldrich) and phenylphosphonic acid chloride (Aldrich) with the corresponding alcohol, following a published procedure.²⁵ 4-Methoxyphenyl methylarylphosphinates with aryl = phenyl and 4-methylphenyl were prepared in a similar manner by the reaction of the phenol and acid chloride. Tetraethoxyphenylphosphorane was prepared by using the sulfenate ester route of Denney and co-workers,²⁶ reacting ethyl phenylsulfenate with diethyl phenylphosphonate.

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(18) McClelland, R. A.; Ahmad, M. *J. Am. Chem. Soc.* **1978**, *100*, 7031–7036.

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(24) Sawyer, C. B. *J. Org. Chem.* **1972**, *37*, 4225–4226.

(25) Edmunson, R. S.; Wrigley, J. O. L. *Tetrahedron* **1967**, *23*, 283–290.

(26) Chang, L. L.; Denney, D. B.; Denney, D. Z.; Kazior, R. L. *J. Am. Chem. Soc.* **1977**, *99*, 2293–2297.

Phosphonium ions **7–10**, **12**, and **14** were prepared by dissolving the appropriate phosphinate or phosphonate ester in dry CH_2Cl_2 (distilled from concentrated H_2SO_4) to give a solution 0.1–1.0 molar in concentration. Methyl trifluoromethanesulfonate (MeOTf (Aldrich)) was added and the solution allowed to stand at ambient temperature. The progress of the methylation was monitored by recording ¹H NMR and ³¹P NMR spectra of the solution.²⁷ As an example, methyl methylphenylphosphinate exhibits a ¹H NMR spectrum with its P-methyl doublet at 2.02 ppm and its O-methyl doublet at 3.80 ppm. Addition of MeOTf results in a decrease in intensity of these peaks, with new doublets now in a 1:2 ratio appearing at 2.46 and 4.16 ppm. A corresponding change is seen in the ³¹P NMR with the phosphinate ester signal at 29.4 ppm giving way to the phosphonium ion signal at 78.4 ppm. Lewis and Colle²⁸ have reported ³¹P chemical shift of 78.5 ppm for this ion. The reactions achieve their equilibrium position within a day; as reported by Lewis and Colle²⁸ the methylations do not proceed completely to the phosphonium ion. Approximate values of the equilibrium constant for $\text{X}_3\text{P}=\text{O} + \text{MeOTf} \rightarrow \text{X}_3\text{P}^+-\text{OMe}\cdot\text{OTf}^-$ were determined from relative NMR peak intensities and are 5 for the cations **7**, **8**, **9**, and **12**, 1 for the cation **10**, and 0.5 for the cations **14** and **15**. In the last three cases an excess, sometimes as much as 10-fold, of MeOTf was employed in order to achieve an excess of phosphonium ion in solution. Phosphonium ions **7** and **12** were also prepared by reacting in CH_2Cl_2 the phosphinate ester and an equivalent amount of trimethyloxonium tetrafluoroborate. In this case the phosphonium ion as its BF_4^- salt could be precipitated by the addition of excess ether (distilled from sodium). These salts, however, proved highly hygroscopic and tended to turn to an oil even on standing under strictly anhydrous conditions. The phosphonium ion **13** was prepared by the P-methylation in CH_2Cl_2 of methyl diphenylphosphinite (Aldrich) with MeOTf as described by Colle and Lewis.²⁹ The phosphonium ion **11** was prepared in two ways, by ethylation of diethyl phenylphosphonate with triethyloxonium tetrafluoroborate and by the addition of tetraethoxyphenylphosphorane directly to aqueous solutions. This phosphorane produces the ion extremely rapidly when added to water.¹⁵

