Acid-Catalyzed Hydrolysis of Diethyl α-Arylvinyl Phosphates[1]

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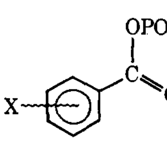
Abstract: The rates of HCl-catalyzed hydrolysis of α-arylvinyl diethyl phosphates have been correlated with Brown–Hammett σ^+ constants with $\rho = -2.1$ at 70°. The entropies of activation fall in the range -8.1 to -14.5 eu. The products from the *m*-nitro derivative were *m*-nitroacetophenone and a mixture of diethyl- and ethylphosphoric acids. These results are uniquely consistent with an $A_{SE}2$ mechanism for hydrolysis involving rate-determining protonation on carbon. The corresponding vinyl acetates under the same conditions react through both $A_{SE}2$ and $A_{AC}2$ paths. The utility of various acidity functions for correlating the data is considered.

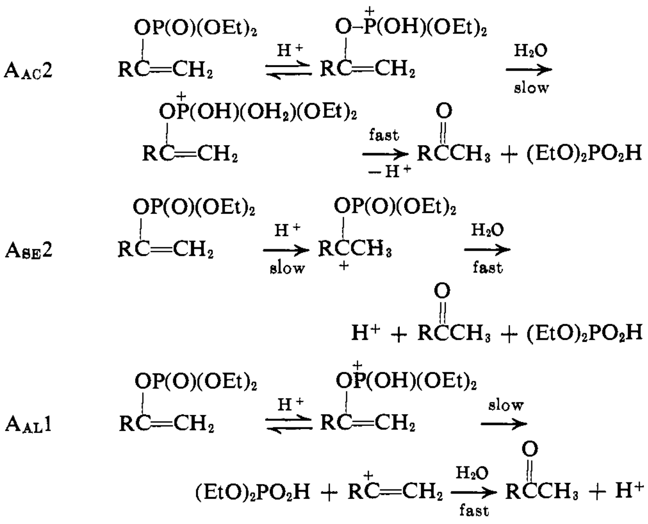
Because of their biological importance, vinyl phosphates have been the object of several recent investigations,[2,3] including studies of the hydrolysis of these compounds.[3–5] This report deals with the acid-catalyzed hydrolysis of a series of α-arylvinyl phosphates (**1**).[6,7]



1a, X = H
b, X = *p*-MeO
c, X = *p*-Me
d, X = *p*-Br
e, X = *m*-NO$_2$
f, X = *p*-NO$_2$

There are three mechanisms (Chart I) which may *a priori* be considered reasonable for these compounds. They are designated $A_{AC}2$, $A_{SE}2$, and $A_{AL}1$, according to the terminology of Ingold,[7b] including his use of the designation AC for reactions at both acyl and phosphoryl groups. The $A_{AC}2$ path is the normal mode for acid hydrolysis of carboxylate esters, and would be characterized by P–O cleavage. This reaction has also been observed for vinyl acetate esters without strongly electron donating groups on the double bond, particularly in less concentrated acid solutions.[7a]

Chart I. Possible Hydrolysis Mechanisms of Diethyl Vinyl Phosphates



The $A_{SE}2$ route[8,9] involves rate-determining proton transfer to the double bond followed by rapid hydration. This path has been proposed for the HCl-catalyzed hydrolysis of diethyl α-phenylvinyl phosphate (**1a**),[4c] and is favored for vinyl acetates with good electron donors on the double bond, particularly in very strong acids.[9]

The $A_{AL}1$ route consists of equilibrium protonation followed by slow cleavage to form a carbonium ion, and is the route followed by *tert*-butyl acetate,[7] and *tert*-butyl dihydrogen phosphate.[10] For **1** this route would give a vinyl cation.[6]

$$tert\text{-}\mathrm{BuOPO_3H_2} \overset{H^+}{\rightleftharpoons} tert\text{-}\mathrm{BuOPO_3H_3^+} \xrightarrow{\text{slow}} tert\text{-}\mathrm{Bu^+} + \mathrm{H_3PO_4}$$

Results

The desired diethyl α-arylvinyl phosphates (**1**) were prepared by Perkow reactions[3b,11] of the appropriate α-chloroacetophenones and triethyl phosphite. The compounds were all liquids subject to thermal decomposition on distillation so they were purified by chromatography. Spectral and analytical data (Tables I and II) confirmed their structure and purity.

Rates of HCl-catalyzed hydrolysis of the phosphates were followed by measuring the change in absorbance at several wavelengths using a recording ultraviolet spectrophotometer. Reactions were run at the lowest

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(1) Presented at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March–April 1971, Abstracts, No. ORGN 41. This investigation was supported by Public Health Service Research Grant No. 1 RO1 GM 16818 from the National Institute of General Medical Sciences.

