was washed four times with water, dried over K_2CO_3, filtered, and concentrated at room temperature to a yellowish-green oil. On standing overnight in air, the oil formed crystals. These were filtered out and washed with *n*-hexane. Further concentration of the mother liquor yielded additional crystals. The combined crystalline material was recrystallized from dry ether, affording 0.55 g (0.002 mol, 25%), mp 86.5-88.0 °C (sealed capillary). IR: 3075, 3050, and 3015 (=C—H), 2970, and 2920 (saturated C—H), 2250 (saturated C—D), 1603 (C=C), 1385 and 1369 ($C(CH_3)_2$). NMR: δ 7.37 (aromatic multiplet 100), 1.53 (singlet 52), indicating 98% $(CD_3)_2$. UV: max at 368.0 nm (ϵ 43.82).

Acknowledgments. This research was supported in part by Grant MPS73-04683 A01 from the National Science Foundation. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

References and Notes

(1) S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, **88,** 137 (1966).
(2) S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, **88,** 143 (1966).
(3) W. A. Pryor and K. Smith, *J. Am. Chem. Soc.*, **92,** 5403 (1970).
(4) See the Experimental Section for details.
(5) G. J. Young, *J. Colloid Sci.*, **13,** 67 (1958).
(6) A quantitative analysis of the data in terms of τ_{rot} and τ_{trans} was not attempted, since this laboratory is not equipped for accurate T_1 and T_2 measurements.
(7) Koelsch's radical begins to decay at high temperatures. However, the decay and resulting decrease in concentration were shown not to be responsible for the increased resolution. The resolution was unchanged on running the temperature back down to 105 °C, obtaining a spectrum, raising the temperature to 180 °C, and again obtaining a spectrum.
(8) (a) The spectra were recorded at a power level of 0.10 mW. The line width for diphenyl nitroxide adsorbed on silica is approximately 10 G. However, parameters for the calculation of τ_{rot} from the nitroxide spectra have not been determined for this line width.[8a] The use of the value for a 3-G line width will probably cause τ_{rot} to be overestimated. (b) S. A. Goldman, G. V. Bruno, and J. H. Freed, *J. Phys. Chem.*, **76,** 1858 (1972).
(9) B. Loev and M. M. Goodman, "Progress in Separation and Purification", Vol. 3, E. S. Perry and G. J. Van Oss, Eds., Wiley, New York, 1970, pp 73-95.
(10) T. Kawamura, A. Matsunami, T. Yonezawa, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **38,** 1935 (1965).
(11) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, 1963.
(12) J. H. DeBoer and J. M. Vleeskens, *Proc. K. Ned. Akad. Wet., Ser. B,* **61,** 2 (1958).
(13) J. B. Peri and A. L. Hensley, Jr., *J. Phys. Chem.*, **72,** 2926 (1968).
(14) M. L. Hair, "Infrared Spectroscopy in Surface Chemistry", Marcel Dekker, New York, 1967.
(15) (a) M. R. Basila, *J. Chem. Phys.*, **35,** 1151 (1961). (b) P. A. Leermakers, H. T. Thomas, L. D. Weis, and F. C. James, *J. Am. Chem. Soc.*, **88,** 5075 (1966).
(16) (a) M. V. Kurashev, B. V. Romanouskii, and N. V. Kolesnichenko, *Neftekhimiya*, **17,** 507 (1977). (b) K. J. Skinner, R. J. Blaskiewica, and J. M. McBride, *Isr. J. Chem.*, **10,** 457 (1972); K. J. Skinner, H. A. Hochster, and J. M. McBride, *J. Am. Chem. Soc.*, **96,** 4698 (1974).
(17) BDPA is stable at 55 °C on the pure silicas and decomposes only to the extent of 6-10% in ten or so azocumene half-lives on P_0 silica. Galvinoxyl was too unstable, decreasing to zero concentration in 24 h. The spin trap nitrosobenzene on silica by itself generates a radical signal, presumably due to a nitroxide. *N-tert*-Butyl-α-phenylnitrone[18] failed to trap any cumyl radicals.
(18) E. G. Janzen, *Acc. Chem. Res.*, **4,** 31 (1971).
(19) The central bond of the dicumyls is too weak to permit observation of the molecular ion. There is also a substantial isotope effect on the sensitivity of the mass spectrometric determination, with d_{12} considerably underestimated and d_6 somewhat less so. Part of this error is cancelled in eq 9.
(20) An analogous principle for rotations about bonds predicts that the greater the number of rotational potential energy minima, the lower the energy barrier.
(21) At this fraction of an azobenzene monolayer a rough estimate of the average distance between azobenzene molecules is about 50 Å, or six times the diameter of a cumyl radical.
(22) R. P. Bell, *Chem. Soc. Rev.*, **3,** 513 (1974).
(23) I. D. Gay, *J. Phys. Chem.*, **78,** 38 (1974).
(24) D. Geschke, W. D. Hoffmann, and D. Deininger, *Surf. Sci.* **57,** 559 (1976).
(25) D. Michel, *Surf. Sci.*, **42,** 453 (1974).
(26) J. J. Zupancic, "Radical Reactions on Silica Surfaces: Azocumene," Dissertation, Florida State University, December 1978.
(27) J. S. Fowler, *J. Org. Chem.*, **37,** 510 (1972).
(28) A. C. Cope, T. T. Foster, and P. H. Towle, *J. Am. Chem. Soc.*, **71,** 3929 (1949).
(29) H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *J. Am. Chem. Soc.*, **79,** 1897 (1957).
(30) J. Weinstock, *J. Org. Chem.*, **26,** 3511 (1961).
(31) F. W. Hoover and H. S. Rothrock, *J. Org. Chem.*, **29,** 143 (1964).
(32) A. Lambert, J. D. Rose, and B. C. L. Weedon, *J. Chem. Soc.*, 42 (1949).
(33) F. D. Greene, J. C. Stowell, and W. R. Bergmark, *J. Org. Chem.*, **34,** 2263 (1969).

