system at temperatures between 180 and 230°. Complete high-resolution mass spectra were measured on the CEC 21-110 mass spectrometer.

The low electron voltage spectra also were obtained on the model 21-110B mass spectrometer. Metastable ion measurements reported in Table II were made on an Associated Electrical Industries MS-12 mass spectrometer with a glass inlet system at 200°.

Deuterium Exchange. The appropriate compound was subjected to exchange on a deuterium oxide treated potassium hydroxide–Carbowax vapor phase chromatography column.[34] 4,4-Dimethyl-2-cyclohexenone yielded 76% 6,6-d_2 and 24% 6-d_2; 6,6-dimethylbicyclo[3.1.0]hexan-2-one yielded 75% 3,3-d_2 and 18% 3-d_1; 4,4,6-trimethyl-2-cyclohexenone yielded 79% 6-d_1; and 4-methyl-2-cyclohexenone yielded 58%, 2,4,6,6-d_4 and 34% d_3. 5-Methylbicyclo[3.1.0]hexenone was exchanged to the 3,3-d_2 derivative of greater than 99% isotopic purity by stirring in deuterium oxide and methanol-OD with sodium methoxide.

Synthesis of the Ketones. The syntheses of the ketones used in this study have been described in a separate publication.[19]

Acknowledgment. The authors express their appreciation to Professor A. L. Burlingame for his interest and assistance in this work.

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The Two Mechanisms for the Acid-Catalyzed Hydrolysis of Enol Acetates[1]

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Abstract: Hydrolysis of α-acetoxy-*p*-nitrostyrene (**6**) in 1 *M* sulfuric acid shows the characteristics of normal ester hydrolysis. In D_2O, the solvent isotope effect, k_{H_2O}/k_{D_2O}, is 0.75; the rate of hydrolysis is very similar to the rate of hydrolysis of isopropyl acetate. Increasing the concentration of sulfuric acid causes an increase in rate which is nonlinear with the acidity function H_0, but which closely parallels the increasing rate of hydrolysis of isopropyl acetate. In sulfuric acid concentrations greater than 55%, the rate of hydrolysis of **6** increases very rapidly. In 69% sulfuric acid, the solvent isotope effect, k_{H_2O}/k_{D_2O}, is now 3.25. Thus, the mechanism has changed to one involving initial, and rate-determining, olefin protonation. The effect of substituents in substituted α-acetoxystyrenes further serves to substantiate the two mechanisms, and to delineate the circumstances under which each of the two mechanisms will be dominant.

Recently there has been a good deal of interest in the acid-catalyzed hydrolysis of enol derivatives.[2-4] Studies with enol ethers have shown that these reactions involve rate-determining protonation at carbon and that they show general acid catalysis and a high order of reactivity. Studies of the hydrolysis of enol acetates have been somewhat less extensive. DePuy has studied the alkaline hydrolysis of several enol acetates.[5] The hydrolysis of vinyl acetate in relatively concentrated hydrochloric acid has been examined very carefully by Yrjänä,[6] and he concludes that normal ester hydrolysis is occurring. Though Kiprianova and Rekasheva[7] and Landgrebe[8] propose mechanisms involving initial protonation on carbon, Yrjänä[6] gives very compelling reasons for preferring a mechanism for the hydrolysis which is normal ester hydrolysis, including a consideration of the relative rate of reaction, the entropy of activation and the solvent isotope effect.

It was noted by Hammett[9] that in acid hydrolysis of esters the effect of structure in the alcohol component is very small in marked contrast to the large effect observed in alkaline hydrolysis. Variation from *t*-butyl to benzyl or phenyl caused a change of less than a factor of 2 in rate.

The acid hydrolysis of benzyl acetates[10] has a ρ of only -0.05.

We have examined the rates for the acid-catalyzed hydrolysis of a series of ring-substituted α-acetoxystyrenes and we find that enol acetates may hydrolyze through two different pathways. The first is that proposed by Yrjänä,[6] which is the same mechanism by which most saturated esters hydrolyze. The second involves protonation of the carbon–carbon double bond. Two different factors determine which mechanism is to be active in any given situation. The first is the acidity and the second is the stability of the carbonium ion formed by the protonation of the carbon-carbon double bond.

Experimental Section[11]

Preparation of Materials. The following general procedure was used to prepare the substituted α-acetoxystyrenes used in this study.

