Vinyl Ether Hydrolysis.
The Facile General Acid Catalyzed Conversion of
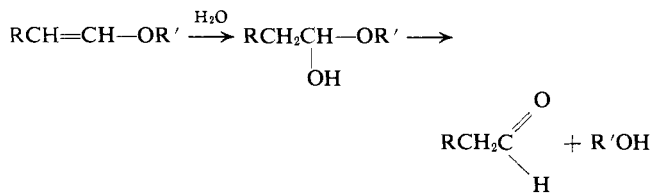## 2-Ethoxy-1-Cyclopentene-1-carboxylic Acid to Cyclopentanone

Thomas H. Fife

Contribution from the Department of Biochemistry, University of Southern California, Los Angeles, California. Received July 1, 1964

The rate of conversion of 2-ethoxy-1-cyclopentene-1-carboxylic acid and its anion to cyclopentanone was studied as a function of pH (1.85 to 7.0) and buffer concentration at 30°. At low pH where the acid is in the un-ionized state, a hydronium ion catalyzed reaction takes place which on the basis of D_2O solvent isotope effects can be considered to involve a rate-determining protonation step. The pH–rate profile in the pH region near the pK_a of the carboxyl group shows a large plateau which can be considered to be due to a rate-determining protonation of the anion by hydronium ion with rates of greater magnitude than for the un-ionized species, or protonation of the double bond in concert with a carboxylate anion catalyzed reaction. The rate of the reaction is greatly increased by increasing buffer concentration with general acids catalyzing the reaction of both the acid and the ethyl ester.

Introduction

It has been established that vinyl ethers generally hydrolyze rapidly in dilute acid at moderate temperatures.[1] This high reactivity is in marked contrast to the stability normally exhibited by dialkyl ethers to these conditions. The hydrolysis of a vinyl ether in H_2O^{18} results in the formation of an alcohol containing no O^{18}; therefore, cleavage occurs between oxygen and the olefinic carbon.[2] A hemiacetal was considered to be a probable intermediate in the reaction. Thus, if

$$RCH{=}CH{-}OR' \xrightarrow{\text{H}_2\text{O}} RCH_2\underset{\overset{|}{OH}}{CH}{-}OR' \longrightarrow$$

$$RCH_2C\overset{\displaystyle O}{\underset{\displaystyle H}{\diagup\!\!\!\diagdown}} + R'OH$$

this scheme is correct, the first stage of vinyl ether hydrolysis is mechanistically similar to the acid-catalyzed hydration of olefins with rates of hydration that are rapid under mild conditions of acidity and temperature. It was thought, therefore, that a study of vinyl ethers might shed light not only on the mechanism of hydrolysis of this interesting class of compounds but also on the mechanism of olefin hydration. In view of the intramolecular carboxyl group and carboxylate anion participation in the hydration of the fumarate monoanion,[3] a study was undertaken of 2-ethoxy-1-cyclopentene-1-carboxylic acid (1) to determine the

effects of neighboring carboxyl group substitution on vinyl ether hydrolysis.

Experimental

Chemicals. 2-Ethoxy-1-cyclopentene-1-carboxylic acid (1) was prepared by the method of Mayer and Gebhardt[4] (m.p. 134°, lit.[4] 134°). Ethyl 2-ethoxy-1-cyclopentene-1-carboxylate was also prepared by the method of Mayer and Gebhardt[4] (b.p. 88° at 3 mm., $n^{25}D$ 1.4812; lit.[4] b.p. 122.5° at 12 mm., $n^{20}D$ 1.4709).

Apparatus. All spectrophotometric studies were conducted on a Model PMQ 11 Zeiss spectrophotometer. All pH measurements were made on a Model 22 Radiometer pH meter at the same constant temperature as employed in the kinetic runs. Constant temperature in the kinetic studies was maintained by circulating water at 30 ± 0.1°, from a Haake Model F constant-temperature circulating bath, through a Zeiss constant-temperature cell holder. In the determination of the pK_a of 1 a Radiometer TTT-1 autotitrator was employed utilizing a Metrohm EA 115 X electrode in an airtight Metrohm cell. The same constant temperature and ionic strength were employed as in the kinetic runs.

Kinetic Measurements. Kinetic studies were carried out in water, D_2O, and 10% dioxane–water at 30 ± 0.1° and at a constant ionic strength of 0.25 M made up with KCl. At pH values less than 3.0 constant pH was maintained by excess hydrochloric acid and at two pH values by a chloroacetate buffer. At values above pH 3.0 buffered solutions were employed with the formate, acetate, phosphate $(H_2PO_4^-/HPO_4^{2-})$, pyridine, and imidazole studied. In experiments in which chloroacetate, pyridine, or imidazole served as the buffer, ionic strength was 1.0 M.

The acid or ester was weighed into a 10-ml. volumetric flask and the flask was filled to the mark with the proper buffer solution and shaken vigorously until the material was completely in solution. The solution was then allowed to come to constant temperature (30 ± 0.1°) by thermostating in a constant-temperature bath. The solution was then quickly transferred to a stoppered cuvette and placed in the thermostated spectrophotometer. In experiments utilizing hydrochloric acid as the catalyst the acid was preheated to 30 ± 0.1° in the constant-temperature bath before being added to the weighed compounds. For very fast rates the sodium salt of the acid was employed so that complete dissolution would be attained quickly.