Mechanism of Hydrolysis of Allenyl Acetates

Doris J. Scheffel, A. Randolph Cole, Dorothy M. Jung, and M. D. Schiavelli*

Contribution from The Department of Chemistry,
College of William and Mary, Williamsburg, Virginia 23185.
Received May 18, 1979

Abstract: The acid-catalyzed hydrolyses of $R_2C{=}C{=}CHOAc$ proceed by two mechanisms depending upon the degree of substitution at C-3. The monomethyl derivative exhibits acidity dependence, activation parameters, and a solvent isotope effect, $k_{H_2O}/k_{D_2O} = 0.87$, characteristic of normal ester hydrolysis, while the dimethyl derivative exhibits behavior characteristic of a slow proton transfer mechanism with $k_{H_2O}/k_{D_2O} = 1.46$. A study of α- and β-secondary isotope effects in the hydrolysis of the dimethyl derivative strongly supports this conclusion. For this compound, $k_H/k_{\alpha\text{-D}} = 1.00$ and $k_H/k_{\beta\text{-}d_6} = 1.08$.

The elegant work of Noyce and Pollack[1,2] has demonstrated that the acid-catalyzed hydrolysis of enol acetates such as ring-substituted α-acetoxy styrenes, isopropenyl acetate, and vinyl acetate may proceed by two different pathways. At low acidities or when strongly electron-withdrawing substituents are present, a "normal" ester hydrolysis pathway is followed. Thus in 6% H_2SO_4, vinyl acetate and α-acetoxy-*p*-nitrostyrene show solvent isotope effects, k_{H_2O}/k_{D_2O}, of 0.73 and 0.75, respectively. These effects strongly imply an equilibrium proton transfer mechanism is involved. In contrast, at higher acidities, each of these compounds shows a marked change in behavior with solvent isotope effects, k_{H_2O}/k_{D_2O}, being 2.69 (59% H_2SO_4) for vinyl acetate and 3.25 (69% H_2SO_4) for α-acetoxy-*p*-nitrostyrene. These data imply a change in mechanism at higher acidity to one which involves slow proton transfer to carbon. Strong support for this conclusion was provided by a study of substituent effects in the α-acetoxy styrenes where $\rho = -1.9$ at $H_0 = -2.6$. Interestingly α-acetoxy-*p*-methoxystyrene exhibits behavior suggestive of rate-limiting proton transfer at both low and high acidities. For this compound $k_{H_2O}/k_{D_2O} = 2.50$. More recent work by Tidwell et al.[3] and Loudon et al.[4] supports the earlier findings of Noyce and Pollack and further demonstrates the fine balance between the two mechanisms proposed.