Kinetics. Instruments employed for kinetic studies were Unicam sp 1800 and Cary 2390 spectrometers and a Durrum Gibson stopped-flow spectrometer. Conventional UV kinetic studies were carried out by injecting 1–3 μL of the CH_2Cl_2 solution containing the phosphonium ion or phosphorane directly into the thermostated UV cuvette containing 2–3 mL of aqueous solution. Final concentrations of phosphonium ion were of the order $5\text{--}10 \times 10^{-4}$ molar. The wavelengths chosen for kinetic studies were in the range 275–280 nm where a significant decrease in absorbance accompanies hydrolysis (see Results and Discussion). First-order rate constants were determined as the slopes of plots of $\ln(A - A_\infty)$ vs. time. In those experiments conducted with cations with the CF_3SO_3^- counterion and with **11** when generated from the phosphorane, excellent linearity over 4–5 half-lives was observed and excellent reproducibility ($\pm 2\%$) in duplicate runs was obtained. Considerable problems were, however, encountered when BF_4^- was employed as the counterion, both with respect to the linearity of individual runs and to the reproducibility. The source of these problems could not be discovered although we did note that the addition of NaBF_4 markedly accelerates the hydrolysis. In any event kinetic experiments using the BF_4^- counterion were abandoned. As described in the materials section an equilibrium mixture of phosphonium ion, ester, and MeOTf was usually present in the CH_2Cl_2 solutions. Kinetic experiments were conducted with the cation **10** prepared with differing relative amounts of the alkylating agent (1:1, 4:1, and 20:1 with respect to ester). No change outside of experimental error was observed in the rate constant, showing that the presence of unreacted ester or MeOTf does not affect the kinetics. The latter species is hydrolyzed as well,³⁰ but since there is no chromophore involved the kinetic studies in question are not affected (providing sufficient buffer is present to neutralize the acid which is formed from the MeOTf hydrolysis). Kinetic studies in the more basic solutions were carried out on the stopped-flow spectrophotometer by adding the phosphonium ion to 0.002 M HCl solution and mixing this solution on the stopped-flow apparatus with the appropriate basic solution.

Products. Products of the hydrolysis of the cation **7** were determined by dissolving the isolated BF_4^- salt in D_2O to give solutions of about 1 molar and recording directly the ¹H NMR spectral changes. The position of bond cleavage in the hydrolysis of this cation was determined by adding the isolated BF_4^- salt prepared by methylating the methoxy-¹⁸O phosphinate with $\text{Me}_2\text{O}^+\cdot\text{BF}_4^-$ to water and to an 0.2 molar acetate

(27) The peak in the ¹H NMR due to the CH_2Cl_2 solvent, a singlet near 5.3 ppm, does not interfere.

(28) Lewis, E. S.; Colle, K. S. *J. Org. Chem.* **1981**, *46*, 4369–4372.

(29) Colle, K. S.; Lewis, E. S. *J. Org. Chem.* **1978**, *43*, 571–574.

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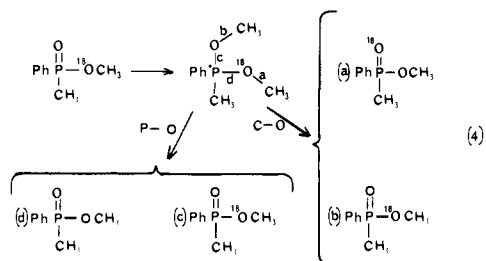
buffer. After a time corresponding to 10 half-lives of hydrolysis, the phosphinate ester was isolated by extraction with CH_2Cl_2 and analyzed directly on a mass spectrometer by measuring the ratio 172:170 corresponding to the molecular ions. The procedure employed here is the same as that used previously,^{31,32} and the excess ^{18}O present in the ester was calculated by using the formula $99.8(R - R_0)/(1.002 + R - R_0)$ where R is the 172:170 ratio of the sample in question and R_0 is the same ratio in a sample of unlabeled material. This equation corrects peak intensities for natural isotopic variation throughout the molecule including that associated with oxygen (0.2% natural abundance).

Products of the hydrolysis of the cation **15** were determined as follows. A CH_2Cl_2 solution of the phosphonium ion was prepared as previously described by methylation of the *p*-methoxyphenyl ester with a 20-fold excess of MeOTf. This solution contains 90% phosphonium ion and 10% unreacted ester. With a mechanical stirrer this solution was shaken with the appropriate aqueous solutions. After a time corresponding to 10–20 half-lives of hydrolysis the CH_2Cl_2 was separated and dried (MgSO_4) and the CH_2Cl_2 removed on a rotary evaporator. The ^1H NMR of the remaining material was recorded in CDCl_3 , the ratio of methyl methyl(4-methylphenyl)phosphinate and 4-methoxyphenyl methyl(4-methylphenyl)phosphinate being determined by integration of the P–Me doublets near 2 ppm. Three aqueous solutions were employed, 35% H_2SO_4 , 0.01 M HCl, and 0.2 M acetate buffer of pH 4.5, and in each case the ratio methyl ester:*p*-methoxyphenyl ester was 10:1.

Results

Products. Products of the hydrolysis of the phosphonium ion **7** were determined by monitoring the course of the reaction in an NMR spectrophotometer. Hydrolysis in both D_2O alone and in a concentrated acetate buffer proceeds cleanly to produce methyl methylphenylphosphinate and 1 equiv of methanol. UV spectral changes with the other alkoxyphosphonium ions are very similar to that observed with **7** (see later). We assume that similar products arise with these, namely the alcohol plus phosphoryl compound – a phosphonate ester from **10** and **11**, a phosphinate ester from **7**, **8**, **9**, and **12**, and a phosphine oxide from **13**.