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Table I

Compound	Bp, °C (mm)	Mp, °C	Calcd, % C	Calcd, % H	Calcd, % Cl or N	Found, % C	Found, % H	Found, % Cl or N
p-Methoxy-α-acetoxystyrene (**1**)	108–110 (1.1)	77–78	68.73	6.30		68.45	6.29	
p-Methyl-α-acetoxystyrene (**2**)	106–108 (5.0)	28.5–30.5	74.97	6.87		74.77	6.69	
α-Acetoxystyrene (**3**)	92–95 (4.5)	...	74.05	6.22		73.84	6.08	
p-Chloro-α-acetoxystyrene (**4**)	116–118 (4.1)	...	61.08	4.61	Cl, 18.03	61.29	4.79	Cl, 17.78
m-Chloro-α-acetoxystyrene (**5**)	114–116 (4.4)	...	61.08	4.61	Cl, 18.03	4.61	4.88	Cl, 18.08
p-Nitro-α-acetoxystyrene (**6**)	120–121 (0.12)	52–53	59.97	4.38	N, 6.76	57.89	4.52	N, 7.04

The appropriate acetophenone (20 g) was mixed with a two- to fourfold molar excess of isopropenyl acetate and about 200 mg of *p*-toluenesulfonic acid as catalyst. The solution was refluxed and acetone was collected by distillation as it formed. The amount of acetone collected did not accurately reflect the extent of reaction, as approximately twice as much was formed as would have been predicted. This was presumably due to decomposition of isopropenyl acetate to acetone and ketene. However, the reaction could be monitored quite conveniently by gas chromatography on a 5 ft × 0.25 in. SE-30 column at about 140°. Since the half-life of all of the reactions was about 2 days, they were stopped at 50–75% completion. Ether was added to the cooled solution to render it homogeneous. The solution was washed with aqueous sodium bicarbonate, dried over magnesium sulfate, concentrated on a rotary evaporator, and distilled through a spinning-band column under reduced pressure. Yields were between 40 and 65%. The properties of the compounds prepared are given in Table I.

Compounds **2–5** were used directly in the kinetics. **1** was recrystallized from ethanol and **6** was purified by gas chromatography before they were used in the kinetic studies.

Nmr and infrared spectra were distinctive and in accord with the structural assignments.

The preparation of sulfuric acid-d_2 has been described previously.[12]

Kinetic Methods. Rates were measured by following the change in absorbance at a wavelength between 280 and 310 mμ at concentrations varying between 5×10^{-5} and 5×10^{-4} *M*. Since the spectra of the starting material and products were similar for compounds **2–5** measurements had to be made on the high-wavelength n–π* band of the ketone and this necessitated the use of concentrations approaching 5×10^{-4} *M*. The spectra of starting material and products were sufficiently different in the case of **1** and **6** so that lower concentrations could be used and kinetic measurements could be made by following the change in absorbance at the main bands.

To 3.00 ml of sulfuric acid of the requisite strength which had been temperature equilibrated in a 1-cm ultraviolet cell 25 μl of an ethanol stock solution of the organic substrate was added to initiate the reaction. Absorbance measurements were generally made to beyond 95% reaction.

To determine the final sulfuric acid concentration weighed aliquots were titrated in duplicate with sodium hydroxide.

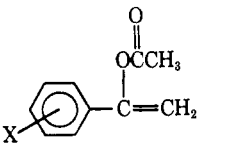
H_0 values were taken from the data of Bascombe and Bell,[13] and Jorgenson and Hartter.[14] The small amount of ethanol was ignored in determining the H_0 values. Solvent isotope effects were calculated at the same mole fraction of acid. Justification for use of mole fraction as a basis for comparison has previously been given.[15]

All compounds gave excellent pseudo-first-order kinetics beyond 95% reaction. Rate constants were calculated by a least-squares computer program. The standard deviations of the rate constants as calculated by the computer showed the precision of the measurements to be good, the error limits obtained generally being less than ±1% of the observed rate constant.

Results

The acid-catalyzed hydrolysis of substituted α-acetoxystyrenes may be conveniently followed kinetically by observing the appearance of the corresponding acetophenone in the ultraviolet. The relatively weak n–π* transition had to be used in some cases as the main bands of the ketone and enol acetate occasionally overlapped. A 0.8% ethanol solution was used in order to facilitate the kinetic measurements. All of the reactions gave excellent pseudo-first-order kinetics and stable infinity points. The final spectrum matched that of the appropriate acetophenone in all respects.