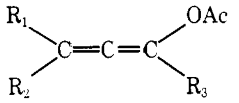
0002-7863/80/1502-0267$01.00/0

Table I. Pseudo-First-Order Rates of Acid-Catalyzed Hydrolysis of **1** and **2** in Aqueous H_2SO_4

compound	T, °C	wt % H_2SO_4[a]	H_0[b]	10^4k_{obsd}, s^{-1}
1	24.64 ± 0.01	0.264	1.40	0.284
		0.462	1.16	0.497
		0.851	0.89	0.940 ± 0.005
		0.960	0.84	0.994
		2.17	0.49	2.39
		3.01	0.34	3.54
		0.477[c]	1.21	0.309
		1.15[c]	0.84	0.745
		1.45[c]	0.72	0.937
		1.96[c]	0.58	1.29
		2.78[c]	0.40	1.93
	44.10 ± .02	0.033	2.21	0.209
		0.048	2.06	0.312
		0.104	1.70	0.560
		0.264	1.40	1.39
		0.539	1.08	2.40
		0.710	0.95	3.71
2	24.69 ± 0.01	2.14	0.50	0.454
		2.97	0.36	0.601
		4.95	0.095	0.964
		7.00	−0.10	1.41
		9.98	−0.35	2.29
		1.66[c]	0.68	0.350
		1.85[c]	0.63	0.415
		4.99[c]	0.06	1.03
		6.17[c]	−0.08	1.43
		7.32[c]	−0.18	1.84
		8.88[c]	−0.31	2.60
		11.21[c]	−0.45	3.35
	44.10 ± 0.02	0.264	1.40	0.270
		0.539	1.08	0.484
		0.940	0.850	0.769
		2.15	0.39	1.96
		2.99	0.35	2.38

[a] 5% (v/v) ethanol. [b] D_0 for D_2SO_4 solutions, assumes $H_0 = D_0$ at same molarity. [c] Wt % D_2SO_4.

We wish to report that the acid-catalyzed hydrolysis of allenyl acetates, **1** and **2**, also appears to occur by the two mechanisms proposed above and that minor structural changes elicit a marked mechanistic change.



1, $R_1 = R_3 = H$; $R_2 = CH_3$
2a, $R_1 = R_2 = CH_3$; $R_3 = H$
2b, $R_1 = R_2 = CH_3$; $R_3 = D$
2c, $R_1 = R_2 = CD_3$; $R_3 = H$

Experimental Section

Allenyl acetates **1** and **2** were prepared by the Ag^+-catalyzed rearrangement of the corresponding propargyl acetates as described earlier.[5] Each sample was purified by preparative GLC immediately prior to use (0.5 in. × 10 ft SE-30, 100 °C). Spectrophotometric rate constants were measured by using a Gilford Model 240 UV-vis spectrophotometer interfaced with a Chronolog 32001 digital clock and Wang Model 600 advanced programmable calculator allowing the acquisition of 200 points per run. Cell temperature control of ±0.01 °C was afforded by a PRT-sensed proportional temperature controller system. Temperature measurement was accomplished with a Hewlett-Packard quartz thermometer.

Table II. Summary of Acidity Dependence Data from Table I: $\log k_{obsd} = mH_0 + \log k_0$

compound	conditions	$-m$	$\log k_0$	r
1	25 °C, 0.26-3.01% H_2SO_4	1.031	−3.110	0.9994
	25 °C, 0.48-2.78% D_2SO_4	0.977	−3.320	0.9996
	44 °C, 0.03-0.71% H_2SO_4	0.970	−2.539	0.9967
2	25 °C, 2.14-9.98% H_2SO_4	0.829	−3.932	0.9999
	25 °C, 1.66-11.21% D_2SO_4	0.851	−3.870	0.9986
	44 °C, 0.26-2.99% H_2SO_4	0.889	−3.342	0.9984

Table III. α- and β-Secondary Isotope Effects at 25.0 °C

compounds	H_0	k_H/k_D[a]
2a/2b	0.89	1.00 ± 0.009[b]
2a/2c	1.40	1.07 ± 0.005[c]
	1.16	1.09 ± 0.008[c]
	0.89	1.07 ± 0.01[c]

[a] Per α-D or per β-d_6 as indicated. [b] Average of paired duplicate runs. [c] Average of paired triplicate runs.

