the solvent in this instance. Calculation of K_{eq} gives $K_{eq} = 4.88 \times 1/30/(1 \times 1 \times 3.0) = 0.54$, agreeing with the value in Table I.

In conclusion, a self-consistent interpretation of the deuterium isotope effects on the hydration of 1-phenyl-1,3-butadiene and the dehydration of 1-phenyl-3-methylallyl alcohol is obtained in terms of the mechanism previously proposed. While this is evidence for the correctness of the mechanism, it should be borne in mind that it involves several important assumptions: first, that the solvation energies of the various species are the same in protic or deuterated solvents; second, that the solvation energies of deuterated and nondeuterated substrates are the same in a given solvent; and third, that the basicities of water and deuterium oxide toward these carbon acids are much the same. Whereas this last assumption is not generally true, it does apply to very strong acids,[24] which these carbonium ions are.

Comparison of k_h for Cases I and II gives a mean primary solvent isotope effect for hydration of 2.97, compared to 2.3–3.3 for styrene.[7] Also, comparison of k_d for Cases II and IVb or I and IIIb gives a combined primary and secondary isotope effect for dehydration of 5.5. The magnitudes of these effects are of interest, because they are a more quantitative indication of the degree of stretching of the C–H bond in the transition state.

(24) R. P. Bell, *J. Chem. Soc.*, 187 (1965).

The Mechanisms for the Acid-Catalyzed Hydrolysis of Vinyl Acetate and Isopropenyl Acetate[1]

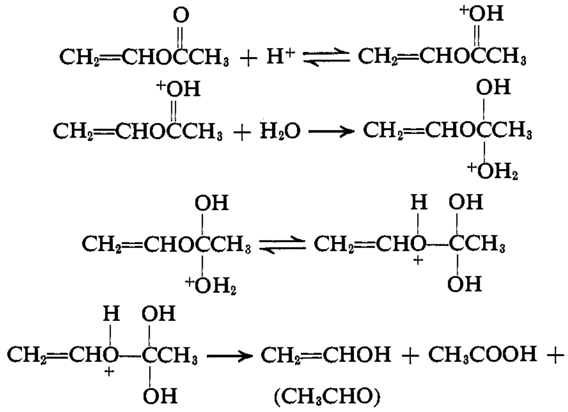
Donald S. Noyce and Ralph M. Pollack

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received July 7, 1969*

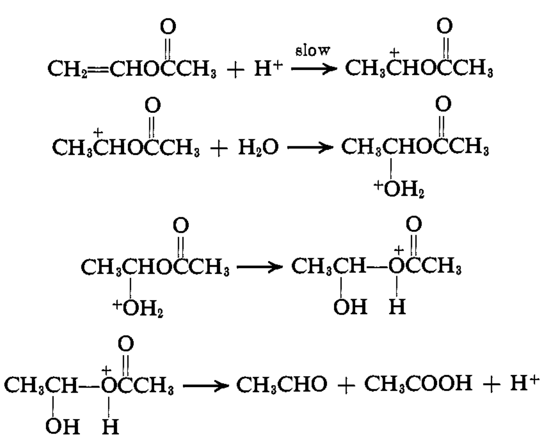
Abstract: In dilute aqueous sulfuric acid, both vinyl acetate and isopropenyl acetate hydrolyze primarily by the same mechanism as ethyl acetate. The alternative ASE2 mechanism, involving rate-determining protonation of the double bond, accounts for less than 0.5% of the rate for vinyl acetate but about 20% of the rate for isopropenyl acetate in 6% sulfuric acid. In this medium, vinyl acetate is hydrolyzed 30% faster than isopropenyl acetate and 75% faster than ethyl acetate. At higher values of the acidity, the ASE2 mechanism becomes progressively more important with the two mechanisms showing equal rates at about 13% acid for isopropenyl acetate and 50% acid for vinyl acetate. The rate of isopropenyl acetate, extrapolated to 60% acid, is about 100 times faster than vinyl acetate at the same acidity and about 1.5 times faster than α-acetoxystyrene. Observed solvent isotope effects (k_{H_2O}/k_{D_2O}) are 0.73 in 6% acid and 2.69 in 59% acid for vinyl acetate; for isopropenyl acetate the values are 1.06 in 6% acid and 3.20 in 40% acid. Effects of methyl and phenyl substitution α to a potential carbonium ion site are discussed.