The question of the position of the bond cleavage^{2,33} was also approached by hydrolyzing an ^{18}O -labeled version of the cation **7** prepared by methylating a methoxy-labeled ester. The resulting cation has two methoxy groups, so that four hydrolyses can occur,



two P–O cleavage reactions and two C–O cleavage reactions. As shown in eq 4, C–O cleavage must produce a phosphinate which retains the label. P–O cleavage on the other hand results in labeled ester and unlabeled ester in equal amounts (ignoring isotope effects), so that overall 50% of the original label would be lost. The starting phosphinate ester contained $11.8 \pm 0.05\%$ excess ^{18}O (average of four measurements). Hydrolysis of the phosphonium ion in water alone results in a phosphinate with $6.7 \pm 0.1\%$ excess ^{18}O (average of two experiments), implying that the hydrolysis occurs with $87 \pm 2\%$ P–O cleavage. This result is interesting in that the acid-catalyzed hydrolysis of the phosphinate ester itself occurs with 91% P–O cleavage.³³ The parallelism³⁴ of the cation and ester results suggests that the phosphonium ion does indeed provide a reasonable model for the protonated ester.

The labeled cation was also hydrolyzed in 0.2 M acetate, pH 4.6, a solution where the kinetics show that an acetate-catalyzed hydrolysis is the dominant reaction. In this experiment the ester

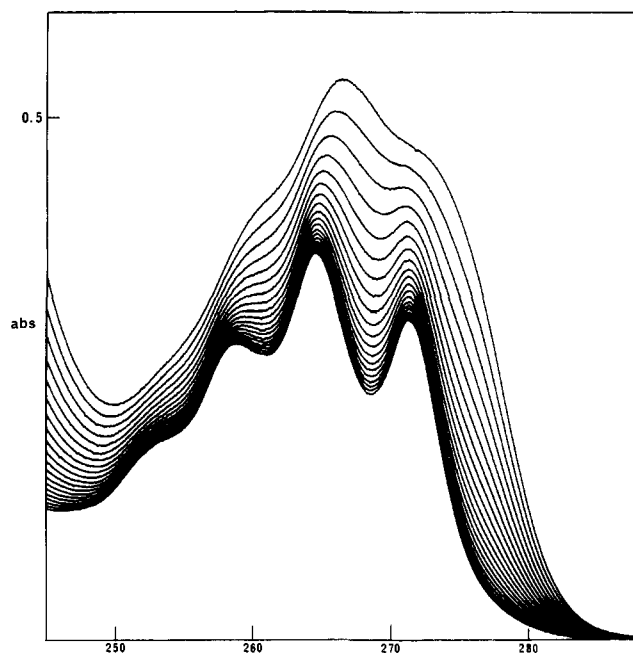


Figure 1. UV spectral changes occurring during the hydrolysis of the phenylmethyldimethoxyphosphonium ion (**7**) in 0.01 M HCl. Spectra were measured for solutions containing 5×10^{-4} molar cation initially. The time interval between each spectra is 10 min.

product was found to contain $5.5 \pm 0.2\%$ excess ^{18}O (average of two experiments), implying, within experimental error, only P–O cleavage. This result is also consistent with the observation of methanol as the product, and not methyl acetate in this solution.

In general we conclude that similar patterns occur for the other catalysts and with the other phosphonium ions. The water reaction involves a mixture of P–O and C–O bond cleavages with a significant if not predominant amount of the former. The buffer-catalyzed hydrolyses occur only with P–O cleavage. The similarity in the Brønsted plots for each of the phosphonium ions (see later) is the principal argument that this common mechanistic behavior does exist. It can also be noted that several studies have been conducted with hydroxide as the nucleophile and only P–O cleavage found.⁶

With the phosphonium ions **14** and **15** hydrolysis can occur in two ways, producing an aryl ester and methanol or a methyl ester and *p*-methoxyphenol. Products were determined from the phosphonium ion **15** in three solutions—35% H_2SO_4 , 0.01 M HCl, and an acetate buffer of pH 4.6. The method of preparation of this phosphonium ion involves methylation of the aryl ester. Since these methylations do not proceed to completion (see Experimental Section), unreacted ester is present and thus appears in the mixture after hydrolysis. A mixture of 90% methyl ester and 10% aryl ester is observed after hydrolysis in each solution. The phosphonium ion solution, however, contained 10% aryl ester, implying that this is the source of this compound in the hydrolysis product. We conclude therefore that the cation itself hydrolyzes with loss of the phenol.

