References and Notes

(1) This investigation was supported by a grant from the National Science Foundation, GP-13845. The work was taken for the most part from the M.S. Theses of L. L. Vestal (1972) and G. R. Cipau (1974).

(2) (a) C. Rüchardt and R. Hecht, *Chem. Ber.*, **98**, 2460 (1965); (b) C. Rüchardt and R. Hecht, *ibid.*, **98**, 2471 (1965).

(3) (a) J. E. Leffler, *J. Amer. Chem. Soc.*, **72**, 67 (1950); (b) P. D. Bartlett and J. E. Leffler, *ibid.*, **72**, 3030 (1950); (c) P. D. Bartlett and F. D. Greene, *ibid.*, **76**, 1088 (1954); (d) D. B. Denney, *ibid.*, **78**, 590 (1956); (e) D. B. Denney and D. G. Denney, *ibid.*, **79**, 4806 (1957); (f) J. E. Leffler and C. C. Petropoulos, *ibid.*, **79**, 3068 (1957); (g) F. D. Greene, H. D. Stein, C. Chu, and F. M. Vane, *ibid.*, **86**, 2080 (1964); (h) H. H. Lau and H. Hart, *ibid.*, **81**, 4897 (1959); (i) J. E. Leffler, R. D. Faulkner, and C. C. Petropoulos, *ibid.*, **80**, 5435 (1958); (j) J. E. Leffler and A. F. Wilson, *J. Org. Chem.*, **25**, 424 (1960); (k) J. E. Leffler and J. S. West, *ibid.*, **27**, 4191 (1962); (l) D. Z. Denney, T. M. Valega, and D. B. Denney, *J. Amer. Chem. Soc.*, **86**, 46 (1964); (m) R. C. Lamb, J. G. Pacifici, and P. W. Ayers, *ibid.*, **87**, 3928 (1965); (n) D. B. Denney and N. Sherman, *J. Org. Chem.*, **30**, 3760 (1965); (o) R. C. Lamb and J. R. Sanderson, *J. Amer. Chem. Soc.*, **91**, 5034 (1969); (p) C. Walling, H. P. Waits, J. Milovanovic, and C. G. Pappianou, *J. Amer. Chem. Soc.*, **92**, 4927 (1970); (q) H. R. Ward, R. G. Lawler, and R. Cooper, *ibid.*, **94**, 545 (1972); (r) J. E. Leffler and A. A. More, *ibid.*, **94**, 2483 (1972); (s) S. Oae, K. Fujimori, and S. Kozuka, *Tetrahedron*, **28**, 5327 (1972), and references cited therein.

(4) R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3432 (1957).

(5) These results are in keeping with our experiences of the past several years using the excess stable radical method, namely, that it is difficult to obtain reproducible data on initiators that decompose slowly above 60°. The method usually works well for low-temperature initiators.

(6) It has been shown that, for decompositions of bis(isobutyryl) peroxide, a peroxide which forms the inversion compound in good yield, the rate constants obtained in a series of nonpolar solvents of different polarizabilities increase with increasing solvent polarizability, *i.e.*, benzene > toluene = *p*-xylene > carbon tetrachloride > cyclohexane. Therefore, for type 1 peroxides, the sequence benzene > ethylbenzene > cyclohexane is in complete agreement with the previously established series (*cf.* Figure 1 in ref 3n).

