

H), 3.52 (s, 3 H), 3.66 (s, 3 H), 4.09 (m, 3 H), 4.75 (s, 1 H), 5.47 (d, 1 H, $J = 8$ Hz), 5.76 (m, 1 H); IR (film) 2960, 1710 (br), 1450, 1380 cm^{-1} ; CIMS, m/z 310 ($M^+ + 1$).

(6R)-6-Carbomethoxy-1-methoxy-6-methyl-1,4-cyclohexadiene. A solution of (2R)-6-[[*N*-carbomethoxy-(*S*)-2-pyrrolidinyl]methoxy]carbonyl]-1-methoxy-6-methyl-1,4-cyclohexadiene (0.582 g, 1.88 mmol) in dry methanol (25 mL) and sodium methoxide (0.610 g, 11.3 mmol) was refluxed for 12 h. The reaction mixture was dissolved in ether (100 mL), and water (100 mL) was added. The organic phase was washed with brine (1 \times 100 mL), dried over sodium sulfate, and chromatographed on neutral alumina (hexane-ethyl acetate, 2:1) to give (6R)-6-carbomethoxy-1-methoxy-6-methyl-1,4-cyclohexadiene (0.275 g, 80%) as a colorless oil, identical with ^1H NMR and IR to the corresponding racemic material **6a**.

(4R)-4-Carbomethoxy-3-methoxy-4-methyl-2,5-cyclohexadien-1-one (53a) was prepared from (6R)-6-carbomethoxy-1-methoxy-6-methyl-1,4-cyclohexadiene as described for the preparation of **8a**. The ^1H NMR, infrared, and mass spectra of **53a** were identical with those of **8a**. The optical rotation of **53a** was $[\alpha]_D^{24} -71.4^\circ$ (c 1.71, methanol).

Irradiation of 53a for 1 h. A solution of **53a** (70 mg, 0.36 mmol) in benzene (7 mL) was purged with nitrogen for 15 min before irradiation at 366 nm for 1 h. The reaction mixture was concentrated, and flash chromatography (silica gel, hexane-ethyl acetate, 1:1) provided bicyclohexenones **54** and **55** and recovered 2,5-cyclohexadienone **53** as 5:1 mixture of enantiomers.

The ratio of enantiomers in each case was determined by ^1H NMR spectroscopy by using the chiral shift reagent tris[3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]europium(III); i.e., $\text{Eu}(\text{hfc})_3$. A 0.28 M stock solution of $\text{Eu}(\text{hfc})_3$ in deuteriated chloroform was prepared, and 5- μL aliquots of the stock solution were added to the NMR sample tubes containing **53**, **54**, or **55**. When base line separation of a diagnostic proton signal was obtained (usually after the addition of several 5- μL aliquots of stock solution), the peaks were integrated. A comparison of the size of the integrals obtained in this manner provided the ratio of enantiomers. In the case of 2,5-cyclohexadienone **53**, the diagnostic proton that had base line separation was the vinyl proton attached to C(5). For bicyclohexenones **54** and **55**, the diagnostic proton

that had base line separation in each case was the vinyl proton attached to C(3).

Irradiation of 53a for 9 h. A solution of **53a** (0.125 g, 0.64 mmol) in benzene (12 mL) was purged with nitrogen for 15 min before irradiation at 366 nm for 9 h. Flash chromatography provided bicyclohexenones **54** (52 mg) and **55** (43 mg). ^1H NMR spectroscopic examination of **54** showed that it was a 3:1 mixture of enantiomers. This mixture gave an optical rotation of $[\alpha]_D^{23} -130^\circ$ (c 0.48, methanol). ^1H NMR spectroscopic examination of **55** showed that it was nearly racemic. This mixture gave an optical rotation of $[\alpha]_D^{31} +14.0^\circ$ (c 0.84, methanol).

Irradiation of the 3:1 Mixture of Enantiomers of 54. A solution of **54** (23 mg) containing a 3:1 mixture of enantiomers in benzene (2.5 mL) was purged with nitrogen for 10 min before irradiation at 366 nm for 4 h. The reaction mixture was concentrated, and flash chromatography (silica gel, hexane-ethyl acetate, 1:1) provided a 1:3 mixture of **55** and **56** (11.3 mg) $[\alpha]_D^{23} -106^\circ$ (c 0.23, methanol). Also recovered was **54** (6.3 mg) as a 3:1 mixture of enantiomers.

4-Ethyl-7-methoxytricyclo[3.3.0^{1,5,6}]oxaocan-3-one (63). The bicyclohexenone **19b** (150 mg, 0.71 mmol) was dissolved in anhydrous ethanol (25 mL). To this solution was added sodium borohydride (108 mg, ~ 4 equiv). After stirring 16 h, the reaction mixture was carefully quenched with 10% HCl. Water was added to dissolve the salts, and the solution was stirred 2 h at room temperature. After extracting with chloroform, the organic layer was washed with water and saturated sodium bicarbonate and then dried over magnesium sulfate to give **63** (103 mg, 100%) as a colorless oil of high purity: ^1H NMR (CDCl_3) δ 0.98 (t, 3 H, $J = 8$ Hz), 1.48 (six line multiplet, 1 H, $J = 8$ Hz), 1.88-2.04 (m, 2 H), 2.12 (d, 1 H, $J = 10$ Hz), 2.18 (t, 1 H, $J = 5$ Hz), 2.94 (t, 1 H, $J = 5$ Hz), 3.45 (s, 3 H), 4.36 (t, 1 H, $J = 7$ Hz), 4.86 (brs, 1 H); ^{13}C NMR (CDCl_3) 10.75, 23.33, 37.72, 37.97, 46.35, 56.39, 80.55, 81.31, 176.91 (one carbon missing); IR (film) 2925, 1760, 1090, 985 cm^{-1} ; CIMS, m/z (rel intensity) 183 ($M^+ + 1$, 10.63), 151 (93.55), 107 (100.00). Anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{O}_3$: C, 65.92; H, 7.74. Found: C, 65.83; H, 7.77.

Acknowledgment. This research was supported by the National Science Foundation (CHE83-19474).

Vinyl Alcohol: Generation and Decay Kinetics in Aqueous Solution and Determination of the Tautomerization Equilibrium Constant and Acid Dissociation Constants of the Aldehyde and Enol Forms

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Abstract: Vinyl alcohol was generated in aqueous solution by Norrish type II photoelimination of 5-hydroxy-2-pentanone and by the acid-catalyzed hydrolysis of a ketene acetal (1-(vinylloxy)-1-methoxyethene) and an ortho ester (2-(vinylloxy)-2-phenyl-1,3-dioxolane), and rates of isomerization of this enol to acetaldehyde catalyzed by hydronium and hydroxide ions and formic and acetic acid buffers were measured. Rates of enolization of acetaldehyde, determined by iodine scavenging and catalyzed by hydronium and hydroxide ions, were also measured. These data lead to two concordant, independent determinations of the tautomerization equilibrium constant for acetaldehyde in aqueous solution whose average is $K_E = (5.89 \pm 0.81) \times 10^{-7}$, $pK_E = 6.23 \pm 0.06$. They also give $K_a^E = (3.13 \pm 0.17) \times 10^{-11}$, $pK_a^E = 10.50 \pm 0.02$, for the dissociation constant of vinyl alcohol ionizing as an oxygen acid, and $K_a^K = (1.85 \pm 0.27) \times 10^{-17}$, $pK_a^K = 16.73 \pm 0.06$, for the dissociation constant of acetaldehyde ionizing as a carbon acid; all equilibrium constants are concentration quotients and refer to aqueous solution at ionic strength 0.10 M. Kinetic solvent isotope effects on both enolization and ketonization suggest that reaction occurs by a stepwise rather than a concerted mechanism.

There has been a resurgence of interest lately in the chemistry of simple enols.¹ This was sparked by the demonstration that vinyl alcohol, the prototype enol, is not especially unstable in aqueous solution,² and it has included invention of new methods for estimating enol contents of simple aldehydes and ketones³ as well as the re-examination of stable, sterically crowded "Fuson"

enols.⁴ We have contributed to this activity by devising methods for preparing enols in aqueous solution under conditions where

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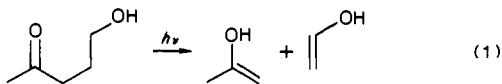
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[†]University of Toronto.