Rates were measured by following the decrease in optical density at 262 and 275 mμ for 2-ethoxy-1-cyclopentene-1-carboxylic acid. The product of the reaction,

(1) E. N. Prilezhaeva, E. S. Shapiro, and M. F. Shostakovskii, *J. Gen. Chem. USSR*, **18**, 1663 (1948).

(2) L. A. Kiprianova and A. F. Rekasheva, *Dokl. Akad. Nauk, SSSR*, **142**, 589 (1962).

(3) M. L. Bender and K. A. Connors, *J. Am. Chem. Soc.*, **84**, 1980 (1962).

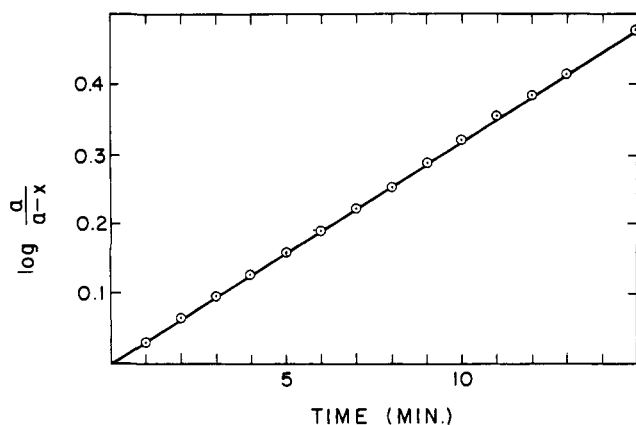(4) R. Mayer and B. Gebhardt, *Chem. Ber.*, **93**, 1212 (1960).

Figure 1. A typical first-order plot for the acid-catalyzed hydrolysis of 1. The rate was measured at pH 2.24, $T = 30°$, and $\mu = 0.25\ M$.

Figure 2. Plot of log k_{obsd} vs. pH for the hydrolysis of 1 in H_2O, $\odot$, and log k_{obsd} vs. pD for the hydrolysis of 1 in D_2O, $\ominus$, at $T = 30°$ and $\mu = 0.25\ M$.

cyclopentanone, has essentially no absorption at the very low concentrations employed. The reactions were followed to 50–75% completion. The pH of each kinetic run was routinely checked at 0 and ∞ time. The pseudo-first-order constants (k_{obsd}) were obtained from the slopes of plots of log $a/(a - x)$ vs. time. Precise first-order plots were invariably obtained. The catalytic constants for the various buffer acids were obtained from the slopes of plots of k_{obsd} vs. the concentration of the catalyzing species.

The rates were determined in 99.8% D_2O by the same procedure followed above, taking care that all solutions remained anhydrous. In the determination of a_D the glass electrode correction formula of Fife and Bruice[5] was employed.

Product Isolation. Thirty milliliters of 0.01 N HCl was added to 4.0 g. of 1 (0.028 mole) and the mixture was warmed gently to affect solution. The solution was allowed to stand for 1 hr. at room temperature and then extracted with ether. The ether extracts were dried over anhydrous sodium sulfate and the ether was evaporated. The residual liquid (1.8 g., 82.6%) had an infrared spectrum identical with that of an authentic sample of cyclopentanone. A semicarbazone derivative was prepared (m.p. 205°) identical with that of cyclopentanone. A mixture melting point determination showed no depression.

Thirty milliliters of phosphate buffer (pH 6.35) was added to 4.0 g. of 1. The material did not immediately dissolve but did so upon standing. The mixture was then allowed to stand for 8 days at room temperature. The solution was extracted with ether and the above procedure was duplicated. The liquid obtained again had an infrared spectrum and semicarbazone derivative (m.p. 205°) identical with that of cyclopentanone.

Results and Discussion

The disappearance of 1 ($T = 30°$, $\mu = 0.25\ M$) at pH values from 1.82 to 7.0 was observed by following the decrease in the absorption at 262 and 275 mμ due to the α,β-unsaturated carbonyl system. First-order kinetics were invariably obtained. A typical example is shown in Figure 1. Variation of the initial concentration of reactant over a threefold range produced no change in k_{obsd}. The product of the reaction

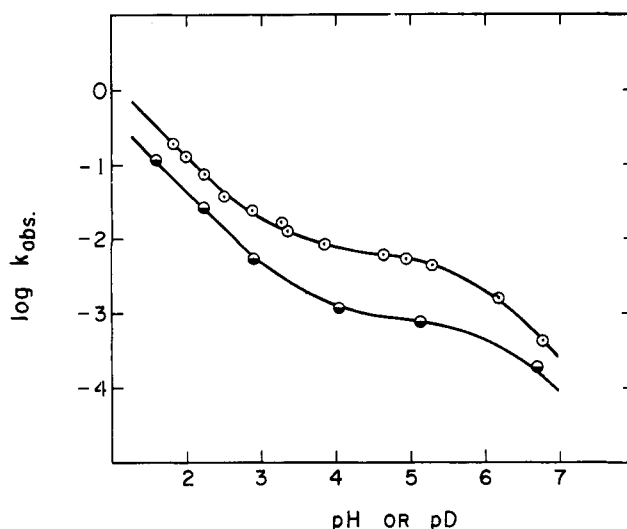(5) T. H. Fife and T. C. Bruice, *J. Phys. Chem.*, **65**, 1079 (1961).