Table IV. Hydrolysis of **2a** in Formic Acid- Sodium Formate Buffer at 44.10 °C

$M_{MCO_2H}/M_{HCO_2^-}$	pH	10^5k, s^{-1}
0.288/0.144	3.39	3.03
0.230/0.115	3.38	2.42
0.173/0.086	3.37	1.73
0.115/0.0576	3.38	1.15

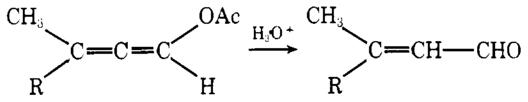
A 1.0×10^{-2} M stock solution of the ester was prepared in distilled 95% ethanol. In a typical kinetic run, 1.0 mL of the stock solution was diluted to 25 mL with aqueous sulfuric acid resulting in a final concentration of 4×10^{-4} M in ester. The appearance of product absorbance at 253 nm was observed as described above. In all other respects, kinetic runs were carried out and rate constants calculated as described earlier.[6]

Results

Excellent pseudo-first-order rate constants with random residual plots were obtained to >95% reaction. Infinity absorbances indicated that the hydrolysis proceeded to >98% completion before decomposition of the product acroleins became important. Values of the acidity functions H_0 and D_0 are available for this medium.[7] Table I presents the LSKIN 1-calculated rate data obtained in this study. Table II summarizes the acidity dependence data and Table III the α- and β-secondary isotope effects obtained from paired runs of isotopically substituted compounds. The activation parameters calculated from these data at $H_0 = 0.0$ at 25 °C for **1** are $\Delta H^{\ddagger} = 14.4$ kcal/mol and $\Delta S^{\ddagger} = -36.2$ eu and for **2a** at $H_0 = 0.80$ at 25 °C $\Delta H^{\ddagger} = 15.7$ kcal/mol and $\Delta S^{\ddagger} = -31.3$ eu. The solvent isotope effects are calculated to be $k_{H_2O}/k_{D_2O} = 0.87$ at $H_0 = 0.0$ for **1** and $k_{H_2}/k_{D_2O} = 1.47$ at $H_0 = 0.80$ for **2a.** Table IV summarizes the effect of changing buffer concentrations on the rate of hydrolysis of **2a.** These data yield $k_{HCO_2H} = 11.0 \times 10^{-5}$ s^{-1} M^{-1} from the least-squares line.[8]

Discussion

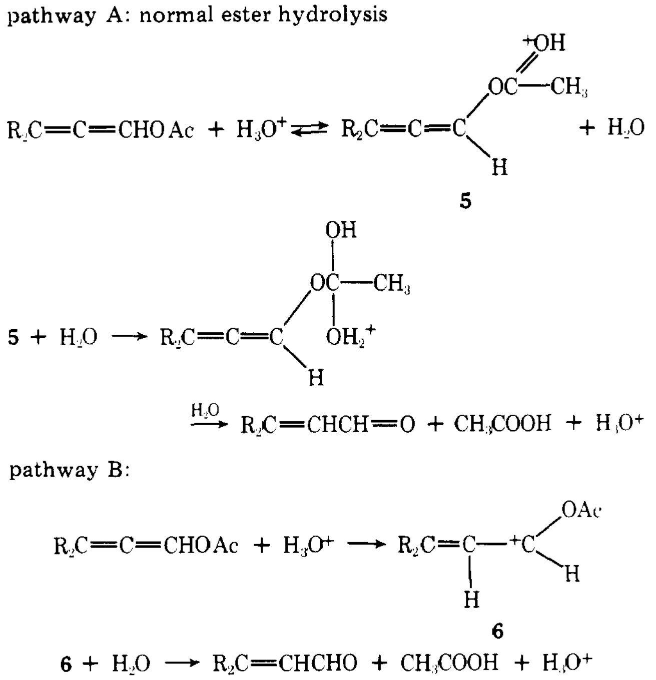
The acid-catalyzed hydrolyses of **1** and **2** yield the corresponding α,β-unsaturated aldehydes **3** and **4** nearly quanti-