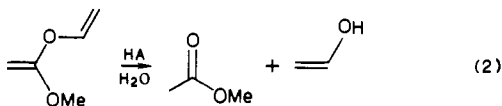
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the kinetics of their reactions may be measured accurately, and we have used these new methods to examine the enols of acetophenone,⁵ isobutyraldehyde,⁶ acetone,⁷ and isobutyrophenone.⁸

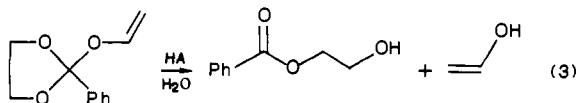
In this paper we report our work on the parent enol, vinyl alcohol. We generated this substance in aqueous solution three different ways, namely by Norrish type II photoelimination of 5-hydroxy-2-pentanone, eq 1, by acid-catalyzed hydrolysis of 1-(vinylloxy)-1-methoxyethene, eq 2, and by acid-catalyzed hydrolysis of 2-(vinylloxy)-2-phenyl-1,3-dioxolane, eq 3. Using these



(1)



(2)



(3)

methods of production, we have measured rates of tautomerization of vinyl alcohol, and we have also measured rates of the reverse reaction, enolization of acetaldehyde. This has allowed accurate determination of the keto-enol equilibrium constant for this system, and it has also provided the acidity constant of the enol ionizing as an oxygen acid and of acetaldehyde ionizing as a carbon acid, all in aqueous solution.

Experimental Section

Materials. 1-(Vinylloxy)-1-methoxyethene was prepared by sodium hydride promoted elimination of 2 equiv of HCl from chloroacetaldehyde 2-chloroethyl methyl acetal, as described by Capon.^{2b} 2-(Vinylloxy)-2-phenyl-1,3-dioxolane was obtained by analogous elimination of HBr from 2-(2-bromoethyl)-2-phenyl-1,3-dioxolane, which in turn was made from 2-methoxy-2-phenyl-1,3-dioxolane by trans-etherification⁹ with 2-bromoethanol. The spectral properties of these substances were consistent with their structures.

Acetaldehyde (BDH) and 5-hydroxy-2-pentanone (Aldrich) were distilled prior to use. All other materials were best available commercial grades. Solutions were prepared with deionized H₂O, purified further by distillation, or D₂O (MSD Isotopes, 99.8 atom % deuterium) as received.

Kinetics, Ketonization. The flash photolysis experiments were done in apparatus of conventional design;¹⁰ the system used at Basel has already been described.^{5b} In the Toronto apparatus, the excitation flash (50 μ s width at half-height) was produced by electrical discharge of 2000-J energy from a Xenon Corp. Model A Micro Pulser power supply through two Xenon Corp. FPA-5-100C xenon flash lamps. The monitoring light was supplied by an Osram Model XBO 150-W xenon lamp, operating from an Oriol Model 68700 universal arc lamp power supply. This light was passed first through a 10-cm water-jacketed (25.0 \pm 0.05 $^\circ$) sample cell and then through an Oriol Model 77250 grating monochromator, and the output from that was detected by an Oriol Model 77341 photomultiplier. The signal from the photomultiplier was

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sent to a Biomation Model 805 transient recorder and A-D converter, and the digitized output was fed into a Commodore PC 10 microcomputer. First-order rate constants were calculated by least-squares fitting to exponential functions.

Flash photolysis measurements were made with use of freshly prepared aqueous solutions of 5-hydroxy-2-pentanone (ca. 0.02 M), and the transient decay was monitored at 220 nm. Only a small portion of the substrate was photolyzed in each flash, and a number of consecutive rate determinations were therefore made with each solution.

Rates of ketonization of vinyl alcohol generated by hydrolysis of the ketene acetal (eq 2) or ortho ester (eq 3) precursor were measured with either a Durrum-Gibson stopped-flow apparatus, operating at 25.0 \pm 0.05 $^\circ$, or Cary 118 and HP 8451A conventional spectrometers, whose cell compartments were thermostated at 25.0 \pm 0.05 $^\circ$. Substrate concentrations of the order of 3 \times 10⁻⁵ M were used and reactions were followed by monitoring the decrease of vinyl alcohol absorbance at 220-230 nm. Rate constants were calculated by least-squares fitting to either the exponential or linear forms of the first-order rate equation.

Kinetics, Enolization. Rates of enolization of acetaldehyde catalyzed by HClO₄ were measured by iodine scavenging under zero-order conditions (100-fold excess of acetaldehyde over iodine) in the presence of iodide ion; iodine was generated by the acid-catalyzed reaction of KIO₃ with KI. In one series of experiments the reaction was followed by monitoring the decrease in absorbance of iodinating agent at the I₂-I₃⁻ isosbestic point, 466 nm (ϵ = 777 \pm 1 cm⁻¹ M⁻¹, measured here), and in another series by monitoring the decrease at the I₃⁻ absorption maximum, 351 nm (ϵ = 26 000 cm⁻¹ M⁻¹).¹¹

The isosbestic point experiments were performed by allowing 3.0 mL of aqueous HClO₄ solution (ionic strength μ = 0.100 M (NaClO₄)) contained in a cuvette to come to temperature equilibrium with the spectrometer cell compartment. Fifteen microliters of neat acetaldehyde was then added and the absorbance at 277 nm was measured in order to determine the exact aldehyde concentration (ϵ_{max} = 7.66 cm⁻¹ M⁻¹, based on stoichiometric concentration¹²). Iodination was then initiated by adding 15 μ L of IO₃⁻/I⁻ solution, and continuous recording of absorbance at 466 nm was begun. There was at first a slight rise in absorbance as the rapid acid-catalyzed conversion of IO₃⁻ and I⁻ to I₂ came to completion; this was followed by a steady decrease which gave good zero-order behavior. First-order rate constants were evaluated by dividing these zero-order rates of change of absorbance by the I₂/I₃⁻ extinction coefficient and the free aldehyde concentration; the latter was calculated from the stoichiometric concentration by using the hydration equilibrium constant K = 1.059.¹² Stoichiometric concentrations of aldehyde in the reaction mixtures were 7-9 \times 10⁻² M, and initial stoichiometric concentrations of I₂ and I⁻ were 1 \times 10⁻³ and 1 \times 10⁻⁴ M, respectively.

The experiments conducted by making measurements at the I₃⁻ absorption maximum were carried out in a similar fashion, but concentrations of aldehyde and I₃⁻ (which must also be known for this method) were determined by a combination of weighings and volumetric delivery from a calibrated spring-driven microsyringe (Hamilton CR-700-20). In a typical experiment, approximately 1 g of perchloric acid solution was weighed into the cuvette. When this solution had reached temperature equilibrium with the spectrometer cell compartment, first 70 μ L of aqueous IO₃⁻/I⁻ solution and then 40 μ L of aqueous acetaldehyde solution were added. (The acetaldehyde solution was stabilized by making it slightly acidic.) The rate of change of absorbance at 351 nm was then recorded. This again proved to be accurately zero order, and first-order rate constants were calculated with the formula $k = -(dA/dt)(1 + K[I^-])/\epsilon_{\text{max}}[A]$, in which A is absorbance, K (= 1.5 \times 10⁻³)¹¹ is the equilibrium constant for the triiodide dissociation reaction I₃⁻ = I₂ + I⁻, ϵ_{max} is the extinction coefficient of I₃⁻, and $[A]$ is the free aldehyde concentration. In these experiments, stoichiometric aldehyde concentrations were 0.16 M and initial stoichiometric concentrations of I₂ and I⁻ were 2-8 \times 10⁻⁴ and 1-5 \times 10⁻³ M, respectively.

The rate of acid-catalyzed enolization of acetaldehyde was also measured in dilute DClO₄/D₂O solution. For accurate comparison with the rate in HClO₄/H₂O solution, the reaction media were prepared by adding identical 30- μ L portions of 2.3 M DClO₄/D₂O to 3.0-mL samples of either H₂O or D₂O in cuvettes; this gave a final L₃O⁺ concentration of 0.0230 M. Initial rates of iodination were then measured at the I₂/I₃⁻ isosbestic point, as described above. No inert electrolyte was added to the reaction mixtures in these experiments, and the ionic strength was therefore equal to the L₃O⁺ concentration (0.023 M).

Rates of enolization of acetaldehyde catalyzed by NaOH were also measured, again by iodine scavenging. This time, however, first-order

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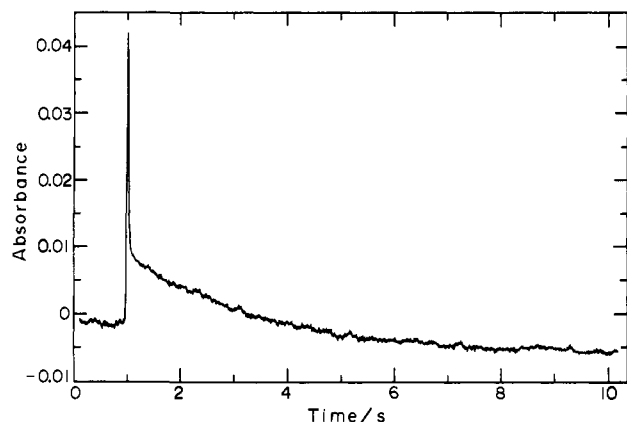


Figure 1. Change in absorbance at 220 nm produced by flash photolysis of 5-hydroxy-2-pentanone in 0.01 M aqueous HCl, $\mu = 0.10$ M (NaCl), $T = 25$ °C.

