The Hydrolysis of Methyl Methylarylphosphinates in Perchloric Acid Solution

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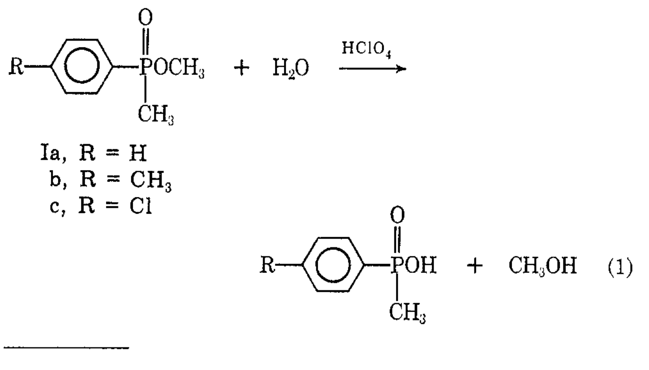
Rates of hydrolysis of methyl methylphenylphosphinate (Ia) and its p-CH_3 (Ib) and p-Cl (Ic) derivatives have been determined at several perchloric acid concentrations and at three temperatures. Ia and Ib show rate maxima at *ca.* 6–7 M $HClO_4$, but no rate maximum was observed for Ic. The apparent pK_{SH^+} value of Ia in perchloric acid is estimated to be −3.27 by nmr methods. Equilibrium protonation of these substrates is best correlated with the H_A function. Rate maxima for Ia and Ib appear at the position of substrate protonation. However, the transition states for hydrolysis of Ia and Ib as well as Ic are likely not to be significantly different from the transition states of organophosphorus esters which display rate maxima not corresponding to substrate protonation.

In recent years the kinetics of the hydrolysis of alkyl and aryl esters of phosphoric acid in mineral acid solutions have been reported.[1–11] Aryl esters containing electron-withdrawing substituents show rate maxima in moderately concentrated acidic media, where substantial substrate protonation has been shown not to occur at the position of maximum rate. This is in contrast to most aryl phosphate esters containing hydrogen or an electron-donating substituent, where no significant acid maximum obtains. Unbranched alkyl phosphates such as methyl phosphate show a smooth increase in rate with acid concentration, and are thought to proceed *via* an A2 mechanism.[6] A recent review has been presented.[11] p-Nitrophenyl diphenylphosphinate[12] and phenyl methylphosphonic acid[13] also show rate maxima in acid solution which cannot be due to substrate protonation. The latter compound is unique in that an electron-withdrawing substituent is not present in the aryl leaving group.

As part of our interest in the nucleophilic reactivity of organophosphorus substrates, we have investigated the hydrolysis of methyl methylphenylphosphinate (Ia) and its p-methyl (Ib) and p-chloro (Ic) derivatives in moderately concentrated perchloric acid solutions at several temperatures (eq 1).



Ia, R = H
b, R = CH_3
c, R = Cl

(1)

Results and Discussion

Stoichiometry.—Substrates Ia, Ib, and Ic were prepared by standard synthetic procedures (see Experimental Section). The most extensive study was carried out on the parent compound, Ia. The reaction of Ia in concentrated perchloric acid solutions gave methylphenylphosphinic acid in nearly quantitative yield (95% by isolation). Thus the stoichiometry is in accord with eq 1. No evidence for other reaction products was found. For Ib and Ic, the change in ultraviolet absorption was that expected for analogous stoichiometry.