(2) For leading references, see J. A. Stubbe and G. Kenyon, *Biochemistry*, **10**, 2669 (1971).

(3) (a) M. Schuler, *Chimia*, **21**, 342 (1967); (b) F. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961).

(4) (a) F. W. Lichtenthaler and F. Cramer, *Chem. Ber.*, **95**, 1971 (1962); (b) K. J. Schray and S. J. Benkovic, *J. Amer. Chem. Soc.*, **93**, 2522 (1971); (c) C. A. Bunton and L. Robinson, *ibid.*, **91**, 6072 (1969); (d) J. F. Marecek and D. L. Griffith, *ibid.*, **92**, 917 (1970).

(5) For a general account of phosphate ester hydrolysis, see C. A. Bunton, *Accounts Chem. Res.*, **3**, 257 (1970).

(6) For references to the chemistry of vinyl esters, see M. Hanack, *ibid.*, **3**, 209 (1970).

(7) For a discussion of acid-catalyzed ester hydrolysis, see: (a) K. Yates, *ibid.*, **4**, 136 (1971); (b) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, Chapter 15.

(8) J. M. Williams, Jr., and M. M. Kreevoy, *Advan. Phys. Org. Chem.*, **6**, 63 (1968).

(9) D. S. Noyce and R. M. Pollack, *J. Amer. Chem Soc.*, **91**, 119 (1969).

(10) A. Lapidot, D. Samuel, and M. Weiss-Broday, *J. Chem. Soc.*, 637 (1964).

(11) I. J. Borowitz, M. Anschel, and S. Firstenberg, *J. Org. Chem.*, **32**, 1723 (1967).

Table I. Analytical Data of Phosphates

Compd	X	Formula	Mol wt	C Calcd	C Found	H Calcd	H Found
1b	*p*-MeO	$C_{13}H_{19}O_5P$	286.27	54.54	54.35	6.69	6.72
1c	*p*-Me	$C_{13}H_{19}O_4P$	270.27	57.77	56.97	7.08	6.89
1d	*p*-Br	$C_{12}H_{16}BrO_4P$	335.14	43.01	43.19	4.81	4.71
1e	*m*-NO_2	$C_{12}H_{16}NO_6P$	301.24	47.85	47.75	5.35	5.49
1f	*p*-NO_2	$C_{12}H_{16}NO_6P$	301.24	47.85	47.91	5.35	5.55
3[a]	*p*-MeO	$C_{13}H_{18}ClO_5P$	320.69	48.69	48.35	5.66	5.78

[a] See Experimental Section.

Table II. Spectroscopic Data[a] of Phosphates, $XPhC(OPO_3Et_2){=}CH_2$

Compd	X	Nmr δ CH_3CH$_2$[c]	Nmr δ CH$_3$$CH_2$[d]	Nmr δ CH_2=	Nmr δ Aryl	Uv max, nm[b]
1a	H	1.30	4.08	5.15[g]	7.3 (m)	244 (248, 4.07)
1b	*p*-MeO[e]	1.30	4.06	5.00[g]	7.02[h]	260 (260, 4.21)
1c	*p*-Me[f]	1.32	4.09	5.10[g]	7.20[h]	250 (251, 4.15)
1d	*p*-Br	1.31	4.11	5.20[g]	7.37 (s)	255 (254, 4.22)
1e	*m*-NO_2	1.36	4.16	5.35[i]	7.7 (m)	230
1f	*p*-NO_2	1.37	4.13	5.38[j]	7.89[h]	298
3	*p*-MeO[k]	1.26	4.00	6.30[g,l]	7.17[h]	