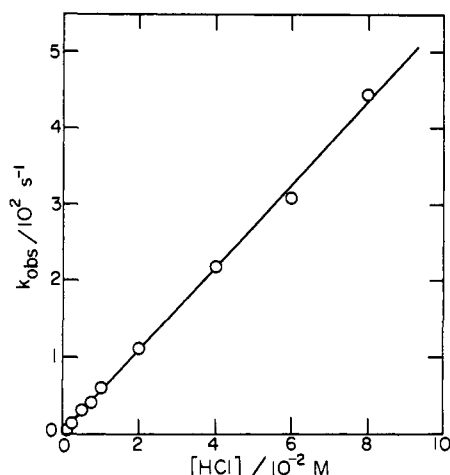


Figure 2. Relationship between hydrochloric acid concentration and observed first-order rate constants for decay of the shorter lived transient species (acetone enol) formed in flash photolysis of 5-hydroxy-2-pentanone in aqueous solution at 25 °C. Each point represents the average of 4–6 determinations.

conditions were used, with a 20% excess of iodinating agent over aldehyde, and the increase in absorbance at 336 nm due to CHI_3 was followed. Runs were conducted by first allowing 2.70-mL portions of aqueous NaOH solution to come to temperature equilibrium with the spectrometer cell compartment. Then, 300 μL of aqueous I_3^-/I^- solution and 15 μL of aqueous acetaldehyde solution were added, and the change in absorbance at 336 nm was recorded. The process followed first-order kinetics accurately for 3–4 half-lives, but the reaction products were not stable and A_∞ changed slowly. First-order rate constants were therefore calculated by fitting the data to an exponential function with a method which leaves A_∞ as an adjustable parameter.¹³ The values of A_∞ obtained in this way and those estimated directly from the kinetic traces never differed by more than 2%.

Results

Ketonization of Vinyl Alcohol Generated by Flash Photolysis.

Flash photolysis of 5-hydroxy-2-pentanone in aqueous solution produces a sudden rise in absorbance at 220 nm, which is complete within the duration of the flash (10–20 μs); the absorbance then decays in a biphasic manner, indicating the formation and subsequent reaction of two transient species (Figure 1). The lifetimes of these two transients differ considerably, and rate constants for the decay of each can be evaluated accurately. Both decays follow first-order kinetics well. Observed first-order rate constants determined in dilute HCl solutions, over the concentration range $[\text{HCl}] = 0.001$ – 0.080 M for the faster reaction and $[\text{HCl}] =$

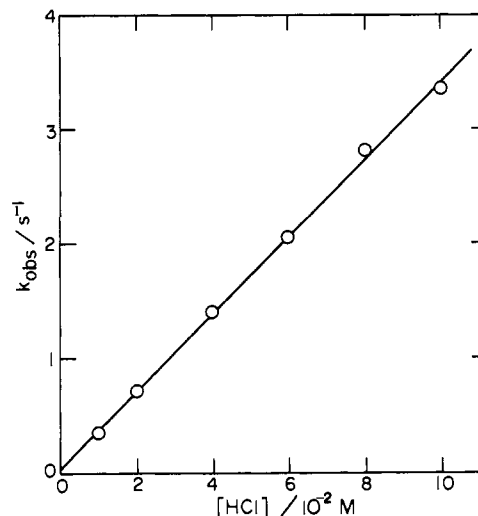
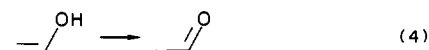


Figure 3. Relationship between hydrochloric acid concentration and observed first-order rate constants for decay of the longer lived transient species (vinyl alcohol) formed in the flash photolysis of 5-hydroxy-2-pentanone in aqueous solution at 25 °C. Each point represents the average of six determinations.

0.01–0.10 M for the slower reaction, are summarized in Table S1.¹⁴

As Figure 2 shows, observed first-order rate constants for decay of the shorter lived transient species are directly proportional to hydrochloric acid concentration; linear least-squares analysis gave the bimolecular rate constant $k_{\text{H}^+}^{\text{K}} = (5.38 \pm 0.08) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. This agrees well with the hydronium ion catalytic coefficient, $k_{\text{H}^+}^{\text{K}1} = (4.72 \pm 0.85) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, expected for the ketonization of acetone enol on the basis of our recently determined keto-enol equilibrium constant for acetone, $K_{\text{E}} = (6.0 \pm 1.1) \times 10^{-9}$,⁷ and the average of 18 determinations of the rate constant for enolization of acetone catalyzed by the hydronium ion, $k_{\text{H}^+}^{\text{E}} = (2.84 \pm 0.07) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$.¹⁵ This good correspondence indicates that the process initiated by flash photolysis is indeed the Norrish type II photoelimination of eq 1, which would give acetone enol in addition to vinyl alcohol. This allows the longer lived transient species to be identified as vinyl alcohol which decays to give acetaldehyde, eq 4. This assignment is reinforced by good



agreement between the lifetime of this transient and that of vinyl alcohol generated here in other ways (vide infra), as well as correspondence of these lifetimes to those of vinyl alcohol determined previously under somewhat different conditions.²

The ketonization of vinyl alcohol should be acid-catalyzed, as is the case for the enol of acetone and other simple aldehydes and ketones,^{2,4–6,8,9} and the first-order rate constants for decay of the longer lived transient observed in these flash photolytic experiments were indeed accurately proportional to hydrochloric acid concentration (Figure 3). Linear least-squares analysis gave the hydronium ion catalytic coefficient $k_{\text{H}^+}^{\text{K}} = 33.8 \pm 1.3 \text{ M}^{-1} \text{ s}^{-1}$.

Rates of ketonization of vinyl alcohol generated by flash photolysis of 5-hydroxy-2-pentanone were also measured at 220 nm in dilute sodium hydroxide solutions; these data are summarized in Table S2.¹⁴ As Figure 4 shows, the rate of reaction is accelerated by sodium hydroxide at low concentrations, but the effect diminishes and k_{obsd} tends toward a limiting value as the sodium hydroxide concentration is increased. This behavior is typical of simple enols.^{3–9} It may be interpreted in terms of a rapid reaction of hydroxide ion with enol to give the much more reactive enolate ion, followed by rate-determining ketonization of enolate

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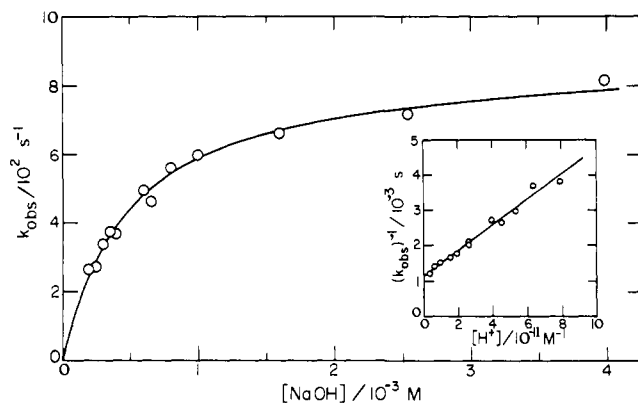
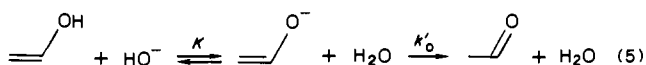


Figure 4. Relationship between sodium hydroxide concentration and observed first-order rate constants for the ketonization of vinyl alcohol generated by flash photolysis of 5-hydroxy-2-pentanone in aqueous solution at 25 °C. Each point represents the average of three determinations. The insert shows these data plotted according to eq 7.

through protonation on β -carbon by water, eq 5: at low hydroxide ion concentrations the equilibrium preceding the rate-determining



step lies to the left and the rate of reaction rises with rising $[\text{NaOH}]$, but as $[\text{NaOH}]$ increases and the equilibrium shifts to the right, this accelerative effect becomes saturated. The rate law for this reaction scheme is given in eq 6, where $[\text{E}]_t = [\text{enol}] + [\text{enolate}]$, K is the equilibrium constant for the first step (and

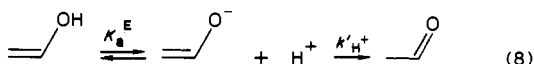
$$\frac{-d[\text{E}]_t}{dt} = k'_0[\text{enolate}] = \frac{k'_0 K [\text{HO}^-][\text{E}]_t}{K[\text{HO}^-] + 1} = \frac{k'_0 K_a^{\text{E}} [\text{E}]_t}{K_a^{\text{E}} + [\text{H}^+]} = k_{\text{obsd}} [\text{E}]_t \quad (6)$$

is equal to the acid dissociation constant of the enol divided by the autoprotolysis constant of water, $K = K_a^{\text{E}}/K_w$), and k'_0 is the rate constant for the second step. This rate law requires $(k_{\text{obsd}})^{-1}$ to be a linear function of $[\text{H}^+]$, eq 7, and the insert in Figure 4 shows that this indeed is the case. Linear least-squares analysis

$$(k_{\text{obsd}})^{-1} = (k'_0)^{-1} + [\text{H}^+]/k'_0 K_a^{\text{E}} \quad (7)$$

of the data gives $(k_{\text{obsd}})^{-1} = (1.13 \pm 0.05) \times 10^{-3} + [(3.62 \pm 0.12) \times 10^7][\text{H}^+]$, which leads to $k'_0 = (8.82 \pm 0.37) \times 10^2 \text{ s}^{-1}$ and $K_a^{\text{E}} = (3.13 \pm 0.17) \times 10^{-11}$; $pK_a^{\text{E}} = 10.50 \pm 0.02$. This acidity constant has not been measured before, but an approximate estimate, $pK_a^{\text{E}} = 11.1 \pm 1.0$, in good agreement with the present result, has been made.^{3b}