Kinetics.—The kinetics of hydrolysis in aqueous perchloric acid solutions were followed by the change in the ultraviolet absorption of aliquots quenched in acetate buffer. The differences in extinction coefficients of reactant esters and product acids were small, but the extinction coefficients of the neutralized acids (methylphenylphosphinate anions) differed significantly from those of the esters. This difference allowed a convenient spectrophotometric analysis. All kinetic data gave linear first-order plots, usually to better than two half-lives. The rate law is given in eq 2, where substrate represents phosphorus ester and k_ψ the pseudo-first-order rate constant, which is dependent on perchloric acid concentration. Rates of hydrolysis of each substrate were determined at three temperatures over a range of perchloric acid concentrations. Data for Ia, Ib, and Ic are given in Table I.

$$\frac{-\mathrm{d[substrate]}}{\mathrm{d}t} = k_\psi[\mathrm{substrate}] \qquad (2)$$

The dependence of rate on perchloric acid concentration at *ca.* 95° is shown in Figure 1 for the three substrates. For Ia and Ib, the value of k_ψ first increases and then decreases with increasing acid concentration. A rate maximum is observed at *ca.* 6–7 M $HClO_4$. However, *the data for Ic do not show a rate maximum*, but rather a monotonic dependence of rate on acid concentration. For Ia and Ib, data at other temperatures show maxima much like those in Figure 1, but for Ic the data at other temperatures do not extend to concentrations above 6 M where a maximum might occur.

For Ia, it is evident (Table I and Figure 1) that, up to 5.5 M $HClO_4$ at 95.1°, the data conform to the rate law

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(1) C. A. Bunton, D. R. Llewellyn, K. G. Oldham, and C. A. Vernon, *J. Chem. Soc.*, 3574 (1958).

(2) C. A. Bunton, M. M. Mhala, K. G. Oldham, and C. A. Vernon, *ibid.*, 3293 (1964).

(3) A. Lapidot, D. Samuel, and M. Weiss-Broady, *ibid.*, 637 (1964).

(4) P. W. C. Barnard, C. A. Bunton, D. Kellerman, M. M. Mhala, B. Silver, C. A. Vernon, and V. A. Welch, *J. Chem. Soc. B*, 227 (1966).

(5) C. A. Bunton, D. Kellerman, K. G. Oldham, and C. A. Vernon, *ibid.*, 292 (1966).

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(10) C. A. Bunton and S. J. Farber, *ibid.*, **34**, 767, 3396 (1969).

(11) C. A. Bunton, *Accounts Chem. Res.*, **3**, 257 (1970).

(12) P. Haake and G. Hurst, *J. Amer. Chem. Soc.*, **88**, 2544 (1966).

(13) E. J. Behrman, M. J. Biallas, H. J. Brass, J. O. Edwards, and M. Isaks, *J. Org. Chem.*, **35**, 3063 (1970).

TABLE I

HYDROLYSIS OF METHYL METHYLPHENYLPHOSPHINATES $CH_3(XC_6H_4)P({=}O)OCH_3$ IN AQUEOUS $HClO_4$

Temp, °C	$[HClO_4]$, M[a]	10^5k[b]	Log k − log $([SH^+]/[S]_{st})$[c]	$-H_0$ + log $[HClO_4]$[d]	Log k + H_A[e]	a_{H_2O}[d]
			X = H[f]			
67.2	1.03	0.086				
	3.08	0.270				
	4.11	0.390				
	5.59	0.556				
	7.09	0.585				
	9.13	0.468				
95.1	0.52	0.63			−5.12	0.980
	1.03	1.21	−2.00	0.34	−5.24	0.957
	2.08	2.49	−2.23	0.57	−5.48	0.897
	3.08	3.74	−2.49	0.88	−5.82	0.820
	4.11	5.30	−2.68	1.21	−5.94	0.715
	5.08	6.44	−2.92	1.63	−6.19	0.587
	5.59	7.20	−3.02	1.88	−6.30	0.518
	6.12	7.51	−3.17	2.18	−6.47	0.450
	6.61	7.40	−3.34	2.43	−6.67	0.382
	7.09	7.56	−3.50	2.70	−6.87	0.316
	8.11	7.30	−3.79	3.40	−7.30	0.194
	9.13	6.10	−4.03	4.31	−7.74	0.110
	10.13	4.58	−4.30	5.26	−8.21	
107.6	1.01	3.19				
	3.04	9.48				
	5.56	18.8				
	7.09	20.6				
	9.13	16.0				
			X = p-CH_3[g]			
67.2	1.01	0.154				
	3.04	0.257				
	5.56	0.447				
	7.09	0.504				
	9.13	0.435				
95.1	1.01	1.36	−2.17	0.31	−5.17	0.960
	3.04	3.18	−2.61	0.86	−5.79	0.824
	5.56	6.05	−3.03	1.86	−6.37	0.524
	7.09	6.55	−3.43	2.70	−6.93	0.316
	9.13	5.25	−3.97	4.31	−7.81	0.110
107.6	3.04	11.5				
	5.56	18.1				
	7.09	23.4				
	9.13	16.4				
			X = p-Cl[h]			
67.4	1.01	0.057				
	2.99	0.157				
	5.52	0.288				
94.4	1.01	1.07	−2.01	0.31	−5.27	0.960
	2.99	2.20	−2.48	0.85	−5.94	0.828
	5.52	4.83	−2.82	1.84	−6.46	0.528
	7.03	6.10	−3.15	2.66	−6.93	0.325
	9.03	8.01	−3.54	4.19	−7.58	0.117
107.9	1.01	3.97				
	2.99	7.74				
	5.52	16.2				