1, R = H
2, R = CH_3

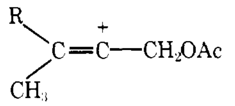
3, R = H
4, R = CH_3

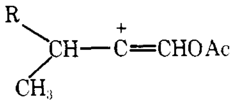
Scheme I



tatively as evidenced by the UV spectrum of the infinity kinetic solutions. Two reasonable mechanisms may be proposed as shown in Scheme I. Two alternative mechanisms may be rejected as unreasonable.[9] These are (1) direct solvolysis of **1** or **2** to an allenyl cation and (2) protonation at a terminal, rather than central, carbon atom of the allene moiety. In the first instance the allenyl cation derived from solvolysis of an allenyl acetate would be expected to yield substantial amounts of propargyl alcohols as products.[13] None are observed. Additionally the rate of solvolysis of **2a** can be estimated from the rate of solvolysis of $(CH_3)_2C{=}C{=}CHBr$ to be at least 10^6 times slower than the observed rate of hydrolysis.[14,15]

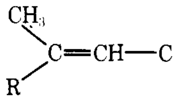
Protonation at a terminal carbon would lead to vinyl cations **7** or **8**, neither of which is expected to be particularly stable in contrast to the allylic cations proposed as intermediates in pathway B nor would they be expected to yield the observed products.


7


8

The pseudo-first-order behavior, the acidity dependence, and the large negative entropy of activation are all consistent with the two pathways proposed. The acid-catalyzed hydrolysis of ethoxypropadiene which is reported by Drenth et al. to proceed by an $A_{SE}2$ mechanism shows a similar acidity dependence and activation parameters.[16] An examination of the solvent isotope effects suggests that **1** and **2** follow different pathways in the hydrolysis reaction. The inverse solvent isotope effect, $k_{H_2O}/k_{D_2O} = 0.87$, observed in hydrolysis of **1** is consistent with an equilibrium proton transfer step as depicted in pathway A. The magnitude of the effect is comparable to that observed in a wide variety of normal ester hydrolyses such as that for vinyl acetate,[2] $k_{H_2}/k_{D_2O} = 0.73$, ethyl formate,[17] $k_{H_2O}/k_{D_2O} = 0.73$ methyl acetate,[18] $k_{H_2O}/k_{D_2O} = 0.60$, or α-acetoxystyrene,[1] $k_{H_2O}/k_{D_2O} = 0.83$.

In contrast, the solvent isotope effect observed in the hydrolysis of **2a** is consistent with an $A_{SE}2$ mechanism, i.e., $k_{H_2O}/k_{D_2O} = 1.46$. This suggests that rate-limiting proton transfer (pathway B) has become important in the hydrolysis of this compound. Additional evidence supporting this conclusion may be gained from a consideration of the relative rates of hydrolysis of **1** and **2**, $k_{2a}/k_1 = 5.37$. In the solvolysis of allyl halides **9** and **10** the addition of a methyl group results in a 1585-fold increase in rate.[19,20] It may be argued therefore that since **1** exhibits reactivity apparently higher than expected a change of mechanism from $A_{SE}2$ (compound **2**) to normal ester hydrolysis is occurring. A similar situation obtains in the hydrolysis of vinyl acetate and isopropenyl acetate where $k_{\text{isopropenyl}}/k_{\text{vinyl}}$ varies from 1.07 at low acidities to 17.8 at moderate acidities. Noyce and Pollack interpreted this change to indicate that the methyl-substituted compound, isopropenyl acetate, hydrolyzes by a normal acid-catalyzed ester hydrolysis mechanism at low acidity and by a slow proton transfer mechanism at higher acidity while vinyl acetate exhibited uniform behavior consistent with normal ester hydrolysis. The solvent isotope effect for isopropenyl acetate varied from $k_{H_2O}/k_{D_2O} = 1.06$ at low acidity to 3.20 at high acidity. In comparison $k_{H_2O}/k_{D_2O} = 3.05$ in the hydrolysis of ethoxypropadiene.[16]