The following compounds were hydrolyzed in sulfuric acid of dilute to moderate strength, at 25.00°. All of the compounds were followed from about 6% sulfuric



1, X = *p*-CH_3O **4**, X = *p*-Cl
2, X = *p*-CH_3 **5**, X = *m*-Cl
3, X = H **6**, X = *p*-NO_2

acid ($H_0 = 0$) until the rates became too rapid to follow conveniently. The results are given in Table II. Note that the rates of compounds **3–6** are virtually identical at lower acidities and that the total range of reactivity of all the compounds is less than a factor of 15 at $H_0 = 0$. At higher acidities the rates of the variously substituted compounds begin to diverge quite markedly. For example, α-acetoxystyrene (**3**) reacts only 30% faster than *p*-nitro-α-acetoxystyrene (**6**) in 6% sulfuric acid but in 40% sulfuric acid the rate ratio is 25. Extrapolation of the rates of the more reactive compounds to higher acidities shows that the difference in rates becomes even greater as the acidity is increased.

The hydrolysis rates of all the compounds studied are very similar to the rates of saturated esters in the dilute acid range. For example, the rate of the normal acid catalyzed hydrolysis of isopropyl acetate[16] is only twice that of *p*-nitro-α-acetoxystyrene at $H_0 = -0.6$. At higher acidities, however, the rate of isopropyl acetate becomes substantially less than any of the substituted acetoxystyrenes.

Discussion

The two mechanisms which have been proposed for the acid-catalyzed hydrolysis of vinyl esters are both *a priori* reasonable and each has good analogies. The first is the mechanism by which most normal esters hydrolyze, involving an equilibrium proton transfer to the ester oxygen and then nucleophilic attack by water leading to products (eq 1–4).

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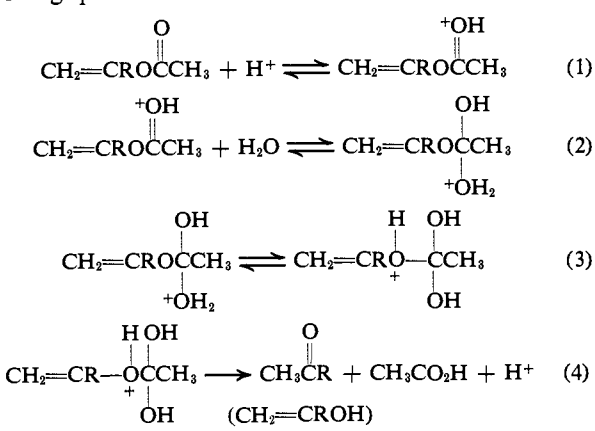
Table II. Rate of Acid-Catalyzed Hydrolysis of Substituted α-Acetoxystyrenes

X	H_2SO_4, %	H_0	k, sec^{-1}	Log k
p-CH_3O	5.71	+0.02	3.33×10^{-4}	−3.48
	12.19	−0.53	1.28×10^{-3}	−2.89
	15.91	−0.79	2.47×10^{-3}	−2.61
	20.24	−1.08	4.71×10^{-3}	−2.33
	23.73	−1.32	8.69×10^{-3}	−2.06
	29.67	−1.76	2.68×10^{-2}	−1.57
p-CH_3	5.64	+0.03	6.67×10^{-5}	−4.18
	12.23	−0.53	2.29×10^{-4}	−3.64
	15.98	−0.79	4.01×10^{-4}	−3.40
	20.22	−1.08	7.80×10^{-4}	−3.10
	23.79	−1.33	1.36×10^{-3}	−2.87
	29.42	−1.74	3.44×10^{-3}	−2.46
	36.40	−2.26	1.35×10^{-2}	−1.87
	40.37	−2.56	2.69×10^{-2}	−1.57
H	5.67	+0.03	3.44×10^{-5}	−4.46
	12.18	−0.53	1.04×10^{-4}	−3.98
	20.14	−1.07	2.60×10^{-4}	−3.59
	29.61	−1.75	9.53×10^{-4}	−3.02
	36.30	−2.25	2.95×10^{-3}	−2.53
	40.29	−2.55	6.24×10^{-3}	−2.21
	45.45	−2.95	1.90×10^{-2}	−1.72
p-Cl	5.67	+0.03	3.03×10^{-5}	−4.52
	12.14	−0.53	8.10×10^{-5}	−4.09
	20.13	−1.07	2.06×10^{-4}	−3.69
	29.30	−1.73	6.31×10^{-4}	−3.20
	36.45	−2.26	1.85×10^{-3}	−2.73
	40.12	−2.54	3.85×10^{-3}	−2.41
	45.54	−2.96	1.15×10^{-2}	−1.94
m-Cl	5.66	+0.03	2.47×10^{-5}	−4.61
	12.34	−0.53	6.38×10^{-5}	−4.16
	19.99	−1.06	1.40×10^{-4}	−3.85
	29.18	−1.72	3.55×10^{-4}	−3.45
	36.17	−2.24	8.01×10^{-4}	−3.10
	40.14	−2.54	1.44×10^{-3}	−2.85
	45.66	−2.97	4.07×10^{-3}	−2.39
	51.61	−3.51	1.34×10^{-2}	−1.87
	55.65	−3.94	3.36×10^{-2}	−1.47
p-NO_2	5.70	+0.02	2.59×10^{-5}	−4.59
	12.08	−0.52	6.30×10^{-5}	−4.20
	20.07	−1.07	1.29×10^{-4}	−3.89
	29.14	−1.72	2.61×10^{-4}	−3.58
	36.03	−2.23	4.39×10^{-4}	−3.36
	40.06	−2.54	5.70×10^{-4}	−3.24
	45.55	−2.96	9.03×10^{-4}	−3.04
	46.43	−3.03	9.97×10^{-4}	−3.00
	51.49	−3.50	1.64×10^{-3}	−2.78
	55.47	−3.92	2.77×10^{-3}	−2.56
	61.11	−4.61	8.04×10^{-3}	−2.10
	66.35	−5.30	2.44×10^{-2}	−1.61
	68.80	−5.64	4.52×10^{-2}	−1.35