Kinetics. Figure 1 shows a typical absorbance change for the hydrolysis. The spectra of the phosphonium ions and ester products are similar, but the cations in every case are more strongly absorbing and show a slight shift to longer wavelength. Quite significant absorbance changes are therefore observed and kinetic measurements performed routinely. All of the phosphonium ions of this study are of sufficient stability in water that their hydrolysis can be conveniently studied by conventional UV spectroscopy.

The disappearance of the phosphonium ions was studied at constant pH in HCl solutions or buffer solutions. Excellent adherence to the first-order rate law was observed. Rate constants determined in HCl or by extrapolation to zero buffer concentration obeyed the simple relationship

$$k_{\text{obsd}} = k_0 + k_{\text{OH}}[\text{OH}^-] \quad (5)$$

(31) McClelland, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 3177–3181.

(32) McClelland, R. A.; Ahmad, M. *J. Am. Chem. Soc.* **1977**, *99*, 5356–5360.

(33) McClelland, R. A. *J. Chem. Soc., Chem. Commun.* **1976**, 226–227.

(34) A difference in temperature does exist—cation (25 °C), ester (69 °C)—so that an exact comparison under identical conditions is not possible.

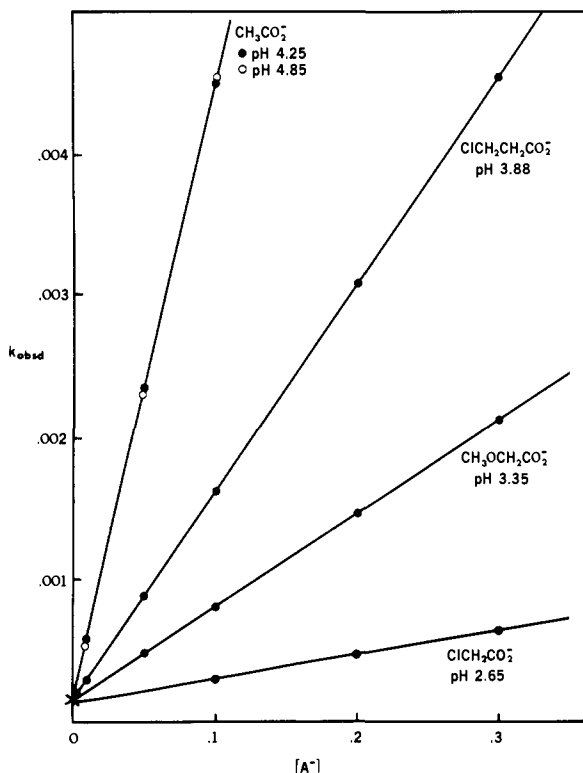


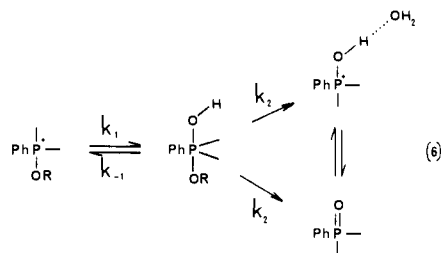
Figure 2. First-order rate constants, s^{-1} , for the hydrolysis of the phenylmethyldimethoxyphosphonium ion (7) as a function of the molar carboxylate concentration. The point X is the average of rate constants measured in HCl solutions.

showing a reaction with water and hydroxide ion. As illustrated in Figure 2, significant rate accelerations due to the base component of the buffer were also observed. Catalytic coefficients k_A were determined as the slopes of plots of k_{obsd} vs. base concentration. The constants k_0 , k_{OH} , and k_A are listed in Tables I and II.

Rate constants were also measured for selected cations in sulfuric acid solutions and sodium perchlorate solutions and are listed in Tables III and IV.

Discussion

By analogy with previous investigations^{1,6,7,9} we assume that a pentavalent hydroxyphosphorane intermediate is involved in the hydrolysis. The exception of course is that portion of the water



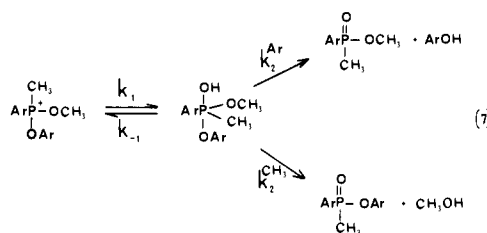
reaction which proceeds with C-O cleavage. We also feel that formation of the intermediate is rate limiting in all cases, so that the observed rate constants refer to k_1 of eq 7. The nature of the rate-limiting step is determined by the relative magnitudes of the rate constants k_{-1} and k_2 for breakdown of the intermediate. The condition for the first step to be rate limiting is that k_2 be greater than k_{-1} . As has been argued previously for the hydrolysis of simple oxocarboxylates,^{18,35} breakdown in the forward direction should be favored. In this direction the hydroxyl group remains on the phosphorus. Proton loss can be concerted with loss of the