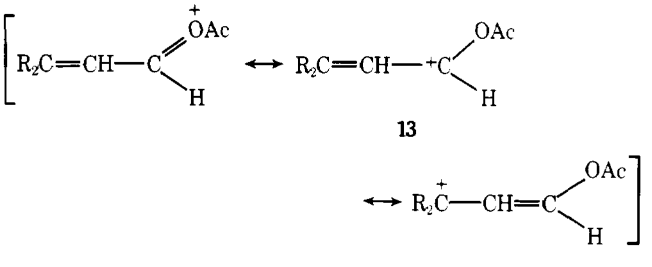

9, R = H
10, R = CH_3

Examination of the α- and β-secondary isotope effects (Table III) lends further strong support to our conclusions. As expected $k_H/k_{\alpha\text{-D}}$ is unity owing to a lack of rehybridization at C-1 in either mechanism. Similar results are observed in the solvolysis of **11** and **12** where the deuterium substitution indicated does not observably affect the rate of solvolysis.[21,22]

$$\underset{\mathbf{11}}{CD_2{=}CHC(CH_3)_2Cl} \qquad \underset{\mathbf{12}}{D{-}C{\equiv}C{-}C(CH_3)_2Cl}$$

It does provide additional support against the two mechanisms previously rejected since each requires rehybridization at C-1. Similarly, secondary deuterium isotope effects associated with a number of polar electrophilic additions to styrene are found to be 0.97–1.00.[23,24]

The β-secondary isotope effect, $k_{2a}/k_{2c} = 1.08 \pm 0.01$, strongly implies the development of positive charge at C-3 as suggested by pathway B. Some rotation about the C-1, C-2 bond must occur if even partial overlap of the developing vacant p-orbital with the allylic π-bond needed for stabilization is to be achieved. The degree of positive charge developed at C-3 and thus the magnitude of $k_H/k_{\beta\text{-CD}_3}$ depends upon three factors. First the cation **13** may be modestly stabilized by the α oxygen of the acetate group, thus reducing demand for π stabilization.[3] Secondly, $k_H/k_{\beta\text{-CD}_3}$ depends upon the extent of proton transfer at the transition state. We did not extend our general acid catalysis work to obtain a Brønsted α for this reaction. The hydrolysis of **2a** does, however, demonstrate general acid catalysis as expected.


13

Finally the extent of rotation about the C-1, C-2 bond determines the degree of interaction of the allylic β-bond with the developing vacant p orbital. Thus, reduced hyperconjugative demand due to the α oxygen, a small degree of proton transfer at the transition state and only partial rotation each may act to reduce the magnitude of the β-secondary isotope effect. The observed effect/β-CD_3 of 1.04 is lower than that observed in the solvolysis of allylic halides, as **14**, where $k_H/k_{\beta\text{-}CD_3} = 1.13$.[25]

$$CD_3CH{=}CHCH(Cl)CH_3$$

14

This implies substantial reduction of hyperconjugative demand at C-3 owing to a combination of the three factors described. Such lowering of hyperconjugative demand with attendant reduction of β-isotope effects is not unusual. Shiner et al.[26] demonstrated such an effect on the solvolysis of the tertiary halides, **15–17**,

$$H{-}C{\equiv}C{-}C(CD_3)_2Cl \qquad CH_3{-}C{\equiv}C{-}C(CD_3)_2Cl$$

15 **16**

$$:^{-}C{\equiv}C{-}C(CD_3)_2Cl$$

17

where solvolytic reactivity increases markedly but the β-d_3 effects drop off from 1.35 to 1.29 to 1.14 along the series **15** → **16** → **17.** A reduced β-d_3 effect, $k_H/k_{\beta\text{-}d_3} = 1.06$, is observed[27] in the hydrolysis of ketals where an α oxygen reduces hyperconjugative demand from the α-CH_3.

Thus we conclude that the acidity dependence, including the observation of general acid catalysis for **2a,** solvent isotope effects, α- and β-secondary deuterium isotope effects, and the activation parameters, strongly support a mechanism of hydrolysis of **2** which involves rate-limiting proton transfer (pathway B).[28] We further conclude therefore that hydrolysis of **1** occurs by a normal ester hydrolysis mechanism (pathway A).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References and Notes