The other mechanism (eq 5-8) involves a rate-determining protonation of the carbon-carbon double



(1)

(2)

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(4)

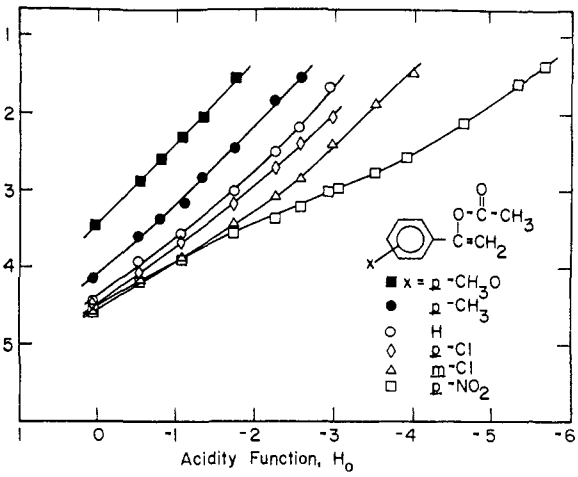
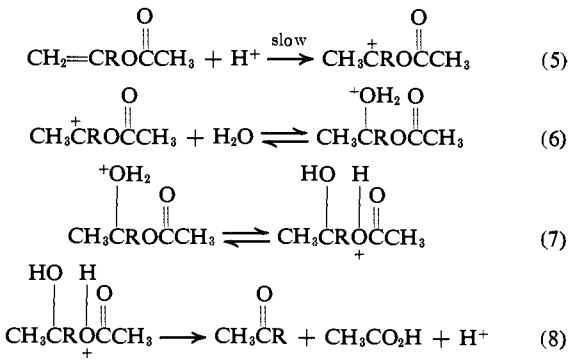


Figure 1. Acidity dependence of rate of hydrolysis of substituted acetoxystyrenes.

bond followed by rapid attack by water and collapse to products. This has been shown to be the pathway through which vinyl ethers are cleaved in acid,[2] and has other analogies in acid-catalyzed reactions such as the isomerization of *cis*-stilbene[17] and hydration of styrene.[18]



(5)

(6)

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These mechanisms can be distinguished in a variety of ways. The three main criteria which will be used in this study are (1) acidity correlation of the reaction rate, (2) effect of the substituent on the rate, and (3) solvent isotope effect.

Acidity Correlations. The two most reactive compounds show a marked dependence on acidity throughout the range studied, whereas the least reactive ones show only a slight dependence on acidity in the lower part of the range, although they, too, are strongly acid-catalyzed if the acidity is increased sufficiently. This difference in response to a variation in H_0 is a strong indication that there is more than one mechanism operating. A plot of log k *vs.* H_0 is given in Figure 1.