Although studies of the acid-catalyzed hydrolysis of saturated esters have been extensive and the mechanisms by which these reactions occur are well understood, less work has been done on vinyl esters. Two mechanisms have been proposed for the hydrolysis of vinyl esters. Scheme I is the same as the mechanism by which the majority of saturated esters hydrolyze in acid, involving equilibrium protonation on the carbonyl carbon followed by attack of water and collapse to products. Scheme II is the ASE2 mechanism, which consists of a rate-determining protonation of the double bond with subsequent fast reaction to products in anal-

Scheme I. Mechanism for Normal Ester



Scheme II. ASE2 Mechanism



---

(1) Supported in part by a grant from the National Science Foundation, GP-6133X.

ogy with the mechanism for acid-catalyzed hydrolysis of enol ethers.[2]

Early studies on vinyl acetate gave conflicting results. In 1962, Kiprianova and Rekasheva[3] hydrolyzed vinyl acetate in a "0.8% water–ethanol solution of sulfuric acid." They reported that the product acetic acid contained only a slight excess of ^{18}O over what would be expected from exchange in the course of experiment. The conclusion drawn is that alkyl-oxygen cleavage occurs, which is consistent only with Scheme II.

In 1965, Landgrebe[4] reported results which are clearly inconsistent with this mechanism. He found that the rate of isopropenyl acetate in 0.1 N HCl at 55° in 50 wt % dioxane–water is only 0.78 that of vinyl acetate. If rate-determining protonation of the double bond were occurring, then isopropenyl acetate should be faster by several powers of 10. Landgrebe also eliminated the possibility of equilibrium protonation on the terminal carbon of the double bond by partially hydrolyzing vinyl acetate in D_2O and finding no deuterium incorporation in recovered starting material.

Yrjänä[5] pointed out further differences between vinyl ester hydrolyses and reactions which occur by double bond hydration. He found that the solvent isotope effect for vinyl acetate in dilute aqueous solution is inverse ($k_{H_2O}/k_{D_2O} = 0.73$). This result should be compared with similar inverse values observed[6,7] for normal ester hydrolyses. In contrast, solvent isotope effects of 2 or greater are normally observed for ASE2 reactions.[8,9] In addition, the rate–acidity profile of vinyl acetate in HCl[5] resembles that for ethyl acetate and is very different from that observed for ASE2 reactions.

Recently,[10] we have shown that for a series of ring-substituted α-acetoxystyrenes, both of the previously discussed mechanisms contribute to the observed rate in varying amounts. In dilute sulfuric acid, the predominant mechanism depends on the ring substituent. Those compounds with electron-donating substituents react primarily by the ASE2 route, whereas those compounds with electron-withdrawing groups react preferentially by the normal ester pathway. As the concentration of acid is increased, the relative importance of the ASE2 pathway becomes greater. At sufficiently high acidity, all of the compounds studied hydrolyze primarily by rate-determining protonation of the double bond.

In this paper we report an extension of the previous study to both vinyl acetate and isopropenyl acetate, in order to determine the relative importance of the two mechanisms in dilute and moderately concentrated sulfuric acid for these compounds.

Experimental Section

Commercial vinyl acetate and isopropenyl acetate were distilled on a spinning band column before use: vinyl acetate, bp 72.5° (lit.[5] bp 72°), isopropenyl acetate, bp 96.0° (lit.[5] bp 97°). The deuteriosulfuric acid was prepared as described earlier.[11]

Rates were measured by following the change in absorbance due to the product in the ultraviolet spectrum. Since the extinction coefficients for acetone and acetaldehyde are very low, relatively high concentrations of substrate had to be used. Concentrations were 2.0×10^{-2} M for both compounds except in the case of vinyl acetate at 61% acid for which the concentration was 8×10^{-3} M. Vinyl acetate was followed at 277 mμ and isopropenyl acetate at 265 mμ. The change in absorbance at these wavelengths was about 0.2–0.3.

To 3.00 ml of sulfuric acid of the requisite strength, which had been temperature equilibrated in a 1-cm quartz uv cell, 25 μl of an ethanolic stock solution of the organic substrate was added to initiate the reaction. The absorbance change was monitored by use of a Gilford 2000 spectrophotometer with a Beckman DU monochromator equipped with thermospacers. Rate measurements were made at 25.00 ± 0.02°.