[a] Each compound showed ir bands at 1640 ($C{=}CH_2$) and 1265 ($P{=}O$) $\pm$ 5 cm^{-1} measured with a Perkin-Elmer 337 grating spectrophotometer on liquid films. [b] Measured in 0.1–1.0 *M* HCl solutions, lit. (A. Arcoria and S. Fisichella, *Ann. Chim.* (*Rome*), **57**, 1228 (1967)) values (with log ε) in parentheses. For comparison, styrene, *p*-methoxystyrene, *p*-methylstyrene, *m*-nitrostyrene, and *p*-nitrostyrene have λ_{max} 245, 260, 252, 240, and 300 nm, respectively (log ε 4.0–4.4): J. R. Joy and M. Orchin, *J. Amer. Chem. Soc.*, **81**, 305 (1959). [c] Triplet, J_{H-H} = 7 Hz, $J_{^{31}P-H}$ = 1 Hz (fine structure). [d] Eight line multiplets (1:3:1:3:3:1:3:1), $J_{^{31}P-H}$ = 8 Hz, J_{H-H} = 7 Hz. [e] δ 3.70 (MeO). [f] δ 2.31 (*Me*Ar). [g] Doublet, $J_{^{31}P-H}$ = 2.2 Hz. [h] AA′XX′ quartets, approximate *J* = 9 Hz, and Δ (parts per million between midpoints of doublets) 0.66, 0.38, 0.47, and 0.48 for **1b**, **1c**, **1f**, and **3**, respectively. [i] Quintet, 2.5-Hz spacing. [j] Multiplet, total width, 10 Hz. [k] See Experimental Section δ 3.75 (MeO). [l] *CHCl*=C.

Table III. HCl–Catalyzed Hydrolysis of Diethyl α-Arylvinyl Phosphates (**1**), $XPhC(OPO_3Et_2){=}CH_2$

Compd	X	*T*, °C	[HCl], *M*	k_{obsd}[a]	h_0	h_R'	$h_0{}^{t}$[b]	k_2[c,d]
1b	*p*-MeO	69.8	0.00160	8.36×10^{-5}	0.0016	0.0016	0.0016	5.22×10^{-2}
		54.4	0.0200	1.92×10^{-4}	0.0200	0.0200	0.0200	9.60×10^{-3}
		41.4	0.0465	1.60×10^{-4}	0.0465	0.0465	0.0465	3.44×10^{-3}
		25.0	0.0200	1.14×10^{-5}	0.0200	0.0200	0.0200	5.70×10^{-4}
1c	*p*-Me	70.2	0.100	5.49×10^{-4}	0.1046	0.0794	0.0741	5.25×10^{-3}
		54.7	0.100	1.47×10^{-4}	0.1046	0.0794	0.0759	1.41×10^{-3}
		41.5	1.000	6.61×10^{-4}	1.585	2.45	1.32	4.17×10^{-4}
		41.5	1.135	7.86×10^{-4}	1.82	3.24	1.62	4.32×10^{-4}
		25.0	1.135	1.05×10^{-4}	1.82	3.24	1.62	5.77×10^{-5}
1a	H	70.2	0.100	1.88×10^{-4}	0.1046	0.0794	0.0741	1.80×10^{-3}
		54.7	0.100	3.17×10^{-5}	0.1046	0.0794	0.0759	3.03×10^{-4}
		41.5	0.100	8.84×10^{-6}	0.1046	0.0794	0.0794	8.45×10^{-5}
		41.5	1.000	1.55×10^{-4}	1.585	2.45	1.32	9.78×10^{-5}
		25.0	1.000	2.07×10^{-5}	1.585	2.45	1.17	1.31×10^{-5}
1d	*p*-Br	70.2	0.100	6.18×10^{-5}	0.1046	0.0794	0.0741	5.91×10^{-4}
		54.7	1.00	2.54×10^{-4}	1.585	2.45	1.45	1.60×10^{-4}
		54.2	1.00	1.89×10^{-4}	1.585	2.45	1.45	1.19×10^{-4}
		41.5	1.00	5.06×10^{-5}	1.585	2.45	1.32	3.19×10^{-5}
		25.0	1.00	9.40×10^{-6}	1.585	2.45	1.17	5.93×10^{-6}
1e	*m*-NO_2	99.0	1.00	1.20×10^{-3}	1.585	2.45	1.95	7.57×10^{-4}
		85.0	1.00	3.14×10^{-4}	1.585	2.45	1.74	1.98×10^{-4}
		69.8	1.135	7.88×10^{-5}	1.82	3.24	2.00	4.33×10^{-5}
1f	*p*-NO_2	99.0	1.00	6.50×10^{-4}	1.585	2.45	1.95	4.10×10^{-4}
		84.9	1.00	1.57×10^{-4}	1.585	2.45	1.74	9.91×10^{-5}
		69.8	1.135	4.05×10^{-5}	1.82	3.24	2.00	2.23×10^{-5}

[a] Sec^{-1}. [b] $H_0{}^{t}$, temperature correct value of acidity function, ref 15 and 16. [c] $M^{-1}\,sec^{-1}$. [d] $k_2 = k_{obsd}/h_0$.

feasible acid concentrations to minimize the deviation of the acidity function[12–17] from the pH scale. Observed pseudo-first-order rate constants (k_{obsd}) at various acid concentrations and temperatures are recorded in Table III. The log of the observed rates of the α-phenyl compound (**1a**) have been reported[4c] to be linearly related to the acidity function H_0' (equivalent to

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(12) The acidity function H_0' is an extension[13] of the H_0 scale[14] using only primary amine indicators, but at the acid concentrations used in this study these scales are identical. H_0 will be used in this report.