In addition to catalysis by hydronium and hydroxide ions, rate profiles for the ketonization of enols generally contain an "uncatalyzed" portion or water reaction near the middle of the pH range, over which the rate of reaction does not change with the acidity of the medium.^{6b,8} The mechanistic interpretation of rate constants in this region is open to question.^{2c,5b,16} Perhaps the most straightforward assignment is equilibrium ionization of the enol to enolate, followed by rate-determining carbon protonation of enolate by hydronium ion, eq 8; since a hydronium ion is generated in the first step of this process and is then used



up in the second step, the overall reaction is independent of hydronium (or hydroxide) ion concentration. In terms of this scheme, observed rate constants determined in this region, k_w , are equal to the product $K_a^{\text{E}} k'_{\text{H}^+}$, and since K_a^{E} is now known from the rate measurements in sodium hydroxide solutions, k'_{H^+} may be evaluated.

In order to determine k_w , rates of ketonization of vinyl alcohol generated by flash photolysis of 5-hydroxy-2-pentanone were

(16) Tapuhi, E.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 5758–5765.

Table I. Evaluation of the "Uncatalyzed" Term in the Rate Law for Ketonization of Vinyl Alcohol in Aqueous Solution at 25 °C^a

method of vinyl alcohol generation ^b	buffer acid	$[\text{H}^+]/10^{-5}$ M	intercept/ 10^{-2} s ⁻¹	$k_w/10^{-2}$ s ⁻¹
FP	CH ₃ CO ₂ H	5.06	4.10	3.88
FP	CH ₃ CO ₂ H	2.67	4.19	4.00
FP	CH ₃ CO ₂ H	1.24	4.26	4.00
H,KA	HCO ₂ H	35.4	5.35	4.18
H,KA	HCO ₂ H	7.07	4.59	4.32
H,KA	CH ₃ CO ₂ H	2.72	4.48	4.29
H,OE	CH ₃ CO ₂ H	2.78	3.98	3.79
H,OE	CH ₂ CO ₂ H	1.43	3.35	3.11
av				3.95 ± 0.14

^a Ionic strength = 0.10 M maintained with NaCl. ^b FP = flash photolysis, H,KA = hydrolysis of ketene acetal, H,OE = hydrolysis of ortho ester.

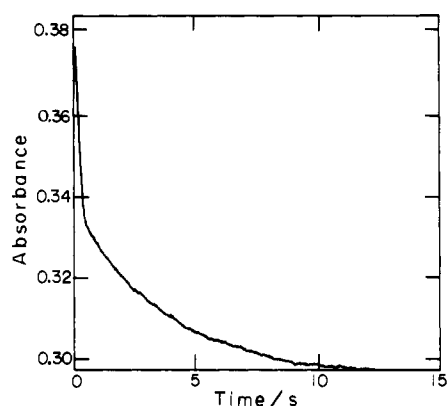
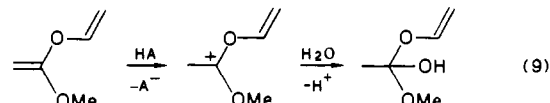


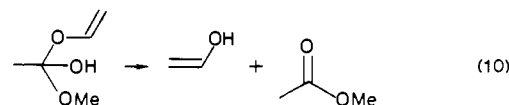
Figure 5. Absorbance change at 225 nm produced by the hydrolysis of 1-(vinyloxy)-1-methoxyethene in aqueous 0.024 M acetic acid buffer solution, buffer ratio = 1.0, at 25 °C.

measured in acetic acid buffer solutions and the data were extrapolated to zero buffer concentration. Series of solutions of constant buffer ratio and constant ionic strength (0.10 M) were used, and buffer concentrations were varied by a factor of 5. These data are summarized in Table S3.¹⁴ Extrapolation to zero buffer concentration was done by linear least-squares analysis; the zero-buffer-concentration intercepts so obtained are listed in Table I. An analysis of these data is given below.

Ketene Acetal Hydrolysis. Vinyl alcohol was also generated in the present study by the acid-catalyzed ketene acetal hydrolysis reaction shown in eq 2. This process had been used before to prepare vinyl alcohol in the pioneering work which demonstrated that this enol can persist in aqueous solution for times long enough to allow rate measurement by conventional (slow) kinetic methods.² Hydrolysis of this ketene acetal can be expected to occur by the standard mechanism for this reaction,¹⁷ which involves rate-determining proton transfer from the catalyst to the substrate followed by hydration of the ensuing dialkoxycarbocation, eq 9; the hydrogen ortho ester thus formed would then break down by



either acid- or base-catalyzed paths to give vinyl alcohol and methyl acetate, eq 10.¹⁸



(17) Kankaanpera, A.; Touminen, H. *Suom. Kemistil. B.* **1967**, *40*, 271–276. Gold, V.; Waterman, D. D. A. *J. Chem. Soc. B* **1968**, 839–849, 849–855. Yeager, M. J.; Schmir, G. L. *J. Org. Chem.* **1975**, *40*, 2940–2946. Kresge, A. J.; Straub, T. S. *J. Am. Chem. Soc.* **1983**, *105*, 3957–3961.

Table II. Summary of Rate Constants for Hydrolysis of the Ketene Acetal Group of 1-(Vinylloxy)-1-methoxyethene in Aqueous Carboxylic Acid Buffer Solutions at 25 °C^a

buffer acid	buffer ratio	$k_{HA}/10^2 \text{ M}^{-1} \text{ s}^{-1}$	$k_{H^+}/10^4 \text{ M}^{-1} \text{ s}^{-1}$
HCO ₂ H	0.44	9.79 ± 0.40	2.07 ± 0.38
HCO ₂ H	0.25	10.3 ± 0.8	2.56 ± 1.80
CH ₃ CO ₂ H	1.00	3.22 ± 0.05	2.11 ± 0.51

^aIonic strength = 0.10 M (NaCl).

We have found that the rate of this ketene acetal hydrolysis reaction can be measured in formic and acetic acid buffer solutions by stopped-flow techniques. The process is accompanied by a drop in carbon-carbon double bond absorbance at 220 nm, but as Figure 5 shows, this change is biphasic. The time constants of the two phases are sufficiently different to allow easy resolution into two separate rate processes. Both the fast and the slow reaction obey the first-order rate law well, and the slower process gives rate constants characteristic of vinyl alcohol ketonization.

Rates of the faster reaction measured in series of buffer solutions of constant buffer ratio and constant ionic strength (0.10 M) but changing (fivefold) buffer concentration are summarized in Table S4.¹⁴ The process shows strong general acid catalysis, as is characteristic of ketene acetal hydrolysis.¹⁷ General acid catalytic coefficients were evaluated by linear least-squares analysis of the relationship between observed rate constants and undissociated acid concentration, and hydronium ion catalytic coefficients were calculated from the intercepts of these relations and the hydronium ion concentrations of the buffers; the latter were obtained by calculation with use of literature values of the acid dissociation constants and activity coefficients recommended by Bates.¹⁹

The results produced in this way are listed in Table II. A Brønsted exponent of $\alpha = 0.49$ may be calculated from the two carboxylic acid catalytic coefficients; this is a typical value for the hydrolysis of ketene acetals of this reactivity. The average value of the hydrogen ion catalytic coefficient is $k_{H^+} = (2.25 \pm 0.16) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, which is three orders of magnitude greater than the hydrogen ion catalytic coefficient for the ketonization of vinyl alcohol. This ketene acetal hydrolysis reaction is thus sufficiently fast to be a good source of vinyl alcohol in mineral acid and moderately acidic buffer solutions. Ketonization, however, is catalyzed by bases as well as by acids, whereas ketene acetal hydrolysis is not, and in more basic solutions the rate difference between the two reactions becomes smaller. In the acetic acid buffer solutions used here, for example, ketene acetal hydrolysis was only 30 times faster than vinyl alcohol ketonization, and in solutions much more basic than that, this ketene acetal would no longer be a useful source of vinyl alcohol.