was isolated at pH 2.0 and 6.35 and was identified as cyclopentanone from the identity of the infrared spectrum of the isolated material with that of pure cyclopentanone and from the identity of the semicarbazone derivative with that of an authentic sample. The reaction may be formally considered a vinyl ether hydrolysis followed by decarboxylation. Mayer and Gebhardt[4] found that at $-10°$, in ethanol–water with H_2SO_4 as the catalyst, the product was the enol form of 2-oxocyclopentanecarboxylic acid. On warming, this compound rapidly decarboxylated. Under these conditions then, hydrolysis of the vinyl ether group preceeded decarboxylation. Decarboxylation of α,β-unsaturated acids has been observed to occur in cases where β-substituents, capable of stabilizing a carbonium ion at that position through a resonance effect, are present.[6] In the case of γ,γ-di-p-anisylitaconic acid,[6] where such resonance stabilization is extreme, 40 min. was required for 90% CO_2 release in boiling 20% hydrochloric acid. Cinnamic acid was found to be decarboxylated much more slowly.[7] On considering, therefore, the findings of Mayer and Gebhardt[4] at high acidity and the rapid rates obtained with 1 under very mild conditions, it is evident that decarboxylation is occurring after hydrolysis of 1 to a β-keto acid and is, therefore, not being seen spectrophotometrically, the observed reaction being destruction of the carbon–carbon double bond. The reaction must involve hydration of the olefin to a carboxyl-substituted hemiacetal, conversion of the hemiacetal to 2-oxocyclopentanecarboxylic acid, and subsequent decarboxylation of the β-keto acid.
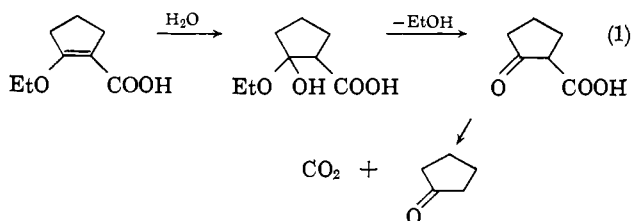
(6) W. S. Johnson and M. W. Miller, *J. Am. Chem. Soc.*, **72**, 511 (1950).

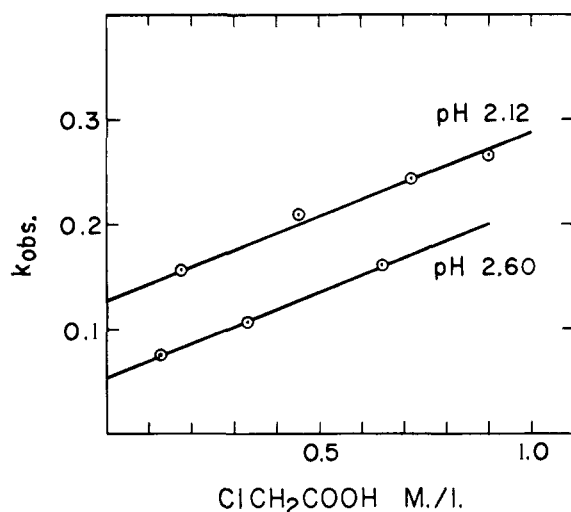(7) W. S. Johnson and W. E. Heinz, *ibid.*, **71**, 2913 (1949).

Figure 3. Plot of k_{obsd} for the hydrolysis of 1 vs. chloroacetic acid concentration at pH 2.60 and 2.12, $T = 30°$, and $\mu = 1.0\ M$.

In Table I the kinetic constants are recorded for 1. The pH–rate profile for the reaction of 1 is shown in Figure 2. The points at pH values greater than pH 3.0

Table I. Rate Constants and Activation Parameters for the Hydrolysis of 2-Ethoxy-1-cyclopentene-1-carboxylic Acid

Sol- vent	pK_a	$k_1,^a$ l. mole^{-1} min.$^{-1}$	ΔH^{*b}	$\Delta S^{*,c}$ e.u.	$k_2,^d$ l. mole^{-1} min.$^{-1}$	$k_0,^e$ min.$^{-1}$
H_2O	5.64	13.2	14.2	−14.5	2762	6.33×10^{-3}
D_2O	6.17	4.57			1140	7.71×10^{-4}
$\dfrac{k(D_2O)}{k(H_2O)}$		0.35			0.41	0.12

^{a} Second-order rate constant for the hydronium ion catalyzed reaction of the acid species of 1. ^{b} Enthalpy of activation for the hydronium ion catalyzed reaction of 1 (kcal. mole^{-1}). ^{c} Entropy of activation for the hydronium ion catalyzed reaction of 1. Calculated at 30° with k_1 having the units l. mole^{-1} sec.$^{-1}$ ^{d} Second-order rate constant for the hydronium ion catalyzed reaction of the anion of 1. ^{e} Rate constant for the uncatalyzed reaction of 1.

were obtained by extrapolation to zero buffer concentration. It can be seen that in the low pH region of the profile, the plot of log k_{obsd} vs. pH is linear with slope of -1.0 showing the reaction in that pH range to be hydronium ion catalyzed. At higher pH values a large plateau is encountered which could be due to an uncatalyzed reaction of the acid, or to a faster acid-catalyzed reaction of the anion, these two possibilities being kinetically indistinguishable.