Table I. Rate Constants for the Hydrolysis of the Phenylmethyldimethoxyphosphonium Ion (7) (25 °C, ionic strength (μ) = 0.5) and the Phenyltriethoxyphosphonium Ion (11) (25 °C, μ = 0.1)

catalyst	k ($M^{-1} s^{-1}$)	
	7	11
H ₂ O	0.00013 s^{-1}	0.00024 s^{-1}
D ₂ O	0.000038 s^{-1}	
CNCH ₂ CO ₂ ⁻	0.0011	
ClCH ₂ CO ₂ ⁻	0.0017	0.0011
CH ₃ OCH ₂ CO ₂ ⁻	0.0067	0.0034
ClCH ₂ CH ₂ CO ₂ ⁻	0.015	
CH ₃ CO ₂ ⁻	0.063	0.022
CH ₃ CO ₂ ⁻ (in D ₂ O)	0.044	
F ⁻	0.02	
(CH ₃) ₂ AsO ₂ ⁻	0.94	0.16
HPO ₄ ²⁻	2.48	0.19
N-methylmorpholine	2.32	
tris		0.14
NH ₃		0.6
CO ₃ ²⁻	36	
(CH ₃ CH ₂) ₃ N	83	5.6
OH ⁻	5.3×10^4	4.9×10^2

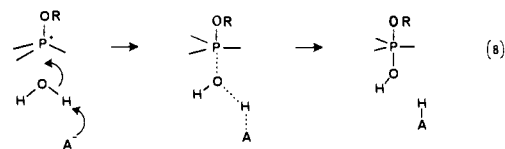
alcohol (or phenol) as in the k_2' reaction, or at the very least, this group can provide a hydrogen bond to solvent water molecules. In the latter case the forward and reverse reactions each result in phosphonium ions, but the argument is that the hydroxyphosphonium ion is more stable because of the solvent interaction. Some evidence that this is the case will be presented later.

There is some evidence pointing to rate-limiting hydration with the cations bearing both an aryloxy group and an alkoxy group.



The products imply that the intermediate undergoes breakdown in the forward direction with only loss of the aryloxy group, so that k_2^{Ar} of eq 7 is greater than $k_2^{CH_3}$. Since similar leaving groups are involved, loss of methoxy and loss of hydroxy should occur at similar rates, or in other words k_{-1} is about the same as $k_2^{CH_3}$. In consequence one can argue that k_2^{Ar} is also greater than k_{-1} so that the intermediate loses only the aryloxy group and its formation is rate limiting. The lack of dependence on acidity of the products from the mixed cation 15 is interesting in light of the mechanism suggested by Kubisen and Westheimer (see eq 2),⁹ since if this were to apply to 15, strong acids such as 35% H₂SO₄ might be expected to produce some methanol and aryl ester. One explanation is that with the mixed phosphonium ion water addition produces a pentavalent intermediate with the phenol apical.³⁶ This is well set up for loss of the phenyl group, but a pseudorotation must occur for loss of methanol.

The hydrolysis involving the base component of the buffer represents general base catalyzed addition of water to form the hydroxyphosphorane. An alternative mechanism involves nu-



cleophilic catalysis where the buffer adds to the phosphonium ion.

(35) Chiang, Y.; Kresge, A. J.; Lahti, M. O.; Weeks, D. P. *J. Am. Chem. Soc.* **1983**, *105*, 6852-6855.

(36) Brierley, J.; Trippett, S.; White, M. W. *J. Chem. Soc., Perkin Trans. I* **1977**, 273-278.