To determine the final sulfuric acid concentration, weighed aliquots were titrated in duplicate against standardized sodium hydroxide. H_0 values were taken from the data of Bascombe and Bell,[12] and Jorgenson and Hartter,[13] as determined by Evett.[14] The small amount of ethanol was ignored in determining H_0 values. Solvent isotope effects were calculated at the same mole fraction of H_2SO_4 and D_2SO_4. Justification for this method as a basis for comparison has been given.[10]

All compounds gave excellent pseudo-first-order kinetics beyond 95% reaction and stable infinity points, with one exception (*vide infra*). Rate constants were calculated by using LSKIN1,[15] a least-squares computer program which calculates the best value of the first-order rate constant, treating the infinity absorbance as a variable parameter. 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 kinetics of the acid-catalyzed hydrolysis of vinyl acetate and isopropenyl acetate may be followed by observing the change in the ultraviolet spectrum due to the appearance of the product, acetaldehyde, or acetone.

The high volatility of acetaldehyde has been reported[5] to cause some difficulty. We found that this problem was overcome by sealing the cells with "Parawax" for the slower runs; there was no problem of volatility with the faster runs.

The runs in concentrated acid, however, presented a problem of a different sort. Whereas all the runs with vinyl acetate below 55% sulfuric acid gave stable infinity points for at least ten half-lives, the runs in 55 and 60% acid gave infinity points which increased with time. In 55% acid the problem was not serious because the increase in absorbance of the infinity point was very much slower than the hydrolysis reaction. In 60% acid with vinyl acetate at 2×10^{-2} M the subsequent upward drift of the absorbance following the initial rapid reaction was much more troublesome. It seems fairly certain that the complicating reaction is the polymerization of acetaldehyde. A polymerization reaction should be of higher order in acetaldehyde, and thus lowering the concentration of substrate should

---

[2] (a) A. J. Kresge and Y. Chiang, *J. Chem. Soc., B*, 53 (1967); (b) A. J. Kresge, D. S. Sagatys, and H. L. Chen, *J. Amer. Chem. Soc.*, **90**, 4174 (1968).

[3] L. A. Kiprianova and A. F. Rekasheva, *Dokl. Akad. Nauk SSSR*, **144**, 386 (1962); *Proc. Acad. Sci. USSR, Phys. Chem. Sect.*, **144**, 393 (1962).

[4] J. A. Landgrebe, *J. Org. Chem.*, 30, 2997 (1965).

[5] T. Yrjänä, *Soumen Kemistilehti, B*, **39**, 81 (1966).

[6] W. E. Nelson and J. A. V. Butler, *J. Chem. Soc.*, 957 (1938).

[7] J. C. Hornel and J. A. V. Butler, *ibid.*, 1361 (1936).

[8] D. S. Noyce, D. R. Hartter, and F. B. Miles, *J. Amer. Chem. Soc.*, **86**, 3583 (1964).

[9] A. J. Kresge and Y. Chiang, *J. Chem. Soc., B*, 58 (1967).

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

[11] D. S. Noyce, H. S. Avarbock, and W. L. Reed, *ibid.*, **84**, 1647 (1962).

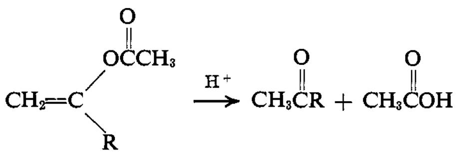
[12] K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1096 (1959).

[13] M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, **85**, 878 (1960).

[14] M. Evett, Ph.D. Dissertation, University of California, Berkeley, 1968.

[15] D. F. DeTar and C. E. DeTar in "Computer Programs for Chemistry," D. F. DeTar, Ed., W. A. Benjamin, Inc., New York, N. Y., 1968, Chapter 6.

Table I. Rates of Acid-Catalyzed Hydrolysis of Vinyl Acetate and Isopropenyl Acetate