In the pH range shown in Figure 2 it can be assumed that any hydroxide ion catalysis would make a negligible contribution to the observed rate since experiments at high hydroxide ion concentration (0.1 M KOH) indicated that 1 was quite stable at 30°, no change in optical density being observed over a 24-hr. period. The rate equation for the observed reaction can then be written as

$$k_{obsd} = [k_1 a_H + k_0]\left[\frac{a_H}{K_a + a_H}\right] \quad (2)$$

where k_1 is the second-order rate constant for the acid-catalyzed reaction of the un-ionized species, k_0 is the

rate constant for either an uncatalyzed reaction of 1 or an intramolecular carboxyl group catalyzed reaction, K_a is the dissociation constant of 1 and a_H is activity of hydronium ion as determined by the glass electrode. The kinetically equivalent hydronium ion catalyzed reaction of both the acid and the anion would have the following equation

$$k_{obsd} = k_1 a_H\left[\frac{a_H}{K_a + a_H}\right] + k_2 a_H\left[\frac{K_a}{K_a + a_H}\right] \quad (3)$$

where k_2 is the second-order rate constant for the acid-catalyzed reaction of the anion. The solid lines in Figure 2 were constructed from eq. 3 using the constants recorded in Table I.[8]

General Acid Catalysis. The observed rate of the reaction was found to be strongly facilitated by buffer. It was found that both carboxylic acids and nitrogen heterocycles were good catalysts for the reaction, with chloroacetate, formate, acetate, phosphate, pyridine, and imidazole buffers showing catalysis when the buffer concentration was increased at constant pH and ionic strength. The catalytic constants are recorded in Table II. As seen in Figure 3 when the pH is

Table II. Catalytic Constants for General Acids at $30 \pm 0.1°$

Catalyst	Solvent	pH or pD	$k_{HA},^a$ l. mole^{-1} min.$^{-1}$	$k_{HA}^{D_2O}/k_{HA}^{H_2O\,b}$
$ClCH_2COOH$	H_2O	2.12	1.55×10^{-1}	
$ClCH_2COOH$	H_2O	2.60	1.60×10^{-1}	
$HCOOH$	H_2O	3.27	4.89×10^{-2}	
$HCOOH$	H_2O	3.34	5.70×10^{-2}	
$HCOOH$	H_2O	3.60	9.10×10^{-2}	
$HCOOH$	D_2O	4.05	1.85×10^{-2}	0.20
CH_3COOH	H_2O	4.64	7.68×10^{-2}	
CH_3COOH	H_2O	4.94	1.44×10^{-1}	
CH_3COOH	H_2O	5.29	2.51×10^{-1}	
CH_3COOH	D_2O	5.14	1.69×10^{-2}	0.22
Pyridinium cation^c	H_2O	5.34	5.55×10^{-2}	
$H_2PO_4^-$	H_2O	6.18	5.31×10^{-2}	
$H_2PO_4^-$	H_2O	6.75	5.30×10^{-2}	
$H_2PO_4^-$	D_2O	6.70	1.35×10^{-2}	0.25
Imidazolium cation^d	H_2O	6.64	2.90×10^{-3}	
Imidazolium cation^d	H_2O	7.0	3.31×10^{-3}	
$HCOOH^e$	10% dioxane– H_2O	3.03	2.15×10^{-2}	
$HCOOH^e$	10% dioxane– H_2O	3.42	2.15×10^{-2}	

^{a} The slope of plots of k_{obsd} vs. the catalyst concentration. ^{b} The ratios were calculated for runs in which the buffer ratio was the same in both D_2O and H_2O. ^{c} The pK_a has the value 5.17 by half-neutralization. ^{d} The pK_a has the value 7.10, by half-neutralization. ^{e} Hydrolysis of ethyl-2-ethoxy-1-cyclopentene-1-carboxylate.

varied for chloroacetate buffers (pH 2.12 and 2.60), parallel slopes are obtained for plots of k_{obsd} vs. chloroacetic acid concentration. At these pH values 1 is almost completely in the un-ionized form so catalysis of the un-ionized species is by general acids. At higher pH values where 1 is partially ionized, plots of k_{obsd}

(8) The value of k_2 (2762 l. mole^{-1} min.$^{-1}$) was assumed in order to give as good a fit to the experimental data as possible. Employing eq. 2, k_0 has the value 6.33 $\times$ 10^{-3} min.$^{-1}$ The data is of course consistent with either eq. 2 or the equivalent eq. 3.