Table II. Rate Constants for the Hydrolysis of the Arylmethyldimethoxyphosphonium Ions **8** (Ar ≡ 4-ClC₆H₄) and **9** (Ar ≡ 4-CH₃C₆H₄) (25 °C, μ = 0.5), the Phenyltrimethoxyphosphonium Ion (**10**) (25 °C, μ = 0.5), the Diphenyldimethoxyphosphonium Ion (**12**) (25 °C, μ = 0.1), the Diphenylmethyldimethoxyphosphonium Ion (**13**) (25 °C, μ = 0.1), and the 4-Methoxyphenoxyphosphonium Ions **14** and **15** (25 °C, μ = 2.0)

	<i>k</i> (M ⁻¹ s ⁻¹)						
	8	9	10	12	13	14	15
H ₂ O	0.00044 s ⁻¹	0.000085 s ⁻¹	0.0048 s ⁻¹	0.00050 s ⁻¹	0.00010 s ⁻¹	0.017 s ⁻¹	0.0066 s ⁻¹
CNCH ₂ CO ₂ ⁻	0.0038	0.00076	0.027			0.085	0.030
ClCH ₂ CO ₂ ⁻				0.0023	0.0013		
CH ₃ OCH ₂ CO ₂ ⁻	0.023	0.0042	0.085	0.0095	0.0063	0.47	0.21
CH ₃ CO ₂ ⁻	0.22	0.042	0.385	0.092	0.062	4.4	0.92
(CH ₃) ₂ AsO ₂ ⁻				1.1	1.6		
CO ₃ ²⁻	91	35					
OH ⁻	8.0 × 10 ⁴	3.6 × 10 ⁴	3.1 × 10 ³	3 × 10 ⁵	2 × 10 ⁵		

Table III. First-Order Rate Constants for the Hydrolysis of Phosphonium Ions **7**, **10**, and **15** in Sulfuric Acid Solutions (25 °C)

% H ₂ SO ₄	<i>k</i> , s ⁻¹		
	7	10	15
0	29 × 10 ⁻⁵	60 × 10 ⁻⁴	54 × 10 ⁻³
5.1	22 × 10 ⁻⁵	56 × 10 ⁻⁴	52 × 10 ⁻³
10.5	16 × 10 ⁻⁵	33 × 10 ⁻⁴	41 × 10 ⁻³
15.5	13 × 10 ⁻⁵	20 × 10 ⁻⁴	31 × 10 ⁻³
20.4	8.4 × 10 ⁻⁵	12 × 10 ⁻⁴	16 × 10 ⁻³
24.2	5.0 × 10 ⁻⁵	4.6 × 10 ⁻⁴	7.9 × 10 ⁻³
29.7	1.4 × 10 ⁻⁵	3.5 × 10 ⁻⁴	4.4 × 10 ⁻³
35.2	1.4 × 10 ⁻⁵	2.0 × 10 ⁻⁴	1.4 × 10 ⁻³
40.2	0.67 × 10 ⁻⁵	0.99 × 10 ⁻⁴	
45.1		0.55 × 10 ⁻⁴	

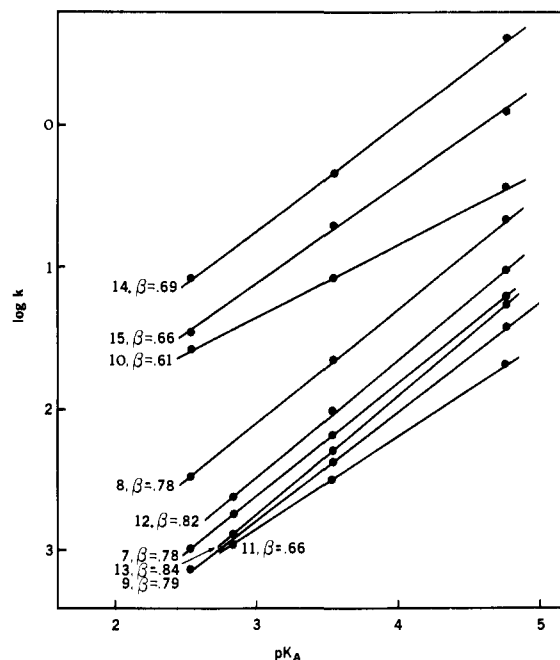
Table IV. First-Order Rate Constants for the Hydrolysis of Phosphonium Ions **7** and **15** in Sodium Perchlorate Solutions (25 °C)

[NaClO ₄]	<i>k</i> , s ⁻¹	
	7	15
0.1	20 × 10 ⁻⁵	54 × 10 ⁻³
0.5	13 × 10 ⁻⁵	
1.0	6.1 × 10 ⁻⁵	16 × 10 ⁻³
2.0	2.7 × 10 ⁻⁵	6.6 × 10 ⁻³
3.0	1.3 × 10 ⁻⁵	1.8 × 10 ⁻³
4.0	0.74 × 10 ⁻⁵	0.8 × 10 ⁻³

The pentavalent intermediate then loses an alkoxy group to give a new phosphonium ion containing the buffer which is then rapidly hydrolyzed. Such a mechanism seems unlikely since if addition were to occur one would expect the base to come off again since it is the better leaving group.