$$CH_2{=}C(OCOCH_3)R \xrightarrow{H^+} CH_3COR + CH_3COOH$$

R	H_2SO_4, %	H_0	k, sec^{-1}	Log k	Log a_{H_2O}
H	5.77	+0.02	1.07×10^{-4}	−3.97	−0.011
	12.38	−0.54	2.71×10^{-4}	−3.57	−0.026
	20.33	−1.09	5.59×10^{-4}	−3.25	−0.057
	29.91	−1.78	1.13×10^{-3}	−2.95	−0.123
	38.07	−2.31	1.96×10^{-3}	−2.71	−0.218
	46.59	−3.05	3.38×10^{-3}	−2.47	−0.373
	55.50	−3.92	8.82×10^{-3}	−2.06	−0.620
	60.85	−4.57	2.75×10^{-2}	−1.56	−0.825
CH_3	5.82	+0.01	8.15×10^{-5}	−4.09	−0.011
	12.58	−0.56	2.54×10^{-4}	−3.60	−0.027
	20.26	−1.08	7.63×10^{-4}	−3.12	−0.056
	29.84	−1.77	2.92×10^{-3}	−2.53	−0.122
	37.97	−2.39	1.19×10^{-2}	−1.92	−0.217
	46.49	−3.04	5.96×10^{-2}	−1.22	−0.371

R	D_2SO_4, %	D_0	k, sec^{-1}	Log k	k_{H_2O}/k_{D_2O}
H	5.61	−0.01	1.53×10^{-4}	−3.82	0.73
	59.08	−4.58	1.05×10^{-2}	−1.98	2.69
CH_3	5.61	−0.01	8.17×10^{-5}	−4.09	1.06
	39.65	−2.64	7.17×10^{-3}	−2.14	3.20

lower the percentage of the competing and subsequent reaction. Reducing the concentration of vinyl acetate to 8×10^{-3} M largely alleviated these difficulties.

Aldol condensation can also explain the fact that the side reaction is more important at the higher acidities. The acid-catalyzed condensation of acetaldehyde should show a linear dependence H_0.[16] As the rate acidity profile for vinyl acetate is very shallow throughout most of the range, a condensation reaction will be more important at higher acidities. This is in agreement with our observations.

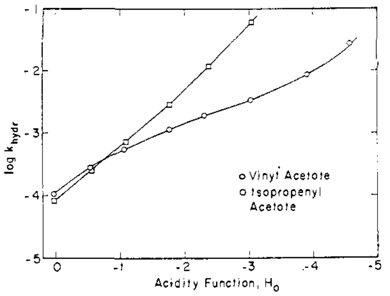


Figure 1. Acidity dependence of the rates of hydrolysis of vinyl acetate and isopropenyl acetate.

Both compounds were hydrolyzed at 25.00° with sulfuric acid concentrations ranging from 6 to 47% for isopropenyl acetate and from 6 to 60% for vinyl acetate, the conveniently accessible range for rate measurements by our techniques. The observed first-order rate constants are given in Table I.

The acidity dependence of the rates for the two esters are distinctly different. While vinyl acetate shows a generally shallow, but complex curve, isopropenyl acetate gives a much sharper response to increasing acidity (Figure 1).

Second-order rate constants may be calculated from the data at 1 M sulfuric acid ($H_0 = -0.30$). The values obtained are 1.86×10^{-4} l. mole^{-1} sec^{-1} for vinyl acetate and 1.61×10^{-4} l. mole^{-1} sec^{-1} for isopropenyl aceate. These values are in satisfactory agreement with those obtained by Yrjänä[5] for hydrolysis in hydrochloric acid, 1.45×10^{-4} l. mole^{-1} sec^{-1} for vinyl acetate and 8.74×10^{-5} l. mole^{-1} sec^{-1} for isopropenyl acetate. Very similar values have been reported for vinyl acetate by Skrabal and Palomaa.[17] Exact comparison cannot be made between present values and previous ones due to the differences in mineral acids used. If comparison is made at the same H_0 value, we obtain 1.51×10^{-4} sec^{-1} at $H_0 = -0.18$ for vinyl acetate; Yrjänä[5] gives a value of 1.42×10^{-4} sec^{-1} at this acidity.

Discussion. The two mechanisms which have been proposed for the acid-catalyzed hydrolysis of vinyl acetate and isopropenyl acetate (*vide supra*) are both reasonable and each has good analogies. In our previous paper[10] we have shown, from a consideration of rate–acidity profiles, substituent effects on the reaction rate, and solvent isotope effects, that both mechanisms contribute to the observed rate in the hydrolysis of α-acetoxystyrenes. These same techniques may be used to determine the relative importance of the normal ester mechanism and the ASE2 mechanisms for vinyl acetate and isopropenyl acetate.

As was discussed previously,[10] a plot of the logarithm of the rate *vs.* the acidity function, H_0, should give very different results for the two postulated pathways. The normal ester mechanism is characterized by a very shallow curve with the rate reaching a maximum value in 55–60% sulfuric acid.[18] In contrast, the rate–acidity

---

[16] D. S. Noyce and W. A. Pryor, *J. Amer. Chem. Soc.*, 77, 1397 (1955).