vs. acid or base concentration do not show parallel slopes when the pH is varied. The slope increases for plots of k_{obsd} vs. acid concentration as the pH increases. This most probably indicates that the anion of 1 is also subject to general acid catalysis with rate constants of greater magnitude than for the un-ionized species, a supposition supported by the magnitude of the second-order rate constants obtained from the slopes of the lines. The constant for acetic acid catalysis at pH 5.29 is greater than those for formic or chloroacetic acid, an order not in accord with the acidities of these acids. With the constants obtained from plots of k_{obsd} vs. acetic acid concentration, the true constants for the general acid catalyzed reactions of the acid and anion can be obtained by plotting k_{HA} vs. the fraction of anion present, as in Figure 4. For such plots the slope is equal to k_{HA}^{anion} and the intercept, at zero anion concentration, equal to k_{HA}^{acid}. With acetic acid as the catalyst $k_{HA}^{acid} = 4.0 \times 10^{-3}$ l. mole^{-1} min.$^{-1}$ while $k_{HA}^{anion} = 8.0 \times 10^{-1}$ l. mole^{-1} min.$^{-1}$, a difference of 200-fold.

The buffer catalysis is much less in D_2O as the solvent as would be expected for general acid catalysis. As seen in Table II the ratio $k_{HA}^{D_2O}/k_{HA}^{H_2O}$ at constant buffer ratio varies from 0.2 to 0.25.

The presence of a carboxyl group in vinyl ethers is not necessary for general catalysis by buffer to occur since the ethyl ester of 1 undergoes rapid reaction in 10% dioxane–water with the reaction being catalyzed by formic acid.

Hydronium Ion Catalysis. In the corresponding acid-catalyzed reaction at low pH, where protonation is by hydronium ion, the rate is slower in D_2O by a factor of 2.9. If a fast pre-equilibrium protonation of substrate were taking place prior to a unimolecular rate-determining step, it would be expected that the rate would be two to three times faster in D_2O than in H_2O.[9] In cases of A-2 reactions where the protonated intermediate breaks down through a rate-determining attack by water, the rate is generally 1.4 to 1.7 times faster in D_2O.[9] The ratio $k_1^{D_2O}/k_1^{H_2O}$ of 0.35 renders it impossible to interpret the hydronium ion catalyzed reaction of the un-ionized species of 1 in terms of the known examples of A-1 and A-2 reactions. The magnitude of this D_2O solvent isotope effect is in accord with that expected for catalysis involving a rate-determining protonation by hydronium ion. The acid-catalyzed isomerization of *cis*-cinnamic acids[10] and the cleavage of vinylmercuric iodide to ethylene and HgI^+,[11] reactions proceeding through a rate-determining protonation of the double bond, also have rates much slower in D_2O than H_2O ($k_{D_2O}/k_{H_2O} < 0.5$). Bunton and Shiner,[12] have calculated theoretical isotope effects for olefin hydration assuming various transition states. According to their calculations a transition state in which the proton interacts electrostatically with both water and olefin would give a maximum k_{H_2O}/k_{D_2O} ratio of 3.6. Thus, assuming an analogy between olefin hydration and vinyl ether hydrolysis, the D_2O solvent isotope effect for 1 is in accord with this model.

(9) F. A. Long, *Ann. N. Y. Acad. Sci.*, **84**, 596 (1960).
(10) D. S. Noyce, H. S. Avarbock, and W. L. Reed, *J. Am. Chem. Soc.*, **84**, 1647 (1962).
(11) M. M. Kreevoy and R. A. Kretchmer, *ibid.*, **86**, 2435 (1964).
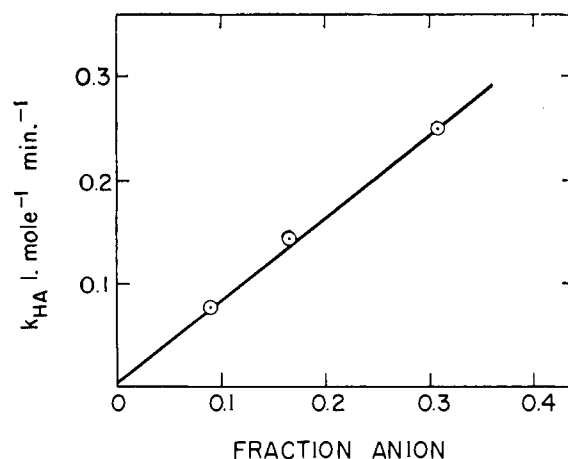(12) C. A. Bunton and V. J. Shiner, Jr., *ibid.*, **83**, 3214 (1961).

Figure 4. Plot of k_{HA} for the acetic acid catalyzed hydrolysis of 1 vs. the fraction of anion present, $k_a/(k_a + a_H)$.