(13) M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, **85**, 878 (1963).

(14) (a) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957); (b) F. A. Long and M. A. Paul, *ibid.*, **57**, 935 (1957).

(15) E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, **88**, 1177 (1966).

(16) C. Rochester, "Acidity Functions," Academic Press, New York, N. Y., 1970.

(17) Values of H_0 at different temperatures measured by Gel'bshtein were taken from ref 16; see also C. D. Johnson, A. R. Katritzky, and S. A. Shapiro (*J. Amer. Chem. Soc.*, **91**, 6654 (1969)) for the temperature variation of the acidity function of sulfuric acid.

Table IV. Activation Parameters for Diethyl α-Arylvinyl Phosphates

Compd	X	$k_2(25°)^a$	$k_2(70°)^a$	ΔH^*, kcal/mol^b	ΔS^*, eu^b
1b	*p*-MeO	5.70×10^{-4}	4.76×10^{-2}	19.5	−8.1
1c	*p*-Me	5.77×10^{-5}	5.59×10^{-3}	19.5	−12.3
1a	H	1.31×10^{-5}	1.60×10^{-3}	21.2	−9.9
1d	*p*-Br	5.93×10^{-6}	5.77×10^{-4}	20.3	−14.5
1e	*m*-NO_2	1.83×10^{-7}	4.39×10^{-5}	24.1	−8.4
1f	*p*-NO_2	8.46×10^{-8}	2.23×10^{-5}	24.6	−8.6

[a] Calculated from data at other temperatures, $k_2 = k_{obsd}/h_0$, M^{-1} sec^{-1}. [b] Calculated from k_2 values.

H_0).[12] Values of h_0 and h_R' (derived at 25°) and temperature-corrected values of h_0 ($\log h \equiv -H$) for the acid concentrations used are also included in Table III.[12–17] None of these acidity functions would be expected to correspond precisely to the reaction involved with the phosphates so each was examined to see which gave the most consistent correlation of the data. The observed rate constants were converted to effective second-order rate constants by the relation $k_2 = k_{obsd}/h$ where h corresponded to the various acidity functions. These values of k_2 were used to calculate activation parameters ΔH^* and ΔS^*, as well as k_2 values at 25 and 70°. There was a maximum difference of less than a factor of 2 between the h values at the concentrations used here, but the values derived from the H_0 scale at 25° appeared (see Experimental Section) to give the most satisfactory treatment and the calculated rate constants and activation parameters reported in Table IV are derived from the H_0 scale. The reported[16,17] temperature dependence of the acidity function of HCl is suspect because the values of H_0 at 25° used in this treatment are significantly different from the accepted values[14,15] (see Katritzky, *et al.*,[17] for a further critique of these data). The correlation of the rates at 25 and 70° with the σ^+ substituent parameters[18] is shown in Figure 1, and the comparison of the correlation at 25° with that of α-arylvinyl acetates at $H_0 = 0$[9] is shown in Figure 2.

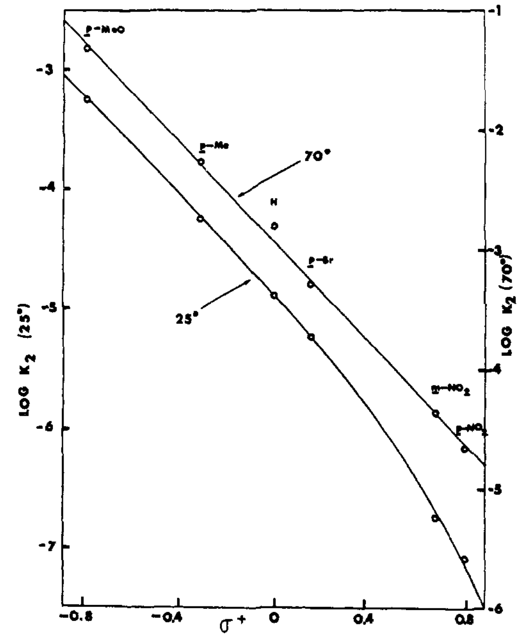

Figure 1. HCl-catalyzed hydrolysis of diethyl α-arylvinyl phosphates.