[17] (a) A. Skrabal and A. Zahorka, *Monatsh. Chem.*, **48**, 459 (1927); (b) M. H. Palomaa, E. J. Salmi, J. T. Jamsson, and T. Salo, *Ber.*, **68**, 303 (1935).

profile for ASE2 reactions is typically linear with a slope, d(log k)/dH_0, of approximately -1.0. Representative values for the slope of some ASE2 reactions are -0.93 for the hydration of phenylbenzoylacetylenes,[19] -1.0 for the isomerization of *cis*-cinnamic acid,[20] and -1.23 for the hydration of styrene.[21,22] These distinctions are exemplified by Figure 1.

Isopropenyl Acetate. For isopropenyl acetate, the rate of hydrolysis shows sharp response to increasing acidity, and is approximately linear with H_0. Closer examination shows that d(log k)/dH_0 is -0.78 in the dilute acid region, but is -1.09 at $H_0 = -3.0$. The slight upward curvature of the plot suggests that the normal ester mechanism is contributing appreciably to the observed rate at low acidities. However, it is difficult to separate the two mechanisms in this instance solely on the basis of acidity behavior.

Consideration of the magnitude of the solvent isotope effects yields much more information about the two mechanisms. An ASE2 mechanism is characterized by an isotope effect, k_{H_2O}/k_{D_2O}, of about 2–4, *e.g.*, 3.2 for the isomerization of *cis*-stilbene[23] and 4.3 for the hydrogen exchange of azulene.[24] In contrast, reactions occurring by a normal ester mechanism usually exhibit an isotope effect of less than unity. Values which have been observed include 0.73 for ethyl formate,[6] 0.60 for methyl acetate,[6] and 0.75 for *p*-nitro-α-acetoxystyrene.[10]

In 40% acid ($H_0 = -2.64$) the solvent isotope effect (k_{H_2O}/k_{D_2O}) for isopropenyl acetate is 3.20 which agrees well with what is expected for an ASE2 mechanism. In much less acidic solutions ($H_0 = -0.01$), the value of the solvent isotope effect is near unity ($k_{H_2O}/k_{D_2O} = 1.06$) indicating that there is a significant contribution to the rate from the normal ester pathway. Hydrolysis is occurring in part by each of the two mechanisms.

Bunnett[25] has suggested a method for plotting rate–acidity data which is particularly useful in analyzing reactions in which there is a change of mechanism with acidity. In this method, log k + H_0 is plotted *vs.* log a_{H_2O} and the slope of the plot defines a parameter w, which is characteristic of the mechanism. Values of w around +4 to +6 are usually obtained for normal ester hydrolyses, although higher values are sometimes observed.[25] For ASE2 reactions, however, w is near zero. Reactions which involve a change of mechanism with acidity often show a sharp break in a Bunnett plot, while a plot in the normal manner of log k *vs.* H_0 shows only a gradual change in slope.

A plot of our rate data for isopropenyl acetate by this method (Figure 2) shows a distinct break, indicating that two mechanisms are contributing to the observed rate. The w value at $H_0 = 0$ is about +3.7 which is consistent with a normal ester pathway, but the w value at $H_0 = -3.0$ is -0.20, suggesting an ASE2 mechanism. Thus, both the small value of the solvent isotope effect at low acidities and the value of w indicate that the rate in dilute acid is predominantly due to a normal ester mechanism. In addition the similarity of rates of both vinyl and isopropenyl acetate at $H_0 = 0$ argues for the normal ester pathway.

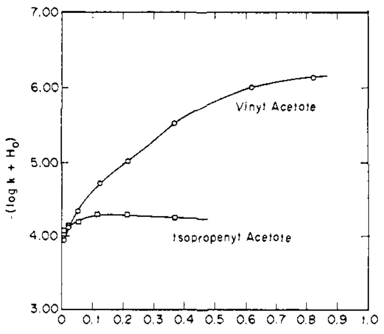


Figure 2. Bunnett plot for vinyl acetate and isopropenyl acetate.

Two procedures may be used to determine the fraction of each mechanism contributing to the hydrolysis of isopropenyl acetate at $H_0 = 0$. The line representing the ASE2 mechanism may be extended to $H_0 = 0$ to give an extrapolated rate due to that pathway, and the rate due to the normal ester mechanism may be found by substracting the ASE2 rate from the observed rate. Analysis by this method indicates that the reaction proceeds 72% by the normal ester mechanism and 28% by rate-determining protonation of the double bond.