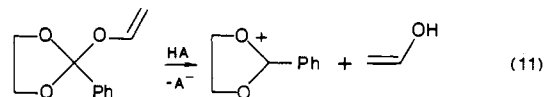
Ketonization of Vinyl Alcohol Generated by Hydrolysis. Measurements of the rate of ketonization of vinyl alcohol produced by ketene acetal hydrolysis of 1-(vinylloxy)-1-methoxyethene were measured in dilute aqueous (H₂O) perchloric acid solutions, over the concentration range [HClO₄] = 0.002–0.016 M by conventional spectrophotometry and over the concentration range [HClO₄] = 0.02–0.10 M by stopped-flow spectrophotometry. Measurements were also made in D₂O solution by the conventional method with DCl as the catalyst with [DCl] = 0.01–0.05 M. These data are summarized in Table S5.¹⁴

Observed first-order rate constants in all three sets of measurements were accurately proportional to acid concentration, and least-squares analysis gave $k_{H^+}^K = 30.2 \pm 0.8 \text{ M}^{-1} \text{ s}^{-1}$ for the stopped-flow measurements and $k_{H^+}^K = 34.9 \pm 1.0 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{D^+}^K = 7.57 \pm 0.10 \text{ M}^{-1} \text{ s}^{-1}$ for the measurements made by conventional spectrophotometry. These two determinations of $k_{H^+}^K$ are in good agreement with the value obtained here for the ketonization of vinyl alcohol produced by flash photolysis, $k_{H^+}^K =$

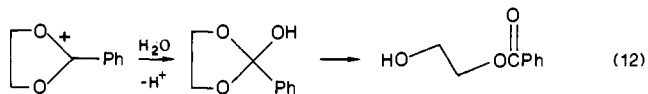
$33.8 \pm 1.3 \text{ M}^{-1} \text{ s}^{-1}$. The average of all three determinations is $k_{H^+}^K = 33.0 \pm 1.4 \text{ M}^{-1} \text{ s}^{-1}$, and the measurements made by conventional spectrometry give the isotope effect $k_{H^+}^K/k_{D^+}^K = 4.61 \pm 0.15$. This isotope effect is consistent with $k_{H^+}^K/k_{D^+}^K = 4.75 \pm 0.08$ measured before in a different laboratory for the ketonization of vinyl alcohol at 15 °C and ionic strength 1.00 M.²⁰ That previous study, however, reports a value of $k_{H^+}^K$ for this reaction at 25 °C and ionic strength 1.00 M which is some 35% greater than the result obtained here. It may be significant in this respect that that previous study also produced a value of k_{H^+} for a closely similar reaction, the hydrolysis of ethyl vinyl ether, which is also significantly greater than several earlier self-consistent literature values.²⁰

Rates of ketonization of vinyl alcohol produced by the ketene acetal hydrolysis reaction were also measured in aqueous formic and acetic acid buffer solutions. Series of solutions of constant buffer ratio and constant ionic strength (0.10 M) were used; buffer concentrations were generally varied by a factor of 5. These data are summarized in Table S6,¹⁴ and the intercepts obtained by extrapolating observed rate constants to zero buffer concentration are listed in Table I.

Vinyl alcohol was also generated in the present study by the ortho ester hydrolysis reaction shown in eq 3. The hydrolysis of cyclic ortho esters such as this is known to proceed through initial loss of the exocyclic alkoxy group,^{9,18,21} which in this case would produce vinyl alcohol, eq 11. Hydration of the 2-phenyl-1,3-



dioxolenium ion and subsequent breakdown of the hydrogen ortho ester thus formed, eq 12, then occur rapidly,¹⁸ leaving the slower



ketonization of vinyl alcohol as a readily observable process. This is borne out by the good correspondence between kinetic results obtained by using vinyl alcohol generated in this way and rate data based on vinyl alcohol produced by other methods (vide infra).

Rates of ketonization of vinyl alcohol made by this ortho ester hydrolysis reaction were measured in acetic acid buffer solutions. Again, series of solutions of constant buffer ratio and constant ionic strength (0.10 M) were used, and buffer concentrations were varied by a factor of 5. These data are summarized in Table S7, and intercepts obtained by extrapolating these results to zero buffer concentration are listed in Table I.

These zero-buffer-concentration intercepts consist mainly of the rate constant for the water reaction, k_w , but they do contain minor contributions from the acid and base catalyzed portions of the rate profile, i.e., from the other two terms of the rate law, eq 13, which governs the nonbuffer catalyzed reaction in this pH

$$k = k_{H^+}^K[H^+] + k_w + k_0/K_a^E/[H^+] \quad (13)$$

region. Since the coefficients of these other two terms have been evaluated, these contributions can be subtracted and values of k_w can be obtained. The results for all of the buffers studied here are listed in the last column of Table I. It may be seen that the agreement between values obtained by using vinyl alcohol generated by different methods is good, which indicates that these different techniques are all reliable methods of preparing vinyl alcohol for kinetic examination. The average of all eight results

(20) Kankaanpera, A.; Lajunen, M. *Acta Chem. Scand.* **1966**, *20*, 1790–1801. Kresge, A. J.; Chiang, Y. *J. Chem. Soc.* **1967**, 58–61. Salomaa, P.; Kreevov, M. M.; Eliason, R. *J. Phys. Chem.* **1968**, *72*, 1313–1316. Kreevov, M. M.; Williams, J. M. *J. Am. Chem. Soc.* **1968**, *90*, 6809–6813. Kresge, A. J.; Chen, H. L.; Chiang, Y.; Murrill, E.; Payne, M. A.; Sagatys, D. S. *J. Am. Chem. Soc.* **1971**, *93*, 413–423.

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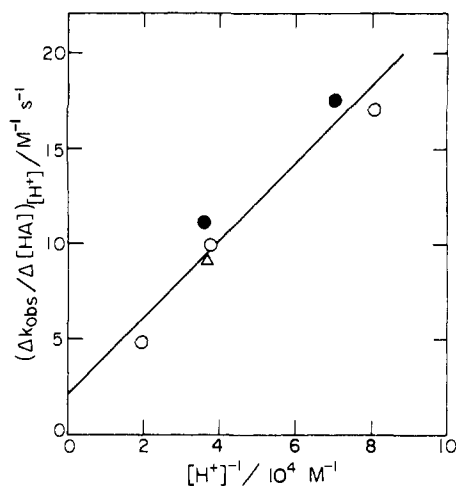
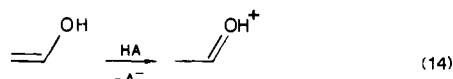


Figure 6. Relationship between buffer catalytic coefficients and hydronium ion concentration for the ketonization of vinyl alcohol in aqueous acetic acid buffer solutions at 25 °C; vinyl alcohol generated by flash photolysis (O), by hydrolysis of ketene acetal (Δ), and by hydrolysis of ortho ester (●).

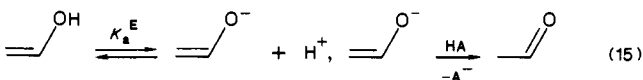
is $k_w = (3.95 \pm 0.14) \times 10^{-2} \text{ s}^{-1}$, from which $k_{\text{H}^+} = (1.26 \pm 0.08) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ can be calculated on the assumption that the mechanism of eq 8 applies.

This rate constant for direct carbon protonation of enolate by the hydronium ion is very much larger than the rate constant for the corresponding reaction of the enol: the ratio of the two is $k_{\text{H}^+} / k_{\text{H}^+}^{\text{K}} = (3.82 \pm 0.29) \times 10^7$. This indicates that converting a hydroxyl activating group on an already quite reactive carbon-carbon double bond ($k_{\text{H}^+}^{\text{K}} = 33 \text{ M}^{-1} \text{ s}^{-1}$) to an oxide ion raises the reactivity of this double bond to electrophilic attack tremendously.

Another test of the consistency of results obtained with vinyl alcohol produced by the three different methods of generation employed here may be made with the buffer-catalyzed portions of rate constants measured in acetic acid buffer solutions. These buffer catalytic coefficients consist of both general acid and general base catalyzed terms, with the general acid component arising from direct reaction of the enol with acid catalyst, eq 14, and the



general base component arising from prior ionization of the enol followed by reaction of the enolate ion with acid catalyst, eq 15.^{6,8} The rate law for this dual-channel reaction scheme in buffer



solutions for which $[\text{H}^+] \gg K_a^{\text{E}}$ is eq 16; it predicts that buffer catalytic coefficients (evaluated as slopes of plots of observed

$$k_{\text{buff}} = \left(\frac{\Delta k_{\text{obsd}}}{\Delta[\text{HA}]} \right)_{[\text{H}^+]} = k_{\text{HA}} + k_{\text{HA}}' K_a^{\text{E}} / [\text{H}^+] \quad (16)$$

first-order rate constants vs. buffer acid concentration) should be linear functions of $[\text{H}^+]^{-1}$. Figure 6 shows that this is indeed the case, and it shows as well that results obtained with vinyl alcohol generated by all three methods employed here form a self-consistent set.