[a] As measured by titration with standard base. [b] Pseudo-first-order rate constants, in sec^{-1}. [c] $[S]_{st} = [SH^+] + [S]$. [d] H_0 and a_{H_2O} values were obtained by interpolation from reported data; see, *e.g.*, C. J. O'Connor, *J. Chem. Educ.*, **46**, 686 (1969). [e] H_A values, at 25.0°, in aqueous $HClO_4$ were obtained from ref 19. [f] $[Ia] = 2.00 \times 10^{-3}$ M. [g] $[Ib] = 2.00 \times 10^{-3}$ M. [h] $[Ic] = 4.00 \times 10^{-3}$ M.

given in eq 3. Further inspection shows that Ia and

$$\frac{-d[\text{substrate}]}{dt} = k_2[\text{substrate}][H^+] \qquad (3)$$

Ib obey eq 3, at the three temperatures studied, up to near the observed rate maxima. Substrate Ic obeys eq 3 under all conditions examined.

Activation parameters for the hydrolysis of Ia–c, each at several perchloric acid concentrations, are given in Table II. For each substrate the values of the activation energies and entropies are almost independent of acid concentration. Ic has a slightly more positive energy of activation and less negative entropy of activation than do Ia and Ib. The values for Ia and Ib are similar to the reported activation parameters for the acid-catalyzed hydrolyses of aryl phosphates,[4,8-11] phosphinates,[12] and phosphonates,[13] which display rate maxima.

pK_{SH^+} Measurements.—In an attempt to determine the equilibrium ionization constants for the con-

TABLE II

ACTIVATION PARAMETERS FOR THE ACID-CATALYZED HYDROLYSIS OF Ia–c

Substrate	$[HClO_4]$, M	E_a, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1} × 4
Ia	1.03	23.3	−20
	3.08	22.1	−21
	5.59	22.6	−19
	9.13	22.9	−18
Ib	3.04	24.2	−16
	7.09	22.4	−19
	9.13	22.9	−18
Ic	1.01	27.0	−10
	2.99	25.0	−14
	5.52	25.6	−11

jugate acids of Ia and Ib, their ultraviolet spectra in concentrated $HClO_4$ were determined. However, for both Ia and Ib a gradual absorbance change was observed with increasing acid concentration, making accurate pK_{SH^+} measurements difficult. It is known that the change in absorption values of esters upon protonation can be ascribed to both solvent effects and protonation.[14]

Further, the observation of variable chemical shifts for the two different methyl groups supports the interpretation,[15,16] indicating a high degree of solvation of the phosphoryl group. Toward protonation, the phosphoryl function acts in fashion similar to the carbonyl function in amides[17] and the sulfonyl function in sulfoxides.[18] These three classes of oxygenated compounds obey the H_A function better than the H_0 function.[16]