The other procedure assumes that the isotope effect which is observed at $H_0 = 2.64$ is representative of the ASE2 mechanism and is invariant with acidity. An isotope effect for the normal ester mechanism of 0.75 can be safely assumed since a value close to this has been observed for all the α-acetoxystyrenes[10] as well as for vinyl acetate. Analysis of the observed solvent isotope effect of 1.06 at $H_0 = 0$ then indicates that the reaction is 87% normal ester and 13% ASE2.

The values calculated from the isotope effect are probably closer to the actual percentages since the extrapolation in the first method is fairly severe and a slight error in the slope used involves a relatively large error in the percentages. It is clear from both analyses, however, that the predominant mechanism for isopropenyl acetate at low acidities is the same one through which the majority of esters hydrolyze.

Vinyl Acetate. In contrast to isopropenyl acetate, the rate profile for vinyl acetate is a shallow curve until about $H_0 = -3.5$, at which point it breaks sharply upward reaching a limiting slope of -0.95. This type of plot was observed previously for *p*-nitro-α-acetoxystyrene.[10] The rate-acidity profile for vinyl acetate is virtually identical with that obtained in hydrochloric acid over the range of acidities studied by Yrjänä.[5] Unfortunately Yrjänä did not extend his measurements beyond $H_0 = -3.3$, presumably due to limitations of his experimental methods. Had he been able to follow the reaction at slightly higher acidities, he would have seen a dramatic break in the plot.

At low acidities, the normal ester mechanism completely accommodates the data for vinyl acetate, much like the situation for *p*-nitro-α-acetoxystyrene. Only this mechanism can account for the shallow curve with

---

(18) K. Yates and R. A. McClelland, *J. Amer. Chem. Soc.*, **89**, 2686 (1967).

(19) D. S. Noyce and K. E. DeBruin, *ibid.*, **90**, 372 (1968).

(20) D. S. Noyce, P. A. King, F. B. Kirby, and W. L. Reed, *ibid.*, **84**, 1644 (1962).

(21) W. M. Schubert, B. Lamm, and J. R. Keefe, *ibid.*, **86**, 4727 (1964).

(22) W. M. Schubert and B. Lamm, *ibid.*, **88**, 120 (1966).

(23) D. S. Noyce, D. R. Hartter, and F. B. Miles, *ibid.*, **90**, 4633 (1968).

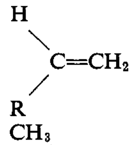
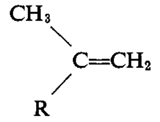
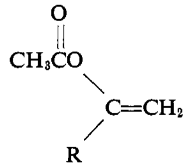
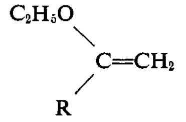
(24) L. C. Gruen and F. A. Long, *J. Amer. Chem. Soc.*, **89**, 1287 (1967).

(25) J. F. Bunnett, *ibid.*, **83**, 4956, 4968, 4973, 4978 (1961).

Table II. Second-Order Rate Constants for Vinyl Acetate and Isopropenyl Acetate in Dilute Acid

Compound	k, l. mole^{-1} sec^{-1} ASE2	 AAc2
Vinyl acetate	8×10^{-7}	1.9×10^{-4}
Isopropenyl acetate	5×10^{-6}	1.0×10^{-4}

Table III. Effects of Phenyl and Methyl Substitution in the α Position on Double Bond Reactivity

Compound	Relative rate (R = H)	$k_{R=CH_3}/k_{R=H}$	$k_{R=C_6H_5}/k_{R=H}$
	1.00[a]	2.4×10^{3} [a]	3.7×10^{4} [b]
	2.4×10^{3} [a,c]	1.0×10^{4} [c]	6.3×10^{3} [c]
	5×10^{4} [d]	6.3×10^{1} [e]	4.0×10^{1} [e]
	10^{11} [f]	3.0×10^{2} [g]	5.9×10^{1} [g]