In order to explain the different rate profiles it is first necessary to consider what would be expected for the two proposed mechanisms. Zucker and Hammett[19] first proposed that if a transition state contains the elements of water in addition to a proton and the substrate, then the logarithm of the reaction rate should be linear with the logarithm of the concentration of

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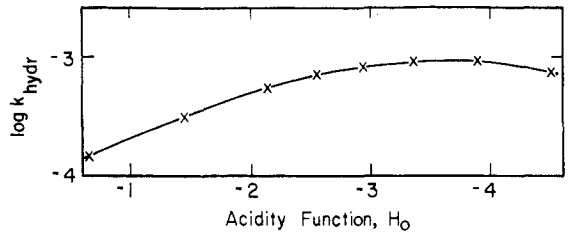

Figure 2. Rate–acidity profile for hydrolysis of isopropyl acetate. Data are from ref 16.

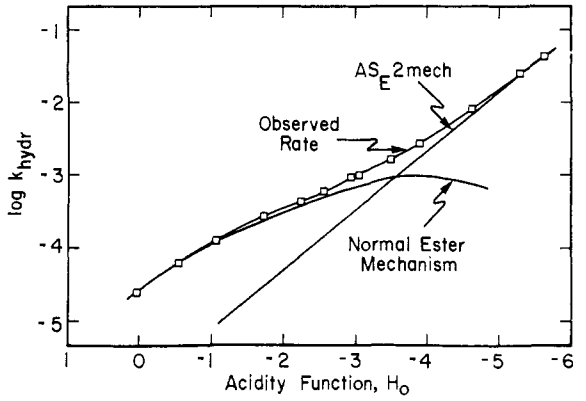

Figure 3. Two mechanisms for the hydrolysis of *p*-nitro-α-acetoxystyrene.

hydronium ion rather than H_0. It is to be noted here that log C_{H^+} and H_0 do not begin to differ appreciably until about 10% sulfuric acid so that this criterion is useless in dilute acid. Normal ester hydrolyses do not follow this criterion exactly but they do show much better correlation with hydronium ion concentration than with H_0.[20] For most esters the reaction rate reaches a maximum around 50% sulfuric acid and then decreases.[16] This is attributed to the increasing scarcity of water, which is needed as an attacking species, in solutions of concentrated acid.

Figure 2 is a plot of log *k vs.* H_0 for isopropyl acetate which is typical of most saturated esters. For a reaction involving rate-limiting proton attack on carbon (ASE2 mechanism) correlation with H_0 is generally observed. The acid-catalyzed isomerization of *cis*-stilbene has been shown to be an ASE2 reaction,[17] and it is linear with H_0 having a slope of −1.25. Other ASE2 reactions which follow H_0 include the hydration of substituted styrenes (slope varies from −1.23 to −1.33 depending on substituent),[18] and the hydration of phenylpropiolic acid (slope = −1.0).[15]

Let us first consider the acidity dependence of the two most reactive compounds. Both compounds **1** and **2** are markedly acid-catalyzed giving an almost linear plot of log *k vs.* H_0. The slopes of the plots for both compounds are between −1.00 and −1.10. There is perhaps a very slight upward curvature of these plots. The very good correlation of these compounds with H_0 supports a mechanism of the ASE2 type and appears incompatible with a normal ester hydrolysis mechanism.

The rate profiles of the other four compounds, **3–6** are not as simple. These show markedly decreasing slope in the low acid range but then curve sharply upward at higher acid concentrations.

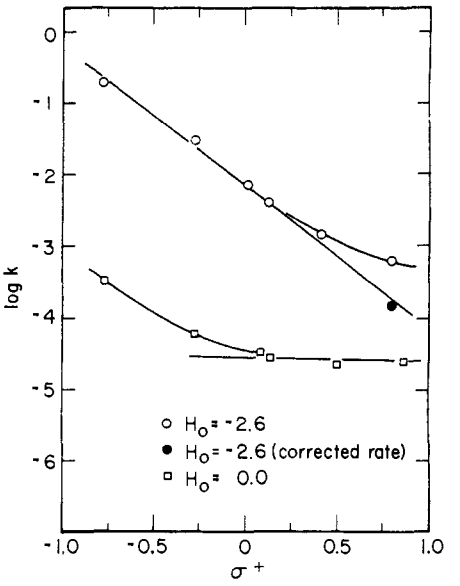

Figure 4. Substituent effects on rate of hyrolysis of α-acetoxystyrenes.