(1) D. S. Noyce and R. M. Pollack, *J. Am. Chem. Soc.,* **91,** 119 (1969).
(2) D. S. Noyce and R. M. Pollack, *J. Am. Chem. Soc.,* **91,** 7158 (1969).
(3) S. Y. Attia, J. P. Berry, K. M. Kochy, Y.-K. Leung, E. P. Lyznicki, Jr., V. J. Nowlan, K. Oyama, and T. T. Tidwell, *J. Am. Chem. Soc.,* **99,** 3401 (1977).
(4) M. Novak and G. Marc Loudon, *J. Org. Chem.,* **42,** 2449 (1977).
(5) D. G. Oelberg and M. D. Schiavelli, *J. Org. Chem.,* **42,** 1804 (1977).
(6) M. Edens, D. Boerner, C. R. Chase, D. Nass, and M. D. Schiavelli, *J. Org. Chem.,* **42,** 3403 (1977).
(7) D. S. Noyce and M. D. Schiavelli, *J. Am. Chem. Soc.,* **90,** 1020 (1968).
(8) A maximum value of $k_{H_3O^+}$ for **2a** of 4.9×10^{-10} M^{-1} s^{-1} calculated from these data is unreasonably small. At $H_0 = 0.0$, $k_{obsd} = 4.6 \times 10^{-4}$ s^{-1} at 44 °C. This value should approximate $k_{H_3O^+}$. A small change in the slope of the k_{obsd} vs. [HCO_2H] would yield adequate agreement. If, for example, k_{HCO_2H} were in error by only 5%, the value of $k_{H_3O^+}$ predicted from these buffer data would be 4.2×10^{-4} M^{-1} s^{-1}.
(9) Pathway B does not specify whether hydrolysis occurs with alkyl or acyl oxygen fission. In the acid-catalyzed hydrolysis of styryl phosphates,[10,11,12] ^{18}O labeling has demonstrated C–O cleavage as the apparently exclusive mode of reaction. Our studies do not provide an answer to this question but C–O cleavage at the original allenyl carbon is likely.
(10) C. A. Bunton and L. Robinson, *J. Am. Chem. Soc.,* **91,** 6072 (1969).
(11) R. D. Frampton, T. T. Tidwell, and V. A. Young, *J. Am. Chem. Soc.,* **94,** 1271 (1971).
(12) E. P. Lyznicki and T. T. Tidwell, *J. Am. Chem. Soc.,* **94,** 3676 (1972); *ibid.,* **95,** 4935 (1973).
(13) M. D. Schiavelli, E. P. Gilbert, W. A. Boynton, and C. J. Boswell, *J. Am. Chem. Soc.,* **94,** 5061 (1972).
(14) D. J. Scheffel, P. J. Abbott, G. J. Fitzpatrick, and M. D. Schiavelli, *J. Am. Chem. Soc.,* **99,** 3769 (1977).
(15) D. S. Noyce and J. A. Virgilio, *J. Org. Chem.,* **37,** 2643 (1972).
(16) I. De Jonge and W. Drenth, *Recl. Trav. Chim. Pays-Bas,* **92,** 420 (1973).
(17) W. E. Nelson and J. A. V. Butler, *J. Chem. Soc.,* 957 (1938).
(18) J. Hornel and J. A. V. Butler, *J. Chem. Soc.,* 1361 (1936).
(19) R. H. De Wolfe and W. G. Young, *Chem. Rev.,* **56,** 753 (1956).
(20) H. C. Brown, C. G. Rao, and M. Ravindranathan, *J. Org. Chem.,* **43,** 4939 (1978).
(21) V. Belancic-Lipovac, S. Borcic, and D. E. Sunko, *Croat. Chem. Acta,* **37,** 61 (1965).
(22) V. J. Shiner, Jr., J. W. Wilson, G. Heinemann, and N. Solliday, *J. Am. Chem. Soc.,* **84,** 2408 (1962).
(23) C. L. Wilkins and T. W. Regulski, *J. Am. Chem. Soc.,* **94,** 6016 (1972).
(24) W. M. Schubert and B. Lamm, *J. Am. Chem. Soc.,* **88,** 120 (1966).
(25) J. G. Jewett and R. P. Dunlap, *J. Am. Chem. Soc.,* **90,** 809 (1968).
(26) V. J. Shiner, Jr., and G. S. Kriz, *J. Am. Chem. Soc.,* **86,** 2643 (1964).
(27) V. J. Shiner, Jr., and S. Cross, *J. Am. Chem. Soc.,* **79,** 3599 (1957).
(28) A Bronsted α may be calculated to be 0.11 from the meager general acid catalysis data given. This implies a small degree of proton transfer at the transition state and is consistent with the small solvent isotope effect observed. An alternative explanation is that two mechanisms are active in the hydrolysis of **2**, one with a large solvent isotope effect and the other with an inverse effect. While our data do not rule out such an explanation, one might expect to observe nonlinearity in the acidity dependence plot at very low or very high acidities. Within the range of our experiments such is not the case.