Least-squares analysis of these data gives $k_{\text{HA}} = 2.05 \pm 1.42 \text{ M}^{-1} \text{ s}^{-1}$ as the intercept of the plot of Figure 6 and $k_{\text{HA}}' K_a^{\text{E}} = (2.04 \pm 0.28) \times 10^{-4} \text{ s}^{-1}$ as the slope. Dividing the latter by the known value of K_a^{E} gives $k_{\text{HA}}' = (6.52 \pm 0.95) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. The larger uncertainty in k_{HA} than in k_{HA}' reflects the fact that most of the buffer-catalyzed reaction in these acetic acid buffers is occurring via the route involving enolate shown in eq 15, and little is taking place by the direct reaction of the enol given in eq

14. The ratio of the two rate constants $k_{\text{HA}}' / k_{\text{HA}} = (3.2 \pm 2.3) \times 10^6$, though not especially well defined because of this imbalance, is nevertheless a large number. This is consistent with the much greater reactivity of enolate over enol toward reaction with the hydronium ion which was noted above.

Enolization. Rates of enolization of acetaldehyde were determined by using iodine to scavenge the enol as it formed. Measurements in dilute perchloric acid solutions performed at the $\text{I}_2\text{-I}_3^-$ isosbestic point were made over the concentration range $[\text{HClO}_4] = 0.02\text{-}0.10 \text{ M}$ and those at the I_3^- absorption maximum over the concentration range $[\text{HClO}_4] = 0.02\text{-}0.08 \text{ M}$. Corrections for the rapid acetaldehyde hydration reaction, eq 17, which converts a significant amount of substrate into a nonreactive form,



were made by multiplying observed rate constants by the factor $(1 + K_h)$ where $K_h (=1.059)^{12}$ is the equilibrium constant for the hydration reaction. These rate data are summarized in Table S8.¹⁴

The iodination of carbonyl compounds under acidic conditions is sometimes appreciably reversible. Calculations based upon an estimate of the equilibrium constant for the present system,²² however, indicate that iodination should be more than 99.9% complete under all of the conditions employed here. This conclusion is supported by the effect of iodide ion concentration upon the iodination reaction rate. Iodide ion is a product of the iodination reaction, and the rate in the reverse direction will therefore be directly proportional to iodide ion concentration. Thus, if reversibility were significant, iodination rate constants should vary with changes in $[\text{I}^-]$. No such variation was found in the present case when $[\text{I}^-]$ was changed by a factor of 4.

First-order specific rates of enolization determined by both the isosbestic point method and the absorption-maximum method of measurement were accurately proportional to perchloric acid concentration. Least-squares analysis gave the hydronium ion catalytic coefficients $k_{\text{H}^+}^{\text{E}} = (1.67 \pm 0.01) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ (isosbestic point method) and $k_{\text{H}^+}^{\text{E}} = (1.80 \pm 0.09) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ (absorption maximum method); the weighted average of these two values is $k_{\text{H}^+}^{\text{E}} = (1.68 \pm 0.01) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$.

This result is consistent with $k_{\text{H}^+}^{\text{E}} = 1.06 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ reported recently for the iodination of acetaldehyde in moderately concentrated aqueous sulfuric acid solutions;²³ correction of that rate constant for acetaldehyde hydration gives $k_{\text{H}^+}^{\text{E}} = 2.18 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, which is some 30% greater than the presently measured value, but rates of enolization are known to be faster in sulfuric than in perchloric acid because of additional catalysis by the HSO_4^- ion.²⁴ There is also an earlier report of the rate of iodination of acetaldehyde measured in hydrochloric acid solutions,²⁵ but the rate constant cited there, $k_{\text{H}^+}^{\text{E}} = 1.65 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, when corrected for hydration, gives $k_{\text{H}^+}^{\text{E}} = 3.40 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, which is in poorer agreement with the present result. An estimate of the hydronium ion catalytic coefficient for the enolization of acetaldehyde has also been made from measurements of the rate of the acid-catalyzed conversion of acetaldehyde to crotonaldehyde $k_{\text{H}^+}^{\text{E}} = 1 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$,²⁶ which when corrected for hydration gives $k_{\text{H}^+}^{\text{E}} = 2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, in substantial agreement with our results.

Some additional measurements of the rate of acid-catalyzed enolization of acetaldehyde were made in $\text{DClO}_4/\text{D}_2\text{O}$ solution by the isosbestic point method in order to provide an estimate of the solvent isotope effect on this reaction. These measurements were performed at a single perchloric acid concentration (0.023 M) and were paired with measurements in $\text{HClO}_4/\text{H}_2\text{O}$ at the same acidity. Two runs were made in each solvent; the results are the following: H_2O , $k = (4.37, 4.50) \times 10^{-7} \text{ s}^{-1}$; and D_2O , $k = (7.07, 7.07) \times 10^{-7} \text{ s}^{-1}$. These rate constants are corrected

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(26) McTigue, P. T.; Gruen, L. C. *Aust. J. Chem.* **1963**, *16*, 177-179.

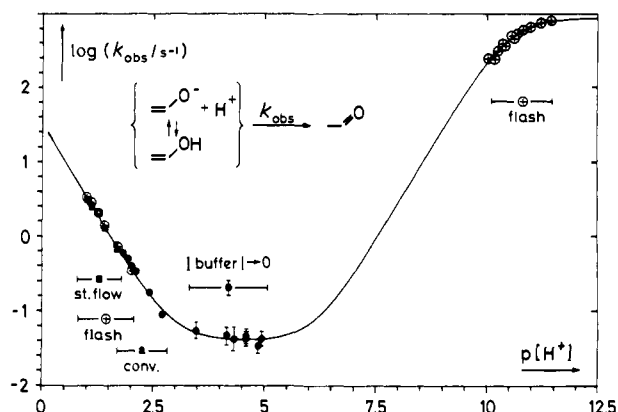


Figure 7. Rate profile for the conversion of vinyl alcohol to acetaldehyde.

for acetaldehyde hydration with the corrections made with $K_h = 1.059$ in H_2O ¹² and $K_h = 1.19$ in D_2O ; the latter is based upon the assumption that the solvent isotope effect on K_h measured at 15 °C ($K_{H_2O}/K_{D_2O} = 0.89$)¹² applies also at 25 °C.

Conversion of these results into the isotope effect $k_{H^+}^E/k_{D^+}^E$ requires a further adjustment for the small amount of reaction occurring by an "uncatalyzed" route with rate constant k_0 . A value of this rate constant in H_2O , $k_0 = (5.8 \pm 0.8) \times 10^{-8} s^{-1}$, is available from the measurements made over a range of perchloric acid concentrations described above. The isotope effect on this rate constant is likely to be small; a value of $(k_0)_{H_2O}/(k_0)_{D_2O} = 1.9$ has been measured for acetone,²⁷ and use of this number for acetaldehyde leads to $k_{H^+}^E/k_{D^+}^E = 0.57$. The result is not very sensitive to the value taken for the isotope effect on k_0 ; for example, use of $(k_0)_{H_2O}/(k_0)_{D_2O} = 1.0$ rather than 1.9 gives $k_{H^+}^E/k_{D^+}^E = 0.59$ and use of $(k_0)_{H_2O}/(k_0)_{D_2O} = 4.0$ gives $k_{H^+}^E/k_{D^+}^E = 0.56$. It appears safe, then, to conclude that $k_{H^+}^E/k_{D^+}^E = 0.57 \pm 0.02$.

Rates of enolization of acetaldehyde were also measured in sodium hydroxide solutions, over the concentration range $[NaOH] = 0.03$ – 0.09 M. Observed rate constants were corrected for the acetaldehyde hydration reaction, eq 17, and also for the reaction of the hydrate with hydroxide ion, eq 18. This correction has the



form indicated by eq 19, in which $K_h (=1.059)$ ¹² is the hydration equilibrium constant, and K_h^- is the equilibrium constant for the

$$k_{corr} = k_{obsd} \{1 + K_h(1 + K_h^-[HO^-])\} \quad (19)$$

reaction of hydrate with hydroxide ion (eq 18). The latter was taken as equal to the acid ionization constant of the hydrate, $K_a = 2.53 \times 10^{-14}$ M,²⁸ divided by the autoprotolysis constant of water on the assumption that the activity coefficients of the hydroxide ion and the hydrate conjugate base are equal at the ionic strength used (0.10 M); this gives $K_h^- = K_a/K_w = 2.53 M^{-1}$. These rate data are summarized in Table S9.¹⁴

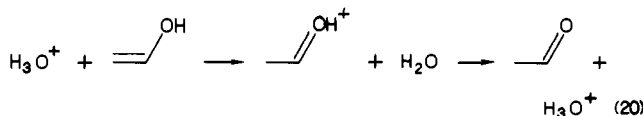
The first-order specific rates of enolization obtained in this way were accurately proportional to hydroxide ion concentration; least-squares analysis gave the hydroxide ion catalytic coefficient $k_{HO^-}^E = 1.17 \pm 0.02 M^{-1} s^{-1}$. The rate of iodination of acetaldehyde catalyzed by hydroxide ion has not been measured before, but the hydroxide ion catalytic coefficient for the enolization of acetaldehyde has been estimated from a study of the kinetics of the hydroxide ion promoted aldol condensation of acetaldehyde with formaldehyde;²⁹ that result, corrected for substrate hydration, gives $k_{HO^-}^E = 0.2 M^{-1} s^{-1}$ which is substantially less than the presently measured value.