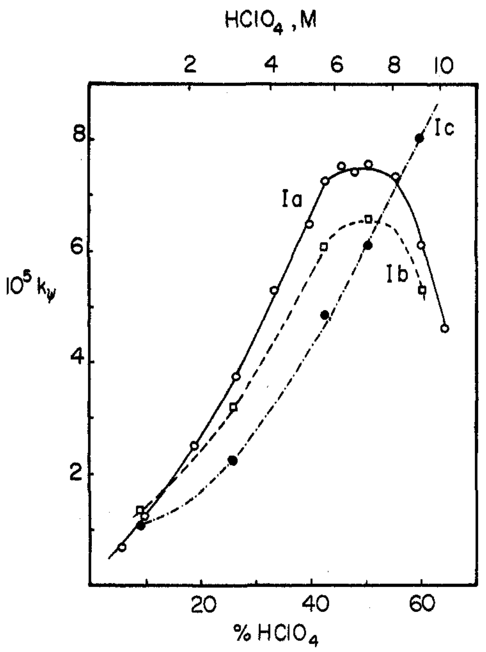

Figure 1.—Plot of $k \times 10^5$ (in sec^{-1}) against perchloric acid concentration (at top) and against per cent perchloric acid (at bottom) for the hydrolysis of Ia (○) and Ib (□) at 95.1°, and of Ic (●) at 94.4°.

TABLE III

DEPENDENCE OF CHEMICAL SHIFTS OF p-CH_3 GROUP AND OF PROTONATION RATIOS ON AQUEOUS $HClO_4$ CONCENTRATION FOR METHYL METHYLPHENYLPHOSPHINATE (TEMPERATURE 25.0°)

$[HClO_4]$, M^a	Hz^b	$[SH^+]/[S]^c$	$-H_A$	Log $([SH^+]/[S]) + H_0$	$-\{H_0 + \log [HClO_4]\}$
0.64	98.8 ($\Delta\nu_S$)				
2.04	98.7$_5$	0.0016	0.86	−3.67	0.56
2.44	98.4	0.0127	1.03	−2.96	0.68
3.04	98.3	0.0160	1.30	−3.14	0.87
4.03	98.1$_5$	0.0209	1.62	−3.49	1.19
6.00	94.3$_5$	0.163	2.32	−3.68	2.12
8.13	87.3	0.567	3.12	−4.58	3.42
8.87	79.6	1.524	3.41	−4.77	4.01
10.09	72.6$_5$	4.628	3.85	−5.42$_5$	5.10
11.70	67.1	158	4.50	−5.62	6.75
	67 ($\Delta\nu_{SH^+}$)^d				

^{a} As determined by titration. ^{b} As measured from $(CH_3)_3NH^+$ internal standard. ^{c} $[SH^+]/[S] = (\Delta\nu_S - \Delta\nu)/(\Delta\nu - \Delta\nu_{SH^+})$. ^{d} Estimated value.

The pK_{SH^+} value of Ia in perchloric acid was estimated by the nuclear magnetic resonance method.[12,13,19] Nmr measurements were made on solutions of Ia in 0.6–11.7 M $HClO_4$. Chemical shifts (ν) of the methyl group directly bonded to phosphorus[15] were measured (at 25°) relative to $(CH_3)_3NH^+$, the internal standard.[16,18,19] Data are given in Table III. Plotting these data in the form