[a] Propylene and ethylene compared by extrapolation to 145° and 100 bars from B. T. Baliga and E. Whalley, *Can. J. Chem.*, **42**, 1019 (1964); **43**, 2453 (1965). [b] Rate of styrene (ref 21 and 22) compared with α-methylstyrene [N. C. Deno, F. A. Kish, and H. J. Peterson, *J. Amer. Chem. Soc.*, **87**, 2157 (1965)] at $H_0 = -2.0$ and α-methylstyrene compared with propylene by footnote *c* and then ethylene by footnote *a*. [c] 29.5% (by weight) $HClO_4$, 38.0° [R. W. Taft, Jr., Office of Naval Research Contract No. 656(03), Project NRO 55-295 Final Report (1960)]. [d] Present work, extrapolated to $H_0 = -2.0$ and compared with α-methylstyrene (Deno, *et al.*, in footnote *b*). [e] Present work, extrapolated to $H_0 = -4.0$. [f] Reference 9, compared with vinyl acetate extrapolated to $H_0 = 0$. [g] Reference 2b.

H_0, the solvent isotope effect of 0.73 at $H_0 = -0.01$, and the fact that the rate of isopropenyl acetate is comparable to vinyl acetate.

At the very highest acidities the sharp dependence on acidity, coupled with the solvent isotope effect of 2.69 at $H_0 = -5.68$ and the fact that isopropenyl acetate hydrolyzes approximately 100 times faster in concentrated acid, is convincing evidence that the reaction is proceeding through the ASE2 pathway under these conditions. If the true isotope effect for the ASE2 reaction is assumed to be 3.20, as for the case of isopropenyl acetate, then an upper limit for the contribution of the normal ester mechanism may be calculated. A calculation of this type indicates that at $H_0 = -5.68$ the reaction is still due about 20% to the normal ester mechanism.

An approximation for the rate of vinyl acetate due to the ASE2 mechanism at all acidities may be obtained by extending the line defined by the tangent to the curve of the rate-acidity profile at high acid concentrations. Upon extending this line through the total range of acidity, it is found that the rates due to the two mechanisms are about equal at $H_0 = -3.2$, and that the rate at $H_0 = 0$ is about 0.5% due to the ASE2 mechanism and 99.5% due to the normal ester mechanism.

A Bunnett plot of the data for vinyl acetate (Figure 2) confirms the previous analysis. The plot is curved, as is expected for a change in mechanism. The limiting slopes (w) are $+8.0$ at about $H_0 = 0$ and $+1.0$ at $H_0 = -5$, which are consistent with the proposed mechanisms.

From the above analysis approximate second-order rate constants for both isopropenyl and vinyl acetates may be obtained for each of the two mechanisms at $H_0 = -0.3$ (1 M H_2SO_4). These are given in Table II.

Rates of the normal acid-catalyzed ester hydrolysis are very similar, even for very wide variation in structure. Yates and McClelland[18] have shown that the rates for the $A_{AC}2$ mechanism for a wide variety of esters are very close to 1×10^{-4} l. mole^{-1} sec^{-1}. The rate for the normal ester hydrolysis of α-acetoxystyrenes may be estimated[16] as 4.1×10^{-5} l. mole^{-1} sec^{-1}. It can be seen that the rates in 1 M acid for both vinyl acetate and isopropenyl acetate fall in the range expected for the normal ester mechanism. It appears that the slight differences in rates are due to steric factors, and a very modest influence of inductive effects.

Relative Rates of Double Bond Protonation. Table III gives the rate increases for α phenyl and α methyl substitution for various ASE2 reactions. For both ethylene and propylene, substitution of the α hydrogen by either a methyl or a phenyl group increases the rate by about 10^4. On the other hand for vinyl acetate and ethyl vinyl ether the rate increase is only about 10^2.

For the two compounds in which the positive charge formed in the carbonium ion is adjacent only to alkyl groups and hydrogens, the effect of both methyl and phenyl groups is quite substantial. In the two compounds in which the charge is adjacent to an oxygen the effect of methyl or phenyl groups is much smaller.

A comparison of the effects of methyl and phenyl groups on double bond protonations and the effects on SN1 solvolyses can also be made. The effect of a methyl group on ASE2 reactions is about the same as the effect of a phenyl group, although the magnitude can vary widely (see Table III). For the four compounds listed, the ratio $k_{C_6H_5}/k_{CH_3}$ varies from 0.2 to 15. Except for $k_{styrene}/k_{propylene}$, the ratio is approximately 0.5. Since the comparisons of styrene to propylene and ethylene had to be made by circuitous and rather extensive extrapolations, these values should be treated with some caution, and it seems safe to say that the effect of a methyl substitution on double bond protonation is very similar to the effect of phenyl substitution.