Discussion

Rate Profile and Reaction Mechanism. The kinetic results obtained here for the conversion of vinyl alcohol to its acetaldehyde

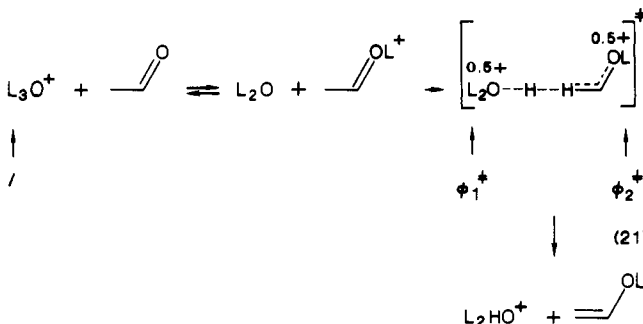
isomer are summarized in the rate profile of Figure 7. This profile refers to catalysis by solvent-derived species only: measurements made in buffer solutions over the region $p[H^+] = 3$ – 5 were extrapolated to zero buffer concentration in order to obtain the points indicated, and all of the other determinations were performed in either hydrochloric acid, perchloric acid, or sodium hydroxide solutions with no other added acidic or basic species.

It can be seen that there is an acid-catalyzed region, over which reaction may be attributed either to rate-determining carbon protonation of the enol by hydronium ion followed by rapid proton loss from the acetaldehyde conjugate acid thus formed, eq 20,⁶ or to a concerted mechanism where these two proton transfers



occur in a single reaction step.² We have discussed this mechanistic question in some detail in our recent report on isobutyraldehyde enol,^{6b} further insight may be gained from the solvent isotope effect we have measured here on the reverse process, the enolization of acetaldehyde, for the principle of microscopic reversibility requires the reaction mechanism for enolization to be the same—stepwise or concerted—as that for ketonization. Solvent isotope effects for these two mechanisms can be predicted by the method of fractionation factors, which expresses a solvent isotope effect as the product of fractionation factors for all exchangeable hydrogens of the initial state, ϕ_i^{IS} , divided by a like product for the transition state, ϕ_j^* : $k_{H_2O}/k_{D_2O} = \prod_i \phi_i^{IS} / \prod_j \phi_j^*$.³⁰

Stepwise enolization is depicted in eq 21, where exchangeable hydrogens are shown as L (L = H or D). The transition state



is written with 0.5 positive charge on each of the oxygen atoms because the second step of this reaction is probably nearly ergoneutral,³¹ and the proton in flight is therefore approximately half-transferred. On this basis, ϕ_1^* and ϕ_2^* can both be given the value $l^{0.5}$ where $l (=0.69)$ ^{30b,32} is the fractionation factor for the hydronium ion. This leads to $k_{H_2O}/k_{D_2O} = 0.57$, which is in remarkably good agreement with the measured value $k_{H^+}^E/k_{D^+}^E = 0.57 \pm 0.02$. It is conceivable that in step two of eq 21 there exists "transition-state imbalance", a phenomenon discussed in detail below. The effect would be to make the carbonyl oxygen in the transition state more positive than 0.5+, with a consequent increase in ϕ_2^* . The critical point to note in this regard is simply that an increase in ϕ_2^* has relatively little effect on the calculation; even if ϕ_2^* were as large as $l^{0.8}$, the calculated value of k_{H_2O}/k_{D_2O} would rise only to 0.64. These predictions are also consistent with

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(31) The pK_a of oxygen-protonated acetaldehyde has been estimated to be -8.67 ;²³ this gives $\Delta G^\circ = 11.8$ kcal mol⁻¹ for the first step of the reaction of eq 21. The acetaldehyde–vinyl alcohol equilibrium constant measured in the present work gives $\Delta G^\circ = 8.5$ kcal mol⁻¹ for the overall reaction, and combination of these two values gives $\Delta G^\circ = -3.3$ kcal mol⁻¹ for the second step.

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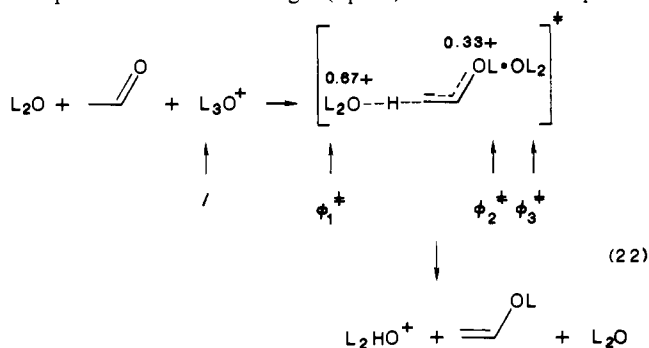
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the fact that hydronium ion isotope effects for preequilibrium proton transfers, such as that of this stepwise enolization, are usually inverse, $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} < 1$.^{30b,33}

The concerted mechanism for acetaldehyde enolization is shown in eq 22. This is an endoergic (uphill) reaction and the proton



leaving carbon is therefore more than half-transferred at the transition state; use of $2/3$ for the extent of this transfer leads to $\phi_1^* = f^{0.67} = 0.78$. The other proton transfer that occurs in this reaction is between two oxygen atoms. When proton transfer between oxygens takes place in a reaction step that also involves heavy atom reorganization, as in the present case, the proton is believed not to be in flight at the transition state but rather to lie in a stable potential well and be situated closer to the more basic oxygen atom.³⁴ This places that proton in the present case on the substrate oxygen rather than on the water oxygen, and that makes this water molecule an uncharged solvent species with a fractionation factor of unity; thus, $\phi_3^* = 1.00$. The proton now on the substrate oxygen atom, however, will have a fractionation factor substantially less than unity because it is strongly hydrogen bonded,^{34b,35} and $\phi = 0.5$ has in fact been assigned to the corresponding hydrogen in the concerted mechanism for the enolization of acetone.²⁷ Use of $\phi_2^* = 0.50$ then leads to $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 1.08$ as the predicted isotope effect for the mechanism of eq 22. This is in much poorer agreement with the observed value than the prediction made for the stepwise mechanism of eq 21, and that suggests that it is the stepwise mechanism which is operating.

A stepwise mechanism is also not inconsistent with the hydronium ion isotope effect measured here for the ketonization reaction itself, $k_{\text{H}^+}^{\text{K}}/k_{\text{D}^+}^{\text{K}} = 4.61 \pm 0.15$. This isotope effect is considerably greater than $k_{\text{H}^+}/k_{\text{D}^+} = 3.43 \pm 0.46$ predicted from a correlation of solvent isotope effects on the hydronium ion catalyzed hydrolysis of a group of vinyl ethers,³⁶ the mechanism of vinyl ether hydrolysis is closely similar to the stepwise mechanism for vinyl alcohol ketonization under consideration here, and the correlation might therefore be expected to apply to ketonization as well. Vinyl alcohol, however, has an O-H bond not present in vinyl ethers, and the oxygen atom of this bond becomes positively charged in the course of vinyl alcohol ketonization (eq 21 in reverse). This will contribute a factor of $1/f^{0.5} = 1.20$ to the isotope effect, which is consistent with the ratio of observed to predicted values: $(4.61 \pm 0.15)/(3.43 \pm 0.46) = 1.34 \pm 0.18$.

In the "uncatalyzed" region of the rate profile from $\text{p}[\text{H}^+] = 3-6$, reaction could occur through rapid ionization of the enol to enolate and hydronium ions followed by rate-determining carbon protonation of enolate by the hydronium ion, eq 8. Here again, however, an alternative mechanism involving a concerted intra-

Table III. Summary of Rate and Equilibrium Constants for the Keto-Enol Interconversion of Acetaldehyde in Aqueous Solution at 25 °C^a

process	constant
	$k_{\text{H}^+}^{\text{E}} = 1.68 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$
	$k_{\text{D}^+}^{\text{E}} = 2.9 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$
	$k_{\text{HO}^-}^{\text{E}} = 1.17 \text{ M}^{-1} \text{ s}^{-1}$
	$k_{\text{H}^+}^{\text{K}} = 3.30 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$
	$k_{\text{D}^+}^{\text{K}} = 7.57 \text{ M}^{-1} \text{ s}^{-1}$
	$k_{\text{H}^+}^{\text{K}'} = 1.26 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
	$k_0^{\text{K}'} = 8.82 \times 10^2 \text{ s}^{-1}$
	$k_{\text{HOAc}} = 2 \text{ M}^{-1} \text{ s}^{-1}$
	$k_{\text{HOAc}'} = 6.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$
	$K_{\text{E}} = 5.89 \times 10^{-7}$; $\text{p}K_{\text{E}} = 6.23$
	$K_{\text{a}}^{\text{E}} = 3.13 \times 10^{-11} \text{ M}$; $\text{p}K_{\text{a}}^{\text{E}} = 10.50$
	$K_{\text{a}}^{\text{K}} = 1.85 \times 10^{-17} \text{ M}$; $\text{p}K_{\text{a}}^{\text{K}} = 16.73$

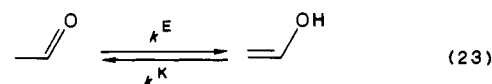
^a Ionic strength = 0.10 M.

molecular proton switch may also be considered.^{2c,5b,16} We know of no evidence at the present time that would allow a choice between these alternatives to be made.