$$\{\log([SH^+]/[S]) + H_0\} \text{ vs. } \{H_0 + \log[HClO_4]\}$$

according to the usage of Bunnett and Olsen,[20] a straight line is obtained (plot not shown), with a slope (ϕ_e value) of 0.51 ± 0.04 and an intercept of −2.76 ± 0.15 which represents the pK_{SH^+} of Ia at infinite dilution in water.[20] Since the ϕ_e value is near to that observed for amides, the H_A function[21] seems appropriate to our type of substrate. Plotting values of $\log([SH^+]/[S])$ *vs.* $-H_A$ yields a straight line with a slope of 1.01 ± 0.06 and an intercept of −3.27 ± 0.20; this is the apparent pK_{SH^+} value (*i.e.*, H_A value at half-protonation) of substrate Ia in perchloric acid. Apparent pK_{SH^+} values for Ia–c in sulfuric acid, as determined by the H_A function, from the nmr spectra of the methyl groups bound to phosphorus are −3.11, −2.94, and −3.17,[16] respectively. Therefore the apparent pK_{SH^+} values of Ia in sulfuric and perchloric acids are the same within the limits of error. We conclude that Ia–c behave as "moderately basic substrates." Also the three values vary in order of the expected electronic effect of substituent on the phenyl group.

Treatment of Kinetic Data.—Having established that all of the three organophosphorus compounds examined should behave as moderately basic substrates in the range of $HClO_4$ concentrations employed in the kinetic runs, rate data in Table I can be handled

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[14] E. M. Arnett and C. Y. Wu, *J. Amer. Chem. Soc.*, **82**, 5660 (1960).

[15] A previous investigation[16] has shown that pK_{SH^+} determinations by nmr, using methyl and methoxy resonances, yield values that can differ by as much as 0.4 pK unit.

[16] R. Curci, A. Levi, V. Lucchini, and G. Scorrano, *J. Chem. Soc., Perkin Trans. 2*, accepted for publication.

[17] (a) K. Yates, J. B. Stevens, and A. R. Katritsky, *Can. J. Chem.*, **42**, 1957 (1964); (b) K. Yates, *Accounts Chem. Res.*, **4**, 136 (1971).

[18] D. Landini, G. Moden, G. Scorrano, and F. Taddei, *J. Amer. Chem. Soc.*, **91**, 6703 (1969).

[19] P. Haake, R. D. Cook, and G. Hurst, *ibid.*, **89**, 2650 (1967).

[20] J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, **44**, 1899, 1917 (1966).

[21] (a) H_A values at 25.0° were obtained by interpolation from the data of H. Wai, Ph.D. Thesis, Toronto University; *cf.* ref 21b. (b) Acidity function values in perchloric acid were obtained from the data of K. Yates and H. Wai, *J. Amer. Chem. Soc.*, **86**, 5408 (1964). Correlations of percentage composition of perchloric acid solutions with molarity are from the data of C. J. O'Connor, *J. Chem. Educ.*, **46**, 686 (1969). All values are at 25°.

accordingly,[20] by making plots of $\{\log k_\psi - \log([SH^+]/[S])\}$ *vs.* $\{-(H_0 + \log[HClO_4])\}$. For compounds Ib and Ic, the log ([SH+]/[S]) values at various $HClO_4$ concentrations were calculated on the basis of the apparent pK'_{SH^+} values in H_2SO_4. Inspection of Figure 2 reveals that satisfactory straight lines are obtained; these give ϕ (slope) values of 0.49 ± 0.02 (r = 0.99), 0.44 ± 0.04 (r = 0.99), and 0.38 ± 0.05 (r = 0.98) for Ia, Ib, and Ic, respectively. Bunnett and Olsen[20] have pointed out that ϕ values from 0.22 to 0.56 are characteristic for reactions in which water is involved as nucleophile in the rate-determining step. Plots of $\{\log k_\psi + H_A\}$ *vs.* $\log a_{H_2O}$ (see Table II and Figure 3) show a clear deviation from linearity at relatively low $HClO_4$ concentrations; however, they are all similar in shape for the three phosphinic esters considered, and this despite the monotonic, no-maximum rate increase of Ic with $HClO_4$ concentration (Figure 3). Furthermore, discarding $\log k_\psi + H_A$ values at aqueous $HClO_4$ concentrations below 20%, good straight lines (correlation coefficient ≥ 0.99) can be drawn through the remaining points, and slopes (r values)[17b] of 2.26 ± 0.04, 2.27 ± 0.17, and 1.90 ± 0.20 can be estimated for Ia, Ib, and Ic, respectively. These values are fairly similar and indicate a strong positive water activity dependence, which is analogous for all of the three phosphorus compounds. Again, no indication of the occurrence of a change in the mechanism of hydrolysis on passing from Ia and Ib to Ic is found.