The correlation with σ^+ at 70° is acceptably linear with $\rho = -2.1$. Rate constants were measured for each compound within half a degree of this temperature, so the correlation is a reliable index of the interaction of the substituent in the transition state. The correlation at 25° (obtained for comparison with the data on vinyl acetates at that temperature[9]) shows distinct curvature but required considerable extrapolation of the rates in several cases. The variation in the correlation for the phosphates at different temperatures reflects the apparently nonsystematic differences in the activation parameters of the different compounds (ln k/T *vs.* $1/T$ plots for each compound were linear within the accuracy of the individual rate measurements). These differences presumably arise from a variety of factors: (1) the uncertainties in the measured rate constants; (2) the use of inexact acidity functions for the reaction under study; and (3) variations of the acidity function with temperature. It was observed[4c] that the measured activation parameters for the α-phenyl compound varied with temperature, and this behavior was attributed to the temperature effect on the acidity of the medium.

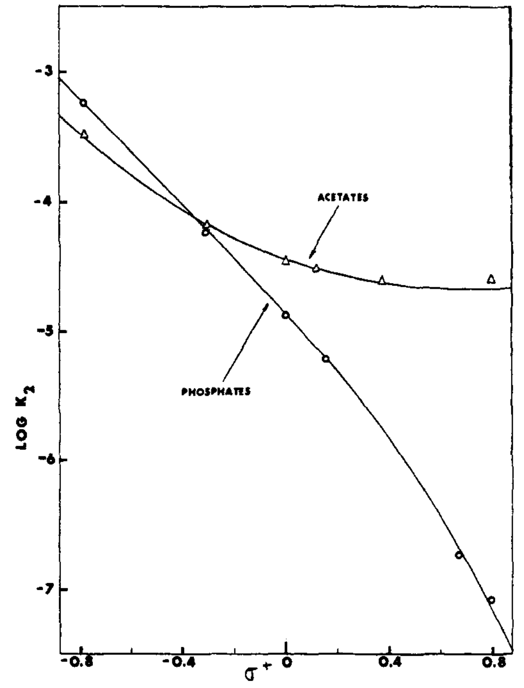

Figure 2. Comparison of acid-catalyzed hydrolysis of diethyl α-arylvinyl phosphates and α-arylvinyl acetates at 25°.

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(18) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, 1, 35 (1963).

The products from the *m*-nitro compound **1e** in 20% dioxane–water (the dioxane was added so as to dissolve an appreciable quantity of **1e**) at 100° and 0.1 *N* HCl were isolated after the reaction by making the solution basic, extracting out the *m*-nitroacetophenone, and acidifying and extracting out the phosphoric acids, which were treated with diazomethane. An essentially quantitative yield of the acetophenone was recovered, and nmr analysis of the mixed methyl ethyl phosphates indicated the presence of $MeEt_2PO_4$ and Me_2EtPO_4 in the ratio of 57:43. This is a reasonable result since the reported[4a] relative rates of hydrolysis by 0.1 *N* HCl in 40% ethanol of triethyl phosphate, diethyl vinyl phosphate, and diethyl α-phenylvinyl phosphate (**1a**) are 1:12:170, respectively, consistent with lower reactivity for cleavage of the ethyl groups than the α-phenylvinyl group. Since the α-*m*-nitrophenylvinyl compound **1e** is less reactive than **1a** by a factor of 36 at 70°, reaction at the ethyl groups may become competitive. The formation of some dimethyl ethyl phosphate from methylation of the phosphoric acids formed indicates the presence of dihydrogen ethyl phosphate in the hydrolysis product, although the greater part of the product was the diethyl derivative. Thus, most of the hydrolysis of the diethyl arylvinyl phosphates proceeds *via* initial cleavage of the vinyl group, although for **1e** and **1f** some of the reaction may first involve cleavage of an ethyl group. Usually dialkylphosphoric acids are less reactive than trialkyl phosphates in acid,[5] so some of the ethylphosphoric acid may have arisen from base-catalyzed hydrolysis of the diethylphosphoric acid during extraction.[18a]

Catalysis of the reaction by the diethylphosphoric acid formed is a complication in concentrated solutions[4a] but will not be significant at the 10^{-5} *M* concentrations used here.