Brønsted plots for the catalysis with carboxylate bases are shown in Figure 3. Brønsted coefficients are very large ranging from 0.61 to 0.84. This implies a transition state with a large amount of proton transfer to the catalyzing base. General base catalysis of the hydration of various carbocations and oxycarbocations has been observed previously. Table V summarizes Brønsted coefficients and rate constants for the water reaction, the latter in a sense providing a measure of the stability of the cation toward hydrolysis. There appears in the carbocation data an approximate trend of increasing β with increasing cation stability. This accords with interpretations in terms of three-dimensional energy diagrams.²² The phosphonium ions show significantly larger β values even when comparing a phosphonium ion and a carbocation of similar reactivity. General base catalyzed hydrations avoid the protonated intermediate by removal of the proton as the bond to oxygen is made. Conceivably the protonated hydroxyphosphorane is of very high energy,³⁸ and the large amount of proton transfer is required to keep the transition state as far away as possible from it.

Considerable variation is seen even in the phosphonium ion β values, and as can be seen in Figure 3 reactivity is not the only factor responsible. There does appear to be a relationship involving the number of oxygen atoms attached to phosphorus, the more

**Figure 3.** Brønsted plots for carboxylate catalyzed hydrolysis of phosphonium ions.**Table V.** Brønsted Coefficients for the General Base Catalyzed Hydration of Carbocations

cation	<i>k</i> _o ^a , s ⁻¹	β	ref
(<i>p</i> -(CH ₃) ₂ NC ₆ H ₄) ₂ C ⁺ C ₆ H ₅	2 × 10 ⁻⁴	0.65	20b,d
<i>p</i> -CH ₃ C ₆ H ₄ C ⁺ (OCH ₃)N(CH ₃) ₂	4.5 × 10 ⁻⁵	0.39	37
tropylium	1.0	0.29	22
(<i>p</i> -MeOC ₆ H ₄) ₃ C ⁺	12	0.3	22
2-(<i>p</i> -methoxyphenyl)-1,3-dithiolan-2-yl	6.1 × 10 ⁻²	0.18	19
Fc ₂ C ⁺ C ₆ H ₅ ^b	2.8 × 10 ⁻⁴	0.12	22
(<i>p</i> -CH ₃ C ₆ H ₄)(CH ₃ O)C ⁺ CH ₃	5 × 10 ⁷	0.09 ^c	16
phosphonium ions	10 ⁻² - 10 ⁻⁴	0.6-0.85	this work

^aRate constant for hydrolysis by water. ^bFc = ferrocenyl. ^cEstimated by competitive trapping.

oxygen the lower β value. This is perhaps best seen with the following series of cations whose water reactivities are similar—PhP⁺(OEt)₃, β = 0.66; PhMeP(OMe)₂⁺, β = 0.78; Ph₂MeP(OMe)⁺, β = 0.84. The variation in β results in some interesting crossovers in reactivity. The three cations PhP(OMe)₃⁺, PhMeP(OMe)₂⁺, and Ph₂MeP(OMe)⁺, for example, have a reactivity order toward water of 48:1.3:1, but with hydroxide ion the order is reversed, 0.016:0.3:1. This results in the situation where a statement regarding the relative hydrolytic stability of these cations depends on the catalyst or reagent. In the above comparison PhP(OMe)₃⁺ is considerably less stable toward water but much more stable toward hydroxide ion.

A Brønsted plot covering a much wider range of catalysts is shown in Figure 4. The water point lies quite near the Brønsted line for the carboxylate ions, suggesting that the same general

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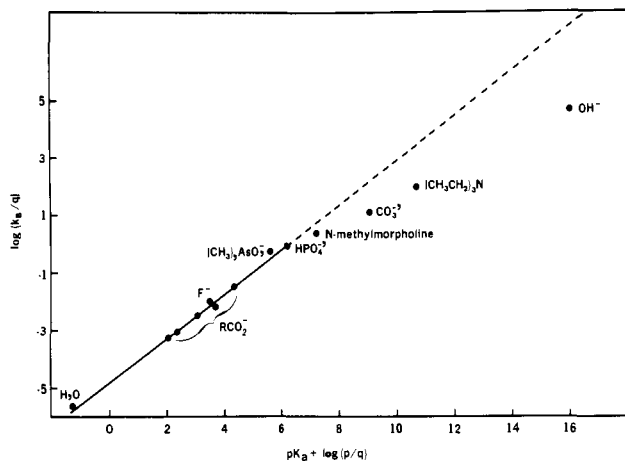


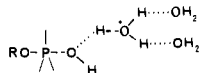
Figure 4. Brønsted plot for the phenylmethyldimethoxyphosphonium ion. The line drawn is based on the points for the carboxylate bases.