Mechanistic Implications.—In substrates Ia–c, $H_2{}^{18}O$ tracer studies have not been performed and the positions of bond cleavage, either P–O or alkyl C–O, have not been determined. The fact that substrates Ia and Ib display rate maxima in moderately concentrated perchloric acid solutions can be taken as evidence for P–O fission. The hydrolysis data of Ia and Ib are similar to that of other substrates which show rate maxima; in the latter cases exclusively P–O bond fission has been demonstrated. In addition Haake and coworkers[12,22] have observed that hydroxide attacks phosphinate esters only at the phosphorus center. One might expect P–O cleavage also to occur for acid-catalyzed hydrolyses. All of the evidence indicates attack at phosphorus, but a labeling experiment to confirm this assignment would be worthwhile.

The acid-catalyzed hydrolyses of aryl phosphates containing electron-withdrawing substituents on the leaving group show rate maxima at acid concentrations not corresponding to complete substrate protonation.[11] *p*-Nitrophenyl diphenylphosphinate[12] and phenyl methylphosphonic acid[13] show similar rate maxima. All of these reactions show characteristic features; *e.g.*, large negative entropies of activation are exhibited. Protonation and strong hydration are thought to be important in the transition state. The high degree of solvation in the transition state is evidence for mechanisms which require slow proton transfer in the rate-determining step.[10,11]

Rate maxima are observed for two (specifically Ia and Ib) of the three substrates studied here. Also the activation parameters for these two differ from those for the third (see Table II) by more than deviations due to experimental error. In part this could result from position of substrate protonation. However, we feel that the observed differences only represent slight variations in mechanistic behavior and that the mechanisms for all three hydrolyses are fundamentally similar. Also the associative character of these reactions is believed to be similar to that for many other strong-acid hydrolyses of phosphorus compounds. Another bit of evidence that the three behave in similar manner is the ultraviolet spectra. Although the spectra were not useful in our system as a means of obtaining good pK_{SH^+} values,[23] the similar spectral changes for Ia–c indicate similar interactions with the acid media.

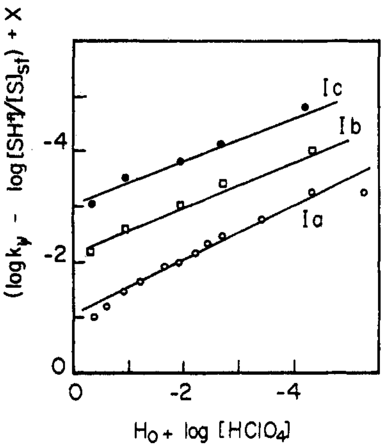

Figure 2.—Typical ϕ plots for hydrolysis of methyl methylphenylphosphinates in aqueous perchloric acid; vertical displacement values x = 1 for Ia, x = 0 for Ib, and x = −1 for Ic.

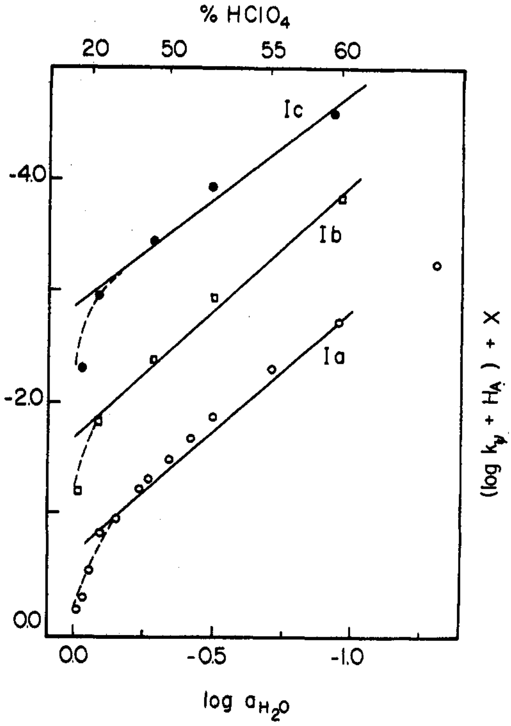

Figure 3.—Typical r plots for hydrolysis of methyl methylphenylphosphinates in aqueous perchloric acid; vertical displacement values x = 5 for Ia, x = 4 for Ib, and x = 3 for Ic.