Discussion

The observed correlation of the rates with σ^+ with $\rho = -2.1$ decisively rules out the $A_{AC}2$ mechanism for these reactions. The $A_{AL}1$ route would also give a correlation with σ^+, but other reactions involving the formation of α-arylvinyl cations, namely the acid-catalyzed hydration of phenylpropiolic acids[19a] and arylacetylenes,[19b] and the solvolysis of α-aryl-β,β-diphenylvinyl iodides[20] give much greater negative values of ρ, −4.77, −3.84, and −3.6, respectively, as expected for the high electron demand of a vinyl cation. The correlation with σ^+ and the value of ρ are both consistent with the $A_{SE}2$ route (for the $A_{SE}2$ reaction of α-arylvinyl acetates the correlation with σ^+ gives $\rho = -1.9$).[9]

The observed values of the activation parameters are also consistent with the $A_{SE}2$ mechanism, particularly the entropy values, which ranged from −8.1 to −14.5 eu. Usually A2 type processes have substantial negative entropies of activation, whereas A1 reactions have positive entropies.[21] However this agreement must be at least partly fortuitous, in view of the known variation of the activation parameters of **1a** in stronger acids,[4c] and the extrapolations involved in the present case.

Bunton and Robinson[4c] have reported that **1a** shows a linear correlation of log *k* with H_0, and has a value of k_{H_2O}/k_{D_2O} of 2.5. Both these results are expected for the $A_{SE}2$ mechanism.

Table V. Rates at 25° of Acid-Catalyzed Hydrolysis of Diethyl α-Arylvinyl Phosphates and α-Arylvinyl Acetates

Substituent	k_2(phosphate)[a]	k_2(acetate)[a,b]	*k*(acetate)/ *k*(phosphate)
p-MeO	5.70×10^{-4}	3.33×10^{-4}	0.58
p-Me	5.77×10^{-5}	6.67×10^{-5}	1.16
H	1.31×10^{-5}	3.44×10^{-5}	2.62
p-NO_2	8.46×10^{-8}	2.59×10^{-5}	306

[a] k_{obsd}/h_0, M^{-1} sec^{-1}. [b] Data of ref 9 at $H_0 = 0$.

Thus, the $A_{SE}2$ mechanism is uniquely consistent with the σ^+ correlation, the magnitude of ρ, the entropies of activation, the solvent isotope effect, and the dependence of log *k* on H_0 for the HCl-catalyzed hydrolysis of diethyl α-arylvinyl phosphates. For *p*-methoxy and *p*-methyl substituents the mechanism of the H_2SO_4-catalyzed reaction of α-arylvinyl acetates is the same and the absolute rates are also similar (Table V). The latter observation indicates only a small difference in the substituent effect of phosphate and acetate on the slow protonation of the adjacent double bond. Reaction at the carbonyl group of the acetate is predominant when the phenyl group is substituted with a para hydrogen or a more electron-withdrawing group at $H_0 = 0$, whereas reaction at the phosphoryl group does not occur even with the *p*-nitro substituent, so that the acetates with electron-withdrawing substituents react much faster than the corresponding phosphates. The low reactivity of the phosphoryl group to $A_{AC}2$-type hydrolysis must arise from either an unfavorable equilibrium constant for the initial protonation or a low rate constant for water attack in the second step of the reaction or both (eq 1) (note that the pentacoordinate species **2** need not

$$(RO)_3PO + H^+ \overset{K}{\rightleftharpoons} (RO)_3\overset{+}{P}OH \xrightarrow[\text{slow}]{k_{H_2O}} \underset{\mathbf{2}}{(RO)_3\overset{+}{P}O_2H_3} \xrightarrow{\text{fast}} \text{products} \quad (1)$$

represent an actual intermediate, but can be only a transition state leading to products). The relative basicities of phosphoryl and carbonyl groups would give an estimate of the influence of the first step. The best estimate that has been made for the base strengths of alkyl phosphates and alkyl acetates is based on measurement of the heats of ionization of the substrates in fluorosulfuric acid.[22] For triethyl phosphate and ethyl acetate this method gives pK_a values for ionization of the corresponding conjugate acids of −4.5 and −6.5, respectively.[22c] Nmr measurements confirm that the protonation of phosphates occurs on phosphoryl oxygen,[23] as shown in eq 1.

(18a) NOTE ADDED IN PROOF. This assumption is apparently correct since repetition of this experiment with **1f** and less exposure to base gave $MeEt_2PO_4$ and Me_2EtPO_4 in the ratio of 88:12.

(19) (a) D. S. Noyce, M. A. Matesich, and P. E. Peterson, *J. Amer. Chem. Soc.*, **89**, 6225 (1967); (b) D. S. Noyce and M. D. Schiavelli, *ibid.*, **90**, 1020 (1968).

(20) L. L. Miller and D. A. Kaufman, *ibid.*, **90**, 7282 (1968).

21) L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, 1, 1 (1963).

(22) (a) E. M. Arnett, R. P. Quirk, and J. J. Burke, *J. Amer. Chem. Soc.*, **92**, 1260 (1970); (b) E. M. Arnett, R. P. Quirk, and J. W. Larsen, *ibid.*, **92**. 3977 (1970); (c) E. M. Arnett, private communication.