The observed acidity dependence for these compounds may be explained by assuming the presence of two mechanisms, one which involves water in the transition state (the normal ester mechanism) and one which does not (the ASE2 mechanism), with the normal ester mechanism predominating as the acidity is lowered or the substituent becomes more electron withdrawing. The ASE2 mechanism takes over as the substituent becomes more electron donating or the acidity is raised.

Let us analyze the rate–acidity of profile for *p*-nitro-α-acetoxystyrene (**6**) in terms of this postulate. This profile is shown in Figure 3. In the higher acidity range the log *k vs.* H_0 plot approaches a straight line with slope −0.83 or less. Upon extending this line into the low acid range, we get an approximation to the rate profile expected from the ASE2 mechanism. Correcting the experimental rate profile gives a curve representing the other mechanism. It can be seen by comparing the resulting curve to that for isopropyl acetate (Figure 2) that this curve is characteristic of a normal ester hydrolysis mechanism. Thus, the rate profile can be considered as a sum of two rate profiles each one representing a different mechanism. The other compounds may be treated in the same manner.

Substituent Effects. As can be seen from Figure 1 the rates at higher acidities are strongly dependent on the substituent, whereas at lower acidities the dependence is much less. For example, compounds **3–6** virtually the same rate in 6% H_2SO_4 but there is a range of reactivity of greater than 20 at 46% H_2SO_4. Plots of log *k vs.* Brown's σ^+ substituent constants[21] at two acidities are shown in Figure 4. These plots bear out the contention that two different mechanisms are operating. At H_0 = −2.6 (which involves only a slight extrapolation for **1**) compounds **1–5** give a good correlation with σ^+ but with **6** reacting too rapidly. If, however, we use a corrected rate for **6** by taking the

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(21) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 80, 4979 (1958).

rate due to the ASE2 mechanism only (from Figure 3) then all of the compounds lie on the line. Measured in this way, ρ is -1.9. It is to be noted at this point that the correlation with σ^+ constants is substantially better than with σ constants indicating that electron deficiency in the transition state is conjugated with the substituent. The magnitude of this ρ should be compared to other reactions of the type which give related carbonium ions. For the hydration of styrene, ρ is -3.4[18] and for α-methylstyrene, ρ is -3.2.[22] Other representative results are the isomerization *cis*-cinnamic acids ($\rho = -4.3$),[23] the hydration of phenylbenzoylacetylene ($\rho = -4.3$),[24] and the hydration of phenylpropiolic acids ($\rho = -4.7$).[15] It is to be expected that the value of ρ for the acetoxystyrenes should be substantially less negative than for the other ASE2 reactions since the carbonium ion is stabilized by resonance with the ester oxygen. To the extent that the positive charge is delocalized onto oxygen, delocalization into the ring will be less effective. The same type of effect is observed in the equilibrium ionization of benzhydrols and triarylcarbinols in sulfuric acid. The ρ for the former reaction is -4.74 whereas the ρ for the latter is -3.44.[21] However, the magnitude of the ρ for the hydrolysis of α-acetoxystyrenes at $H_0 = -2.6$ is still substantially negative, indicating a carbonium ion reaction.

On the other hand, at $H_0 = 0$, the rates of **3–6** are virtually the same. This is, of course, inconsistent with the ASE2 mechanism in which a carbonium ion center develops adjacent to the ring. However, this independence of rate on substituent is typical of normal ester hydrolysis since all of the charges which are formed in this mechanism are on atoms substantially removed from the ring. For example, the ρ for the acid-catalyzed hydrolysis of benzyl acetates in aqueous acetone is -0.05.[10]

Isotope Effects. The most striking evidence for a duality of mechanism comes from a consideration of the solvent isotope effects as a function of both acidity and substituent. The data for runs in deuterated media are given in Table III. The rate-acidity profiles for compound **6** in both H_2SO_4 and D_2SO_4 are plotted together (Figure 5). Comparison of rates was made at the same mole fraction of acid (see Experimental Section). The ratio k_{H_2O}/k_{D_2O} varies from 0.75 at low acidities to 3.25 at higher concentration of acid. Not only does the magnitude of the isotope effect change with the acidity but the direction changes also. At high acidities the rate is larger in H_2O, whereas in more dilute acid the rate is larger in D_2O. The direction of the solvent isotope effect is a very useful tool in separating the two mechanisms. An inverse isotope effect is characteristic of an equilibrium protonation prior to the rate-determining step, which is of course what is involved in the normal ester mechanism. Representative values for this mechanism are 0.73 for ethyl formate[25] and 0.60 for methyl acetate[26] which agree well with the value of 0.75 which is observed in dilute acid for **6**.