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[22] P. Haake, R. D. Cook, W. Schwarz, and D. R. McCoy, *Tetrahedron Lett.*, 525 (1968).

[23] J. T. Edward and S. C. R. Meacock, *J. Chem. Soc.*, 2000 (1957), and references cited therein.

Points of Interest.—The ϕ values (Bunnett and Olsen) for the protonation of amides in sulfuric acid are between 0.42 and 0.55.[20] Values for Ia–c in sulfuric acid lie between 0.50 and 0.65.[16] For Ia in perchloric acid $\phi = 0.51$. Clearly for these substrates the hydration requirements of SH^+ relative to S are high.[20]

Treatment of the hydrolysis data of Ia–c by the Bunnett and Olsen method (Figure 2) for "moderately basic substrates" yields for the rate-determining step ϕ values (0.49, 0.44, 0.38) which are characteristic of reactions for which water is involved in this step.

Experimental Section

Materials and Substrates.—The general procedure used in the synthesis of methyl methylarylphosphinates was according to the method of Arbuzov and Rozimov.[24] Arylphosphonous dichlorides were allowed to react with methanol in ether in the presence of *N,N*-dimethylaniline, producing dimethyl arylphosphonites $ArP(OCH_3)_2$. These compounds were rearranged in the presence of methyl iodide to the desired esters. A modification of the Arbuzov–Rozimov procedure[25] was employed owing to the rapidity and exothermicity of the reaction. Thus roughly equal portions of dimethyl arylphosphonite esters were added to 25 50-ml flasks. Two drops of reagent grade methyl iodide were added to each of the flasks; the flasks became hot and were cooled in water. The contents of the flasks were combined and each flask was rinsed with ether, the rinsings being added to the product.

Some specifics of the preparation and properties of each substrate are as follows. Methyl methylphenylphosphinate (Ia) had bp 133–134° (10 mm), n^{25}D 1.5270 [lit.[25] bp 142° (14 mm), $n^{25.8}$D 1.5260]. *Anal.* Calcd for $C_8H_{11}PO_2$: C, 56.47; H, 6.52; P, 18.21. Found: C, 56.20; H, 6.75; N, 18.07.

For methyl methyl-*p*-methylphenylphosphinate (Ib), *p*-methylphenylphosphonous dichloride was not available and was synthesized from *p*-bromotoluene by the method of Weil, Prijs, and Erlenmeyer.[26] From the dichloride the substrate was obtained by the modified Arbuzov–Rozimov procedure, bp 148–149° (11 mm), n^{25}D 1.5190 [lit.[27] bp 151–152° (13 mm), n^{15}D 1.5280]. *Anal.* Calcd for $C_9H_{13}PO_2$: C, 58.69; H, 7.12; P, 16.82. Found: C, 58.47; H, 7.31; P, 15.94.

For methyl methyl-*p*-chlorophenylphosphinate (Ic), *p*-chlorophenylphosphonous dichloride was synthesized[26] and the substrate was prepared in the usual manner, bp 156–157° (10 mm), n^{25}D 1.5347 [lit.[28] bp 144° (5 mm), nD 1.5363]. *Anal.* Calcd for $C_8H_{10}PClO_2$: C, 46.97; H, 4.93; P, 15.14; Cl, 17.33. Found: C, 46.60; H, 5.00; P, 15.18; Cl, 16.82.