The base-catalyzed portion from $\text{p}[\text{H}^+] = 6-11$ may be attributed to a rate-determining carbon protonation of the enolate ion, this time with water as the proton donor, eq 5. The fact that this catalysis becomes saturated and the rate of reaction reaches a constant value above $\text{p}[\text{H}^+] = 12$ would seem to require a two-step mechanism, and a concerted process here can thus be excluded.

This rate profile also illustrates the good agreement obtained among isomerization rate determinations made by the three different kinetic techniques and the three different methods of generating vinyl alcohol used in this study.

Tautomerization Equilibrium. The equilibrium constant for the conversion of acetaldehyde to its enol isomer, eq 23, may be expressed as the ratio of forward to reverse rate constants: K_{E}



$= k^{\text{E}}/k^{\text{K}}$. Since each of these rate constants has been measured in the present work, both for catalysis by the hydronium ion and for catalysis by the hydroxide ion, this equilibrium constant can now be evaluated.

For catalysis by the hydronium ion, $K_{\text{E}} = k_{\text{H}^+}^{\text{E}}/k_{\text{H}^+}^{\text{K}}$. These two rate constants have been measured as such (Table III), and the data give $K_{\text{E}} = [(1.68 \pm 0.01) \times 10^{-5}]/[(3.30 \pm 0.14) \times 10^1] = (5.08 \pm 0.22) \times 10^{-7}$; $\text{p}K_{\text{E}} = 6.29 \pm 0.02$.

The situation for catalysis by the hydroxide ion is somewhat less straightforward because hydroxide ion catalysis of the ketonization reaction becomes saturated (see Figure 4). This saturation was attributed to a shift in the equilibrium preceding the rate-determining step shown in eq 5, and the rate data were analyzed in terms of this mechanism, but this ketonization reaction may also be handled in a less mechanistic way, similar to the treatment used for the hydronium ion process, with K_{E} as a ratio of operational rate constants, i.e., $K_{\text{E}} = k_{\text{HO}^-}^{\text{E}}/k_{\text{HO}^-}^{\text{K}}$. The rate constant $k_{\text{HO}^-}^{\text{K}}$ is then equal to the product of the equilibrium and rate constants shown in eq 5, $k_{\text{HO}^-}^{\text{K}} = Kk_0^{\text{K}'}$, and, since $K = K_{\text{a}}^{\text{E}}/K_{\text{w}}$, $k_{\text{HO}^-}^{\text{K}} = k_0^{\text{K}'}/K_{\text{w}}$ and $K_{\text{E}} = k_{\text{HO}^-}^{\text{E}}/k_0^{\text{K}'}$. The product $k_0^{\text{K}'}/K_{\text{w}}$

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bonyl compounds show this effect as well: for a series of ring-substituted 3-benzylpentane-2,4-diones, $\alpha = 0.77$ while $\beta = 0.44$.⁵⁰

Now consider variations in the R_1 group of eq 26. This group is more remote than R_2 from the central carbon on which negative charge builds up in the transition state, but it is closer than R_2 to the enolate oxygen atom where the charge is relocated in the final state. Lagging charge relocation will therefore cause R_1 to have less of an effect on the rate constant than expected from its effect on the equilibrium constant and the magnitude of β . The result will be a diminished value of α , as is observed.

Another manifestation of transition-state imbalance may be obtained by comparing rate and equilibrium constants for the ionization of acetaldehyde determined here with those for isobutyraldehyde.⁶ Isobutyraldehyde is the stronger acid, $pK_a^K = 15.49$ as opposed to $pK_a^K = 16.73$ for acetaldehyde, and yet the specific rate for proton transfer from isobutyraldehyde to hydroxide ion, $k = 0.142 \text{ M}^{-1} \text{ s}^{-1}$, is less than that for the same reaction of acetaldehyde, $k = 1.17 \text{ M}^{-1} \text{ s}^{-1}$. These data give the "abnormal" Brønsted exponent $\alpha = -0.3$.⁵¹

A similar situation is found for the ionization of the analogous nitro compounds, nitromethane and 2-nitropropane, where $\alpha =$

-0.5 .^{49b} This phenomenon has also been attributed to lagging negative charge relocation in the transition state, which exalts the effect of methyl substitution on the reaction rate, but this time the effect is coupled with methyl-group stabilization of the carbon-nitrogen double bond of the nitronate ion.

A similar explanation may be advanced for the case of acetaldehyde and isobutyraldehyde. Methyl-group stabilization of the carbon-carbon double bond dominates in the final state enolate ion because the methyl groups are now remote from the relocated negative charge; isobutyraldehyde is thus a stronger acid than acetaldehyde. In the transition state, on the other hand, the not yet delocalized negative charge is near the site of methyl substitution and the destabilizing, electron-supplying polar effect of methyl dominates. The effects of methyl substitution upon rate and equilibrium constants are thus in opposite directions, and a negative value of α results.

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Supplementary Material Available: Tables S1-9 of rate data (10 pages). Ordering information is given on any current masthead page.

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Experimental and Theoretical Evidence for Nonlinear Coordination of "sp-Hybridized" Carbon Atoms: The Gas-Phase Structure of Trifluoroethyldynesulfur Trifluoride, $\text{CF}_3-\text{C}\equiv\text{SF}_3$

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Abstract: We report an extensive series of studies, both experimental and theoretical, which probe the shape of CF_3CSF_3 and its skeletal bending potential. Gas phase and matrix IR and Raman spectra have been recorded and assigned, and a force field has been obtained. The vibrational assignment is most simply based on a C_{3v} model with a linear $\text{C}-\text{C}\equiv\text{S}$ skeleton, but small deviations from linearity cannot be excluded. The gas-phase molecular structure has been studied by electron diffraction. A range of molecular models has been considered, including the effects of internal rotation of the CF_3 group and of large-amplitude bending at the two-coordinate carbon. A linear skeleton is incompatible with the diffraction data. The barrier to linearity is greater than 2 kJ mol^{-1} but cannot be determined precisely. The average $\text{C}-\text{C}\equiv\text{S}$ angle is $155 (3)^\circ$ (3σ uncertainties in parentheses) for all acceptable models; this is a substantially greater deviation from linearity than found in solid CF_3CSF_3 . The electron diffraction model is supported by broad band microwave spectroscopy, which yields $B + C = 1.545 \text{ GHz}$ in very good agreement with the structure derived by electron diffraction. Other geometrical parameters (r_a values) are $\text{C}-\text{F} = 1.329 (4) \text{ \AA}$, $\text{C}-\text{C} = 1.45 (2) \text{ \AA}$, $\text{S}\equiv\text{C} = 1.434 (14) \text{ \AA}$, $\text{S}-\text{F} = 1.561 (3) \text{ \AA}$, $\text{FCF} = 108.4 (5)^\circ$, and $\text{FSF} = 93.2 (9)^\circ$. Ab initio calculations have been performed for $\text{HC}\equiv\text{SF}_3$, $\text{FC}\equiv\text{SF}_3$, $\text{CH}_3\text{C}\equiv\text{SF}_3$, and $\text{CF}_3\text{C}\equiv\text{SF}_3$. All are linear at carbon with use of SCF wave functions but are predicted to bend, though to very different extents, when electron correlation is included at the MP2 level. Calculations on $\text{HC}\equiv\text{SH}_3$ showed that the MP2 method *underestimates* the influence of electron correlation on the skeletal bending potential.

The first compound containing a $\text{C}\equiv\text{S}$ triple bond has recently been prepared,^{2,3} and its geometric structure has attracted some interest by theoreticians and experimentalists. Ab initio calcu-

lations in the HF approximation⁴ and a low-temperature X-ray study³ result in very short $\text{C}\equiv\text{S}$ (1.404 and $1.420 (5) \text{ \AA}$, respectively) and $\text{C}-\text{C}$ bonds (1.439 and $1.434 (7) \text{ \AA}$) and in FSF angles near 90° (92.7° and $90.9^\circ-94.3^\circ$). These studies differ, however, with respect to the configuration of the $\text{C}-\text{C}\equiv\text{S}$

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