In contrast, the rates of SN1 solvolyses are enhanced considerably more by phenyl groups than by methyl groups. Streitwieser has generalized,[26] "A rough approximation is that a phenyl group is as effective in stabilizing a carbonium ion as are two methyl groups." Since both types of reactions presumably give identical carbonium ions one might expect similar effects of phenyl and methyl groups on the rates of both types of reaction.

This discrepancy might be partially resolved by taking into consideration the effects of substituents on the ground states of the substrates. In particular, both a methyl group and a phenyl group are known to stabilize double bonds. If the stabilization of the double bond by a phenyl group were *much* greater than by a methyl group, then the relative rate enhancement by a phenyl group should be less. A comparison of the heats of hydrogenation of model compounds will show whether the difference in ground state stabilization can account for the difference in relative rates. Heats of hydrogenation[27] for α-methylstyrene (26.07 kcal), isobutylene (28.11 kcal), and propylene (29.71 kcal) show that the stabilization of the ground state due to a phenyl group is approximately equal to that provided by two methyl groups. Since the same ratio holds for stabilization of carbonium ions, the relative effects of methyl and phenyl groups on double bond protonations should be the same as they are on SN1 solvolyses.

Although the above approximations are rather rough, the authors feel that they fairly represent the true situation. Further evidence for an effect in the ground state due to a phenyl group which is about twice that due to a methyl group is the fact that the phenyl/hydrogen and methyl/hydrogen ratios are similar for all of the compounds in Table III, even though the magnitude of the ratios vary widely.

Thus, it is apparent that the similarity in rates of methyl substituted and phenyl substituted compounds in ASE2 reactions cannot be explained by recourse only to ground state stabilities. Perhaps this result is indicative of substantially different transition states in the ASE2 reactions and corresponding SN1 solvolyses, and that treating both transitions states as like the product carbonium ions is not as good an assumption as is widely believed.

---

[26] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 43.

[27] American Petroleum Institute, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

General Acid Catalysis of Ketal Hydrolysis. The Hydrolysis of Tropone Diethyl Ketal

Edwin Anderson[1] and Thomas H. Fife

Contribution from the Department of Biochemistry,
University of Southern California, Los Angeles, California.
Received July 7, 1969

Abstract: The hydrolysis of tropone diethyl ketal has been studied in water at 15°. A pronounced general acid catalysis by the acid species of the buffer can be observed. The rate constant for catalysis by Tris (H^+) is less in D_2O than H_2O ($k_{DA}/k_{HA} = 0.67$). The mechanism undoubtedly involves partially rate-determining protonation by the general acid. Thus, if the carbonium-ion intermediate is of great stability general acid catalysis can be obtained even with ketals of aliphatic alcohols. At pH values greater than 10 the rate of hydrolysis is independent of pH. This pH-independent reaction has a D_2O solvent isotope effect (k_{D_2O}/k_{H_2O}) of 0.86.

It has been generally accepted that the acid-catalyzed hydrolysis of simple acetals and ketals involves an A1 mechanism with preequilibrium protonation of the substrate by hydronium ion followed by a unimolecular, rate-determining breakdown of the protonated intermediate to an alcohol and a resonance-stabilized carbonium ion.[2] Intramolecular participation by a neighboring carboxyl group[3,4] or acetamido group[5] has been postulated to occur in the hydrolysis of phenolic acetals and glycosides. Intramolecular participation was not observed, however, in the hydrolysis of a series of carboxyl-substituted ketals of aliphatic alcohols.[6] General acid catalysis by buffer acids has been found in the hydrolysis of 2-(substituted phenoxy)tetrahydropyrans when the substituent group is electron withdrawing.[7]

---

[1] Postdoctoral fellow, Department of Biochemistry, University of Southern California.

[2] E. H. Cordes, *Progr. Phys. Org. Chem.*, 4, 1 (1967).

[3] B. Capon, *Tetrahedron Lett.*, 911 (1963).

[4] B. Capon and M. C. Smith, *Chem. Commun.*, 523 (1965).

[5] D. Piszkiewicz and T. C. Bruice, *J. Amer. Chem. Soc.*, **89**, 6237 (1967).

[6] T. C. Bruice and D. Piszkiewicz, *ibid.*, **89**, 3568 (1967).

[7] T. H. Fife and L. K. Jao, *ibid.*, **90**, 4081 (1968).