Long, Pritchard, and Stafford[13] have shown that if the transition state of an acid-catalyzed reaction is composed of only substrate and proton, the ΔS^* may be positive or a small negative number. If, however, a molecule of water is also bound in the transition state, ΔS^* will be a large negative number, generally less than -20 e.u. While ΔS^* in the present case, -14.5 e.u. for the acid-catalyzed reaction of the un-ionized species, is slightly more positive than one might expect for a reaction involving water in the transition state, still it is sufficiently negative so that this assumption would not appear unreasonable when considered in conjunction with the D_2O solvent isotope effect. Other rate-determining proton transfer reactions in aqueous solution have been found to have large negative ΔS^* values.[11,14]

It is reasonable in view of the above discussion to consider that the most likely scheme for the acid-catalyzed reaction is

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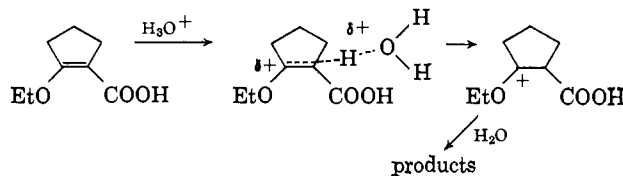
Intramolecular Catalysis. It is apparent from Figure 2 that the presence of the neighboring carboxyl group (or carboxylate anion) is facilitating the reaction. The second-order rate constant, k_2, is 209 times greater than k_1. This difference represents the maximum increase in k_{obsd} due to either ionization of the carboxyl group or to general acid catalysis by the un-ionized species.

In Table I are recorded the catalytic constants for the reaction in D_2O as the solvent. The ratio $k_0^{D_2O}/k_0^{H_2O}$ is 0.12 while $k_2^{D_2O}/k_2^{H_2O}$ is equal to 0.41 so that the value in either case is characteristic of general catalysis.

The finding that the rate of buffer catalysis by general acids increases greatly upon ionization of 1 supports the contention that the plateau rate is due to a much faster reaction of the anionic species (eq. 3) rather than

(13) F. A. Long, J. G. Pritchard, and F. E. Stafford, *ibid.*, **79**, 2362 (1957).
(14) D. S. Noyce, P. A. King, F. B. Kirby, and W. L. Reed, *ibid.*, **84**, 1632 (1962).
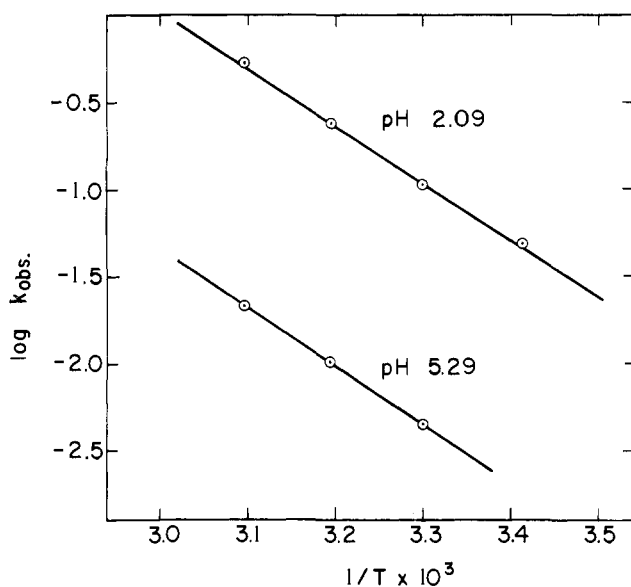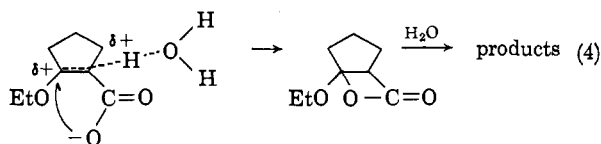
Figure 5. Temperature dependence of k_{obsd} for the hydrolysis of 1. Plot of k_{obsd} vs. $1/T \times 10^3$ at pH 2.09 (HCl catalyst) and 5.29 (acetate buffer with k_{obsd} obtained by extrapolation to zero buffer concentration); $T = 30°$, $\mu = 0.25$ M. Each point in the case of the HCl-catalyzed reaction is the average of three determinations. With the acetate buffers four buffer concentrations were studied in duplicate or triplicate to obtain each point.

to an uncatalyzed reaction of the acid or to an intramolecular protonation by the carboxyl group (eq. 2). Hydronium ion would certainly catalyze the reaction of the anion if general acids will do so, which of course must be the case since plots of k_{obsd} vs. the concentration of a general acid catalyst would show decreasing slopes with increasing pH near the pK_a of 1 if only the unionized species were reacting.

Possible mechanisms for the fast anionic reaction consistent with its associated D_2O solvent isotope effect are: (1) a rate-determining protonation of the anion by hydronium ion, or (2) a concerted protonation and carboxylate anion catalyzed reaction as in eq. 4 where the anion is acting as a nucleophile. This

mechanism, involving formation of a β-lactone, is similar to that favored by Bender and Connors[3] for hydration of fumaric acid.