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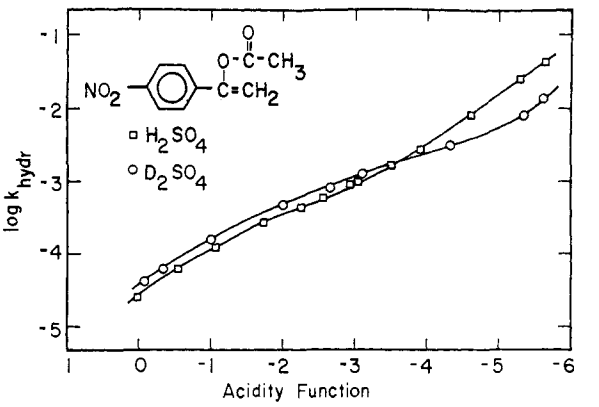

Figure 5. Solvent isotope effects on the hydrolysis of *p*-nitro-α-acetoxystyrene.

A normal isotope effect in the range of 2–4 is characteristic of a rate-determining proton transfer from solvent to substrate. Representative values for k_{H_2O}/k_{D_2O} for ASE2 reactions are 2.6 to 3.2 for isomerization of *cis*-stilbene,[17] 1.9 to 4.0 for the hydration of styrenes,[18] 3.7 to 5.3 for the isomerization of cinnamic acids,[23] and 2.95 for hydration of ethyl vinyl ether.[2]

Table III. Rate of Hydrolysis of Substituted α-Acetoxystyrenes in D_2O–D_2SO_4

Compd	D_2SO_4, %	D_0	k, sec^{-1}	Log k
1	6.22	−0.08	1.62×10^{-4}	−3.79
2	6.17	−0.07	6.19×10^{-5}	−4.21
3	6.16	−0.07	5.14×10^{-5}	−4.29
4	6.14	−0.07	4.73×10^{-5}	−4.33
5	6.16	−0.07	4.23×10^{-5}	−4.37
6	6.18	−0.07	4.14×10^{-5}	−4.38
	8.83	−0.33	6.31×10^{-5}	−4.20
	17.80	−1.00	1.62×10^{-4}	−3.79
	31.26	−2.01	4.60×10^{-4}	−3.34
	39.62	−2.65	8.25×10^{-4}	−3.08
	45.31	−3.12	1.25×10^{-3}	−2.90
	57.04	−4.35	3.10×10^{-3}	−2.51
	64.94	−5.37	8.11×10^{-3}	−2.09
	66.90	−5.64	1.39×10^{-2}	−1.86

The intervention of both mechanisms at low acidity can be shown conclusively by the variation of solvent isotope effect with substituent at $H_0 = -0.07$ (Table IV).

Table IV. Solvent Isotope Effects at $H_0 = -0.07$

X	k_{H_2O}[a]	k_{D_2O}	k_{H_2O}[a]/k_{D_2O}
p-OCH_3 (**1**)	4.06×10^{-4}	1.62×10^{-4}	2.50
p-CH_3 (**2**)	8.13×10^{-5}	6.19×10^{-5}	1.31
H (**3**)	4.26×10^{-5}	5.14×10^{-5}	0.83
p-Cl (**4**)	3.64×10^{-5}	4.73×10^{-5}	0.77
m-Cl (**5**)	3.12×10^{-5}	4.23×10^{-5}	0.74
p-NO_2 (**6**)	3.09×10^{-5}	4.14×10^{-5}	0.75

[a] Values for k_{H_2O} are interpolated from Figure 1.

Only the compounds with electron-donating substituents have isotope effects greater than 1.00 at this acidity. The last four compounds all have isotope effects of approximately 0.75 which is characteristic of the normal ester mechanism. This is consistent

with the fact that there is very little difference in the rates of these compounds at this concentration of acid.

The isotope effect of 2.50 which is observed for compound **1** is similar to the value of 3.25 for compound **6** at higher acidities indicating an ASE2 mechanism. However, if we assume that the rate of compound **6** at $H_0 = 0$ in D_2SO_4 represents the rate at which all of the compounds react in this acidity by the normal ester mechanism, then we can calculate the isotope effect due just to the ASE2 mechanism for compound **1**. This assumption seems quite warranted by the fact that at $H_0 = 0$ compounds **3**–**6** all react at virtually the same rate in H_2SO_4 and that they all have similar isotope effects. Furthermore, a deuterated medium will favor the normal mechanism even more. It is also necessary to assume an isotope effect of 0.75 for this mechanism which also seems borne out by Table IV. Using these values the isotope effect due solely to the ASE2 mechanism for compound **1** is 3.10. A similar calculation for compound **2** gives a value of 2.42.