(23) G. A. Olah and C. W. McFarland, *J. Org. Chem.*, **36**, 1374 (1971).

Comparison of the rate constants of α-*p*-nitrophenylvinyl acetate and diethyl α-*p*-nitrophenylvinyl phosphate (**1f**) at 25° indicates a 300-fold greater reactivity for the acetate. Based on the 100-fold greater basicity of the phosphoryl group, the rate of attack of water on the protonated phosphoryl group (k_{H_2O} in eq 1) must be at least 3 × 10^4 slower than the corresponding reaction of the vinyl acetates. The resistance of the phosphoryl group to attack by water is in accord with its known reluctance to change from 4 to 5 coordination.[24]

Experimental Section

General. Elemental analyses were performed at the Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany. Infrared spectra were determined using a Perkin-Elmer 337 grating spectrophotometer, and nmr spectra were measured with a Varian A-60 instrument with tetramethylsilane as an internal standard.

Preparation of Vinyl Phosphates. Elemental analyses and spectral data for the phosphates prepared as described below are given in Tables I and II, respectively. Compound **1a** (X = H) is well known[3b] and was prepared as previously reported.[4c,11] Compounds **1b**,[11,25] **1c**,[25] **1d**,[25] and **1f**[11,25] have been reported elsewhere, although as components of mixtures in some cases.[11]

Diethyl α-phenylvinyl phosphate (1a) was prepared by the literature procedure[4c,11] and purified by chromatography on silica gel with 3% acetone–$CHCl_3$.

Diethyl α-*p*-anisylvinyl phosphate (1b) was prepared by heating 20 g (0.12 mol) of triethyl phosphite with 12 g (0.065 mol) of *p*-methoxyphenacyl chloride (obtained from anisole, chloroacetyl chloride, and $AlCl_3$ in CS_2)[26] in 20 ml of benzene for 1 hr at 90°. After standing overnight at 25°, the solution was evaporated at 25 Torr in a 50° bath. Chromatography of the product on silica gel with 5% acetone in chloroform gave *p*-methoxyphenacyl chloride and methoxyacetophenone in the early fractions and then 6.3 g (0.023 mol, 35%) of **1b** as a yellow oil after removal of the solvent at 0.05 Torr and 25°.

When the *p*-methoxyphenacyl chloride was prepared by chlorination of *p*-methoxyacetophenone with SO_2Cl_2 and the phosphate was prepared as above, there was obtained in an intermediate fraction of the chromatography diethyl α-*p*-anisyl-β-chlorovinyl phosphate (**3**) of unknown stereochemistry at the double bond. This material evidently was derived from some dichlorinated *p*-methoxyacetophenone formed in the chlorination.

Diethyl α-*p*-methylphenylvinyl phosphate (1c) was prepared by heating crude *p*-methylphenacyl chloride (prepared from 0.20 mol of *p*-methylacetophenone and SO_2Cl_2 in $CHCl_3$ at 25°) and 33 g (0.20 mol) of triethyl phosphite at 70° for 2 hr. The product appeared to contain several compounds but **1c** was isolated in about 5% yield after repeated chromatography on silica gel with acetone–$CHCl_3$ and EtOAc–CH_2Cl_2–pentane mixtures.

Diethyl α-*p*-bromophenylvinyl phosphate (1d) was prepared by heating 14 g (0.084 mol) of triethyl phosphite with 37 g (0.074 mol) of *p*-bromophenacyl chloride (obtained from bromobenzene, chloroacetyl chloride, and $AlCl_3$ in CS_2)[27] at 70° overnight without solvent. Volatiles were evaporated at 0.15 Torr and 25° to give 21.5 g of crude product whose nmr revealed only those peaks assigned **1d**, with a small amount of starting material. Chromatography of half of this product on silica gel with 3% acetone–chloroform gave first starting material and then **1d** (8.0 g, 0.024 mol, 57%).

Diethyl α-*m*-nitrophenylvinyl phosphate (1e) was prepared by heating 17 g (0.085 mol) of *m*-nitrophenacyl chloride (from phenacyl chloride and nitric acid)[28] and 15 g (0.090 mol) of triethyl phosphite 2 hr at 70° without solvent to give 20 g of crude product. Chromatography of half this material on silica gel with 3% acetone–chloroform gave 8.0 g (0.027 mol, 63%) of 1e after removal of the solvent at 0.05 Torr and 25°.