Table VI. Hammett ρ Values of the Hydrolysis of the Arylmethyldimethoxyphosphonium Ions

catalyst	ρ	catalyst	ρ
H ₂ O	1.8	CH ₃ CO ₂ ⁻	1.8
CNCH ₂ CO ₂ ⁻	1.8	CO ₃ ²⁻	1.1
CH ₃ OCH ₂ CO ₂ ⁻	1.9	OH ⁻	0.8

base mechanism is in operation here. Catalysts of different charge type, the dianion HPO₄²⁻ and the neutral base *N*-methylmorpholine, also lie near the carboxylate line. This implies that electrostatic effects are relatively unimportant, an observation which has also been made with stable carbocations.³⁹ The more basic catalysts, carbonate and triethylamine, deviate significantly from the line. This is probably related to an earlier transition state with less proton transfer for these catalysts. Evidence for this can also be seen in Table VI, which lists ρ values based on the three cations 7–9. While water and the three carboxylate catalysts produce within experimental error the same value, carbonate and hydroxide have significantly smaller values. The point for hydroxide ion also shows a negative deviation from the Brønsted line. This reagent probably acts by direct addition to the cation and not the general base route, but because of the curve in the Brønsted plot it is difficult to state this conclusively.

As observed by Kubisen and Westheimer with aryloxyphosphonium ions,⁹ the addition of acid or salt results in quite significant decreases in the reactivity of the alkoxyphosphonium ions (Tables III and IV). This can be explained in simple terms by a transition state such as **16** with significant hydronium ion character. Such a transition state could easily have four or more



16

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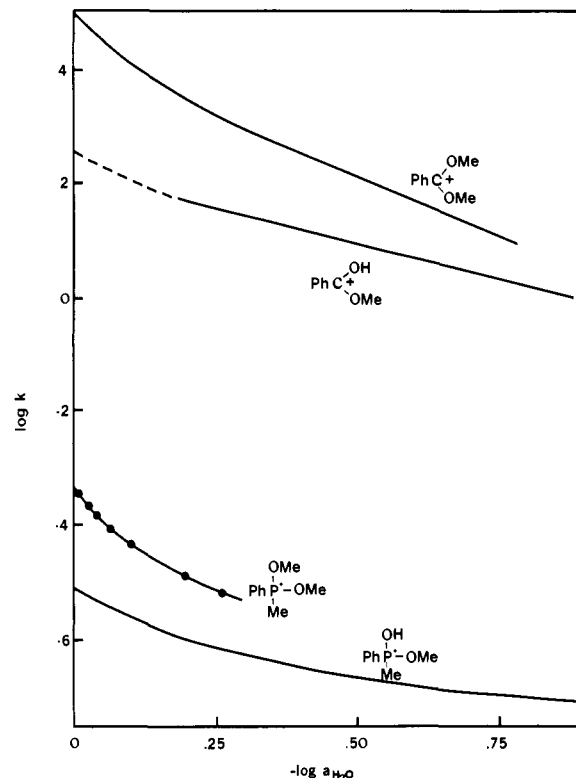


Figure 5. Rates of hydrolysis of cations in sulfuric acid solutions. The curve for the phenyldimethoxycarbocation is based on the extrapolation discussed in ref 18. The curves for the protonated esters are $k_{\text{Hyd}}/f_{\text{SH}^+}$ where k_{Hyd} = the rate constant for the ester hydrolysis and f_{SH^+} the fraction of the ester in the protonated form. Rate and protonation data for the carboxylate ester from ref 40, for the phosphinate ester from ref 5 (rate data extrapolated to 25 °C from higher temperatures).

water molecules tightly bound. In consequence decreases in water activity could raise the energy considerably and thus slow the hydrolysis.

In Figure 5 the reactivity of the alkoxyphosphonium ion **7** in sulfuric acid solutions is compared with that of an analogous hydroxyphosphonium ion (or protonated phosphinate ester). Curves for the two are similar, showing the decrease in rate as the water activity is diminished. The greater reactivity of the alkoxy cation can be explained in terms of the solvation arguments presented earlier; the hydroxyphosphonium ion is hydrogen bonded and consequently more stable towards hydrolysis. Curves for a dialkoxyphosphonium ion and its hydroxy analogue are also shown in Figure 5 and show the same difference associated with this hydrogen bonding. Interestingly the phosphonium ions are about eight orders of magnitude more stable toward hydrolysis.

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