Compound **2** is an interesting case at $H_0 = 0$. Using the rate for compound **6** as an approximation to the normal ester rate it can be shown that in D_2SO_4 the rate is 67% due to the normal ester mechanism, and only 33% due to the ASE2 mechanism. However, in H_2SO_4 the predominant mechanism is ASE2 (62% of the rate). Here is a situation where the predominant mechanism depends on whether the solvent is H_2O or D_2O.

There is one more mechanism (eq 9–12) which is a formal possibility and must be eliminated. This involves a protonation of the ester oxygen and then cleavage to the corresponding vinyl cation. As this mechanism does not involve water in the rate-determining step it would be expected to have an acidity dependence similar to the ASE2 mechanism. It would also have a rather sharp dependence on substituent. However, the isotope effect would have to be inverse

$$CH_2{=}CROCCH_3 + H^+ \rightleftharpoons CH_2{=}CROCCH_3 \quad (9)$$

$$CH_2{=}CROCCH_3 \xrightarrow{\text{slow}} CH_2{=}\overset{+}{C}R + CH_3CO_2H \quad (10)$$

$$CH_2{=}\overset{+}{C}R + H_2O \longrightarrow CH_2{=}CR\overset{+}{O}H_2 \quad (11)$$

$$CH_2{=}CR{-}\overset{+}{O}H_2 \longrightarrow CH_3C(=O)R + H^+ \quad (12)$$

since it involves a preequilibrium protonation. There is no portion of the acidity range in which all of these requirements are simultaneously satisfied for any of the compounds studied.

Another way of eliminating this possibility is by examination of the relative stabilities of the α-phenyl vinyl cation and the benzyl cation. The SN1 rate of solvolysis of $PhCBr{=}CH_2$ in 80% EtOH at 170° is 6.0×10^{-6} sec^{-1},[27] whereas the SN1 rate of solvolysis of $PhCH_2Br$ in 90% EtOH at 30° may be calculated to be approximately 1.2×10^{-6}.[28]

Thus, it can be readily seen that $PhCH_2^+$ is a much more stable entity than $PhC^+H{=}CH_2$. However, the hydrolysis of benzyl acetate by cleavage to the benzyl cation does not become significant until about 65% sulfuric acid. At 65% H_2SO_4 the rate is 1.7×10^{-3} sec^{-1}.[16]

Therefore, the rate of α-acetoxystyrenes by this mechanism would be even slower by several orders of magnitude. As the rate of α-acetoxystyrene extrapolated to 65% H_2SO_4 is about 6.3 sec^{-1}, this mechanism is completely excluded.

(27) C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47**, 194 (1964).

(28) The calculation was performed by assuming a ρ of -5 and using the rate for p-$CH_3OC_6H_4CH_2Cl$ (J. W. Baker, *J. Chem. Soc.*, 2506 (1951)) along with the fact that alkyl bromides react about 40 times faster than alkyl chlorides (A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 82).

Kinetics of the Cerium (IV) Oxidation of Benzaldehyde[1]

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Abstract: The kinetics of the cerium(IV) oxidation of benzaldehyde to benzoic acid were studied in 85% aqueous acetic acid. The first reaction was the formation of a 1:1 benzaldehyde–ceric ion complex. This was followed by an acid-catalyzed decomposition of the complex as well as of a 2:1 benzaldehyde–ceric ion complex which is present in relatively low concentration. Evidence was found for the formation of benzoyl radicals as an intermediate, and the reaction was found to give a kinetic isotope effect.

Cerium(IV) is one of a group of metal ion oxidants which apparently react only *via* one-electron steps. Thus, in the oxidation of thallium(I) by ceric nitrate,[3] kinetic results indicate the intermediacy of the highly unstable thallium(II) species rather than a two-electron step leading to cerium(II). The oxidation of chromium(III) to chromium(VI) by ceric sulfate also was shown to proceed *via* consecutive one-electron steps.[4]

A typical mode of oxidation of aliphatic aldehydes and ketones by one-electron metal ion oxidants involves coordination with the carbonyl group followed by the

(1) This investigation was supported by the National Science Foundation.

(2) Taken in part from the Ph.D. Thesis of P. C. F., 1966. National Institutes of Health Predoctoral Fellow, 1963–1966.

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