Diethyl α-*p*-nitrophenylvinyl phosphate (1f) was prepared by slowly adding 28.5 g (0.143 mol) of *p*-nitrophenacyl chloride to 25.0 g (0.15 mol) of triethyl phosphite with shaking. The reaction was exothermic at 25°. The *p*-nitrophenacyl chloride was obtained by refluxing 33 g (0.20 mol) of *p*-nitroacetophenone with 28 g (0.207 mol) of sulfuryl chloride in 100 ml of chloroform for 2 hr and evaporating the solvent to give 40 g (0.20 mol) of product with nmr absorptions in deuterioacetone at δ 5.07 and 8.24 only. Portions of 10 g of the crude vinyl phosphate were chromatographed on silica gel with 3% acetone–chloroform to give successively *p*-nitrophenacyl chloride, 1f, and triethyl phosphite. After removal of the solvent at 0.05 Torr and 25° 1f was obtained in 40% yield.

Product Analysis from Diethyl α-*m*-Nitrophenylvinyl Phosphate (1e). A solution of 1.01 g (0.00337 mol) of 1e in 500 ml of 0.1 *N* HCl and 120 ml of dioxane was sealed in a glass tube and heated 22 hr at 100°. The solution was cooled and brought to pH 10 with NaOH, and extracted three times with 200-ml portions of $CHCl_3$ which on evaporation gave 0.565 g (0.00342 mol, 101%) of *m*-nitroacetophenone. The aqueous layer was concentrated at 40° and 25 Torr to a volume of 25 ml, acidified with HCl to pH 1, and continuously extracted 4 days with ether. The ether layer was treated with excess diazomethane and evaporated to yield an oil whose nmr spectrum (CCl_4) showed the presence of $POCH_3$ (δ 3.68, doublet, $J_{^{31}P-H}$ = 11 Hz), $PO\mathit{CH}_2CH_3$ (δ 3.96, octet, $J_{^{31}P-H}$ = 8 Hz, J_{H-H} = 7 Hz), and $CH_2\mathit{CH}_3$ (δ 1.33, triplet, J_{H-H} = 7 Hz). The relative integrals of the two low-field signals and the high-field signal were 64.5:35.5, corresponding to the presence of 57% $MeEt_2PO_4$ and 43% Me_2EtPO_4.

Kinetics. Rates were followed by observing the change in absorbance of 10^{-5} *M* solutions using a Cary 14 ultraviolet spectrophotometer. Solutions were prepared by dissolving the vinyl phosphate in the acid solution and placing the samples in constant temperature baths. Aliquots were removed at appropriate intervals and chilled, and the absorbance curves were scanned for all of the samples one after another in 1-cm cells. Runs at 85 and 100° were carried out with the samples in sealed tubes. The absorptions of the vinyl phosphates and the product acetophenones do not differ greatly, so in addition to following the reactions at the absorption maxima (Table II) the rates were also followed at the absorption minima between 220 and 230 nm, according to the procedure of Bunton.[4c] The rates were followed to 2 half-lives, and the infinity spectra closely matched those of the corresponding acetophenones. At least two runs were made at each temperature, and the reported observed first-order rate constants are those averaged for all runs and wavelengths under the same conditions. Maximum deviations at the same wavelength for different runs were ±10%, and at different wavelengths ±20%. Good agreement was observed with the reported[4c] rate constants for **1a**. Thus, the reported value for k_{obsd}/h_0 for **1a** at 25° in 0.1 *M* $HClO_4$ is 1.15 × 10^{-5} M^{-1} sec^{-1} and the comparable value found here is 1.31 × 10^{-5} M^{-1} sec^{-1}. The values of ΔH^* and ΔS^* for **1a** calculated from the reported data in 0.1 *M* $HClO_4$ are 21.3 kcal/mol and −9.6 eu, respectively, as compared to the values found here of 21.2 kcal/mol and −9.9 eu.

The different acidity functions (Table III) were compared in two ways. Thus, the average standard deviations of ΔH^* were 0.03, 0.03, and 0.05 kcal/mol, and the average standard deviations of ΔS^* were 0.10, 0.09, and 0.17 eu, for the rates derived from h_0, $h_0{}^t$, and $h_R{}'$ values, respectively. Values of ρ, and the corresponding correlation coefficients, obtained from plots of log k_2 *vs.* σ^+, were −2.1 (0.999), −2.2 (0.995), and −2.3 (0.992) for k_2 values derived from h_0, $h_0{}^t$, $h_R{}'$ values, respectively.

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(25) See Arcoria and Fisichella, Table II, footnote *b*.

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(28) C. Barkenbus and J. P. Clements, *J. Amer. Chem. Soc.*, **56**, 1369 (1934).