The activation energy calculated from the temperature dependence of k_{obsd} at pH 5.29, in the plateau region of the pH–rate profile (Figure 5), is approximately 0.6 kcal./mole higher than that measured at pH 2.09. The large difference, therefore, between the observed rate at pH values close to the pK_a of 1 and the calculated rate, assuming only a hydronium ion catalyzed reaction of the acid, is due to a more favorable ΔS^*. The ΔS^* associated with k_{obsd}[15] at pH 5.29 is -28.4 e.u. as compared with -38.6 e.u. calculated for the k_{obsd}[15] which would be obtained at pH 5.29 if only an acid-catalyzed reaction of un-ionized species were taking place. The ΔS^* calculated for k_2 is -2 e.u.,
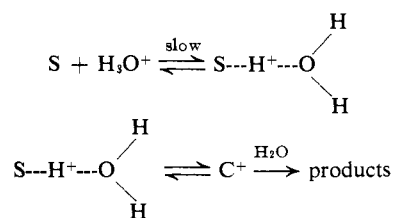
(15) k_{obsd} in sec.$^{-1}$.

assuming the activation energy to be the same as determined at pH 5.29. The acid-catalyzed hydration of 1-alkynyl ethers[16] and 1-alkynyl thioethers,[17] reactions involving a rate-determining protonation step, sometimes have ΔS^* values close to zero, so the value obtained in the present case probably cannot be considered abnormal for this type of a reaction. However, the difference between the ΔS^* values for reaction of the acid species and reaction of the anion is striking. A ring closure reaction as in eq. 4, involving charge neutralization, might result in a less heavily solvated transition state and, therefore, a more favorable ΔS^*.

Conclusions

Upon consideration of the data cited above it would appear that the factor necessary for the occurrence of a facile general acid catalyzed hydration of an olefinic double bond is the presence of a substituent capable of stabilizing an incipient carbonium ion. This undoubtedly occurs in the general acid catalyzed hydration of N-propyl-1,4-dihydronicotinamide[18] through resonance stabilization by the adjoining nitrogen atom. With the fumaric acid monoanion,[3] stabilization can occur by overlap with the nucleophilic carboxylate anion. In the case of 2-ethoxy-1-cyclopentene-1-carboxylic acid, stabilization is possible through both types of effects. The more stable the carbonium ion intermediate the closer the transition state will lie to initial reactants. This in essence corresponds to the postulate of Hammond[19] for deciding whether starting state or product is a better model for the transition state of a given reaction. Considering the following reaction schemes for olefin hydration

$$S + H_3O^+ \rightleftharpoons SH^+ \xrightarrow{\text{slow}} C^+ \xrightarrow{H_2O} \text{products}$$
$$\pi \text{ complex} \quad \text{carbonium ion}$$
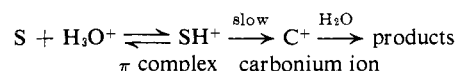
or

the more stable the carbonium ion intermediate, the more closely the transition state will resemble a π-complex[20] or initial state. Considering the proton to be less firmly bound in the transition state therefore, this means that we are approaching a transition state where general acids should compete effectively with hydronium ion if the carbonium ion is sufficiently stable and protonation is the slow step in the sequence. That the transition state for the acid-catalyzed hydrolysis of 1 is a more easily formed complex than is true for the acid-catalyzed hydration of normal olefins can be seen from a comparison of activation energies. The

(16) E. J. Stamhuis and W. Drenth, Rec. trav. chim., 80, 797 (1961).
(17) H. Hogeveen and W. Drenth, ibid., 82, 410 (1963).
(18) C. C. Johnston, J. L. Gardner, C. H. Suelter, and D. E. Metzler, Biochemistry, 2, 689 (1963).
(19) G. S. Hammond, J. Am. Chem. Soc., 77, 334 (1955).
(20) The rate-determining step in acid-catalyzed olefin hydration reactions has been postulated to be rearrangement of a π-complex of olefin and proton to a carbonium ion: R. W. Taft, Jr., ibid., 74, 5372 (1952).

E_a for **1** is 14.8 kcal./mole as compared with isobutene[21] 23.4, trimethylethylene[22] 18.9, crotonaldehyde[23] 18.2, and fumaric acid 22 kcal./mole.[24] The hydrolysis of ethoxyethylene has a reported activation energy of 17.9 kcal./mole.[1] Vinyl ether hydrolysis, therefore, is

(21) H. J. Lucas and W. F. Eberz, *J. Am. Chem. Soc.*, **56**, 460 (1934).
(22) H. J. Lucas and Y. P. Liu, *ibid.*, **56**, 2138 (1934).
(23) S. Winstein and H. J. Lucas, *ibid.*, **59**, 1461 (1937).
(24) L. E. Erickson and R. A. Alberty, *J. Phys. Chem.*, **63**, 705 (1959).
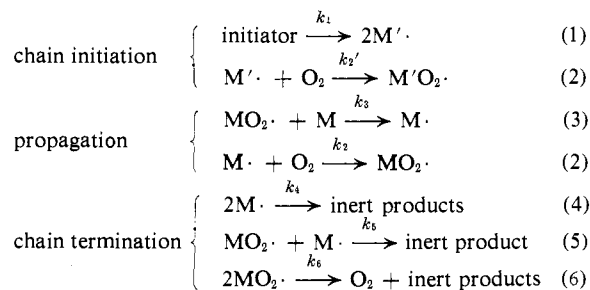
characterized in general by a lower activation energy with **1** having an activation energy even lower than that reported for other compounds of this class.