Purities of substrates were also confirmed by infrared spectra and gas chromatographic measurements. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Nmr absorbances are reported.[18]

Methylphenylphosphinic acid (MPA) was prepared by the hydrolysis of 51.6 g (0.303 mol) of Ia in 1000 ml of refluxing concentrated hydrochloric acid for 36 hr. On cooling the reaction mixture, white needles deposited from solution and were collected on a filter. The volume of the filtrate was reduced on a steam bath and more acid precipitated; 45 g of product (95%) was obtained, mp 133–133.5° (lit.[29] mp 133–134°).

For substrate syntheses the following reagents were obtained: phenylphosphonous dichloride (Technical Grade, Victor Chemical Works), methanol (reagent grade, Mallinckrodt), *N,N*-dimethylaniline (practical grade, Matheson Coleman and Bell), *p*-bromotoluene and *p*-bromochlorobenzene (White Label, Eastman Kodak), and phosphorus trichloride (reagent grade, Mallinckrodt). All other organic and inorganic reagents were of analytical or reagent grade and were used without further purification.

Equipment.—Nmr spectra were determined on a Bruker Model HFX-10 spectrometer. Infrared spectra were recorded using a Perkin-Elmer Model 137 Infracord. Ultraviolet spectra were obtained with Beckman Models DU and DK spectrometers. Gas chromatographic measurements were made on a Perkin-Elmer vapor fractometer, Model 154. Temperatures of the thermostats were checked with NBS thermometers calibrated to ±0.1°.

Spectra.—The ultraviolet spectra of Ia and MPA were determined in various aqueous systems. These spectra were similar in 6 *M* perchloric acid solutions but different in 1 *M* acetic acid–sodium acetate buffers, presumably owing to the ionization of the acid to its anionic form. Extinction coefficients were measured for Ia and MPA in a 1 *M* acetate buffer. Corrections for absorption of the buffer were made. For each compound a linear Beers Law relationship was observed. The following absorption maxima and extinction coefficients were determined: Ia, 270.6 nm (ϵ 616), 264.2 (750), and 258 (560); MPA, 270.6 nm (ϵ 217), 269.5 (300), 263 (387), 257.5 (315), and 252 (216). Compounds Ib and Ic in 1 *M* acetate buffer showed similar spectral changes on hydrolysis. For Ib maxima were at 272 nm (sharpest peak), 266, 260.5 (strongest peak), and 254.5 and for Ic at 275 nm (sharpest peak), 267 (strongest peak), and 257 . No extinction coefficients were determined.

pK_a Measurements. Nmr.—Perchloric acid solutions were prepared by dilution and titrated with standard NaOH solutions. H_0 and H_A values are from reported data.[21] Nmr spectra at 25° were recorded on a Bruker HFX-10 90-MHz instrument with trimethylamine as the internal standard.[16] Temperature was measured by a methanol standard.

For all pK_{SH^+} determinations, solutions in acid were prepared immediately prior to spectral measurement.

Kinetics.—Perchloric acid was added to substrate to form 100 ml of a 0.02 *M* master solution for Ia and Ib and 0.04 *M* for Ic. Aliquots (5 ml) of the solution were pipetted into 15-ml Pyrex vials. The vials were cooled in Dry Ice-CH_2Cl_2 and sealed. They were then placed in a thermostat, removed at various times, and stored at −20° until analyzed. The analysis procedure was as follows. A sample vial was opened and the contents were transferred to a 100-ml volumetric flask. The vial was rinsed with 1 *M* acetate buffer and this was added to the flask, which was then diluted to the mark with buffer. pH values of the resultant solutions were between 4.03 and 4.66 depending on initial $HClO_4$ concentration. The rate of hydrolysis was followed by monitoring the decrease in optical density at 270.6 nm for Ia, 272 for Ib, and 275 for Ic. All optical ddnsity measurements were corrected for buffer absorption. Experiments followed good first-order kinetics. Infinity measurements were taken at ten half-lives and their reliability was checked by the method of Guggenheim.[30,31]

Registry No.—Ia, 6389-79-3; Ib, 39013-59-7; Ic, 13114-08-4.

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