In attempting to deduce the factors responsible for the rapid enzymatic hydration of olefins it would appear that one should look for ways in which the enzyme can stabilize the incipient carbonium ion.

Reactions of Peroxy Radicals with Polynuclear Aromatic Compounds. II. Anthracene in Chlorobenzene

L. R. Mahoney

Contribution from the Scientific Laboratory, Ford Motor Company, Dearborn, Michigan. Received July 13, 1964

The products and kinetics of the reactions occurring in the system anthracene–azobis(2-methylpropionitrile)–oxygen in chlorobenzene have been investigated. At anthracene concentrations greater than 0.1 M a chain oxidation of anthracene occurs with radical addition at the meso positions. A study of the rate of oxygen absorption as a function of oxygen pressure shows that the meso carbon radical is significantly less reactive than other carbon radicals toward oxygen. Above 1.0 × 10⁻⁴ M, anthracene is capable of scavenging all radicals derived from initiator and oxygen. At lower concentrations of anthracene radicals are destroyed by a competing process. The available evidence indicates that the process consists of an attack on chlorobenzene by radicals derived from the bimolecular reaction of 2-cyanopropylperoxy radicals.

In an earlier paper from this laboratory,[1] it was suggested that anthracene undergoes an apparent free-radical chain reaction with oxygen. Although reactive olefins undergo such reactions[2] and compounds related to anthracene undergo photochemical nonchain additions with oxygen,[3] no chain oxidation of polynuclear aromatic hydrocarbons has been reported previously. The present work was therefore undertaken to examine this chain oxidation in detail. The range of anthracene concentrations was also extended well below that required for chain reaction, and the results suggest that the solvent chlorobenzene is involved in termination reactions of radicals derived from azobis(2-methylpropionitrile), *i.e.*, azobisisobutyronitrile (AIBN) and oxygen.

Results and Discussion

The kinetics and products of the reactions of radicals derived from AIBN and oxygen with anthracene in

(1) L. R. Mahoney, *J. Am. Chem. Soc.*, **86**, 44 (1964).
(2) F. R. Mayo, H. H. Miller, and G. A. Russell, *ibid.*, **80**, 2500 (1958).
(3) J. R. Livingston, "Auto-Oxidation and Antioxidants," Vol. I, W. O. Lundberg, Ed., Interscience Publishers, John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 264–287.

chlorobenzene were studied over wide ranges of concentration of anthracene, AIBN, and oxygen. For discussion, the results of this study have been divided into the following two ranges of anthracene concentration: (1) chain-reaction region (greater than 0.1 *M* in anthracene), and (2) radical-scavenging region (from 2 × 10⁻⁶ to 0.1 *M* in anthracene).

I. Chain Reaction. A. Kinetics. The accepted kinetic mechanism for the low temperature liquid phase oxidation of unsaturated hydrocarbons is[2,4]

$$\text{chain initiation} \begin{cases} \text{initiator} \xrightarrow{k_1} 2M' \cdot & (1) \\ M' \cdot + O_2 \xrightarrow{k_2'} M'O_2 \cdot & (2) \end{cases}$$

$$\text{propagation} \begin{cases} MO_2 \cdot + M \xrightarrow{k_3} M \cdot & (3) \\ M \cdot + O_2 \xrightarrow{k_2} MO_2 \cdot & (2) \end{cases}$$

$$\text{chain termination} \begin{cases} 2M \cdot \xrightarrow{k_4} \text{inert products} & (4) \\ MO_2 \cdot + M \cdot \xrightarrow{k_5} \text{inert product} & (5) \\ 2MO_2 \cdot \xrightarrow{k_6} O_2 + \text{inert products} & (6) \end{cases}$$

where $M' \cdot$ and $M \cdot$ are the initiator radical and substrata radical, and $M'O_2 \cdot$ and $MO_2 \cdot$ are the peroxy radicals derived from the initiator and substrata radicals, respectively. At a steady-state radical concentration, the rate of oxygen absorption, $-dO_2/dt$, obeys the general expression

$$-\frac{dO_2}{dt} = \frac{k_3}{(2k_6)^{1/2}} (R_i)^{1/2} (M) \left[\frac{1}{1 + \dfrac{\phi k_4^{1/2} k_3}{k_2 (2k_6)^{1/2}} \dfrac{(M)}{(O_2)} + \dfrac{k_4 k_3^2 (M)^2}{k_2^2 k_6 (O_2)^2}} \right] \quad (7)$$

where $\phi = k_5/(k_4 k_6)^{1/2}$ and R_i is the rate of radical production from the initiator. At sufficiently high concentrations of oxygen, reaction 2 is much faster than reaction 3 so that $(M \cdot) \ll (MO_2 \cdot)$ and termination occurs almost exclusively by reaction 6. The terms

(4) L. Bateman, G. Gee, A. L. Morris, and W. F. Watson, *Discussions Faraday Soc.*, **10**, 250 (1951).