(7) (a) D. J. Brown, *J. Amer. Chem. Soc.*, **62**, 2657 (1940); (b) P. D. Bartlett and N. Nozaki, *ibid.*, **68**, 1688 (1946); (c) *ibid.*, **69**, 2299 (1947); (d) W. E. Cass, *ibid.*, **68**, 1976 (1946); (e) F. G. Edwards and F. R. Mayo, *ibid.*, **72**, 1265 (1950); (f) W. E. Cass, *ibid.*, **72**, 4915 (1950); (g) C. G. Swain, W. T. Stockmayer, and J. T. Clarke, *ibid.*, **72**, 5426 (1950); (h) M. Levy, M. Steinberg, and M. Szwarc, *ibid.*, **76**, 5978 (1954); (i) J. Smid, A. Rembaum, and M. Szwarc, *ibid.*, **78**, 3315 (1956); (j) D. F. DeTar and C. Weis, *ibid.*, **78**, 4296 (1956); **79**, 3041 (1957); (k) D. F. DeTar and D. Wells, *ibid.*, **82**, 5839 (1960); (l) D. F. DeTar, R. A. J. Long, J. Randleman, J. Bradley, and P. Duncan, *ibid.*, **89**, 4051 (1967); (m) D. F. DeTar, *ibid.*, **89**, 4058 (1967); (n) R. C. Lamb, W. E. McNew, Jr., J. R. Sanderson, and D. C. Lunney, *J. Org. Chem.*, **36**, 174 (1971); (o) for a good discussion and other important references on radical-induced decomposition, *cf.* R. Hiatt in D. Swern, Ed., "Organic Peroxides," Vol. 2, Wiley-Interscience, New York, N. Y., 1971, pp 828–833.

(8) "Numerical Analysis Routines," General Electric Co., pp 242–248.

(9) (a) D. S. Tarbell and E. J. Longosz, *J. Org. Chem.*, **24**, 774 (1959); (b) D. S. Tarbell and E. J. Longosz, *ibid.*, **26**, 2161 (1961); (c) T. B. Windholtz, *ibid.*, **25**, 1703 (1960); (d) *cf.* M. Matzner, R. P. Kurkjy, and R. J. Cotter, *Chem. Rev.*, **64**, 645 (1964).

(10) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 325–342.

(11) The uncorrected value for $10^5 k_d = 3.90$ for **1f** (S = *p*-NO_2) in cyclohexane at 75°. The corrected value is presented in Table II.

(12) Thus, when all rate constants are included, the correlation coefficients for the correlations with σ are near 0.97 at all five temperatures. However, if rate constants for **1a** (*p*-OCH_3) are ignored, the *r* values are near 0.997.

(13) *Cf.* J. Shorter, "Correlation Analysis in Organic Chemistry," Oxford University Press, London, 1973, pp 15–16. We have used capital *R* for the Yukawa–Tsuno constant to distinguish it from *r*, which is used in this paper to designate the correlation coefficient.

(14) *Cf.* R. Curci and J. O. Edwards in "Organic Peroxides," Vol. I, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 212–218.

(15) Infrared spectra were obtained using Perkin-Elmer Model 137 and Model 257 spectrophotometers; nmr spectra were obtained using Hitachi Perkin-Elmer Model R-20 and Varian Model A-60 spectrometers; Atlas Model CH-4 and CH-5 mass spectrometers were used to obtain mass spectra.

(16) Rüchardt and Trautwein showed that the acid obtained from bromobenzene by this procedure, mp 109–110°, is actually the meta isomer. The proof consisted of the oxidation of the decarbonylation products of the corresponding aldehyde to *m*-bromobenzoic acid, and by the independent synthesis of β-(*p*-bromophenyl)isovaleric acid, mp 68–69°, from β-(*p*-aminophenyl)isovaleric acid. *Cf.* C. Rüchardt and S. Eichler, *Chem. Ber.*, **95**, 1921 (1962).

(17) A. Hoffman, *J. Amer. Chem. Soc.*, **51**, 2542 (1929).

(18) J. Corse and R. Rohrmann, *J. Amer. Chem. Soc.*, **70**, 370 (1948).

(19) *Cf.* ref 16, as well as paper II in that series: C. Rüchardt, *Chem. Ber.*, **94**, 2609 (1961).

(20) M. S. Newman and H. L. Holmes, "Organic Syntheses," Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1943, p 428.

(21) S. R. Sandler and W. Karo, "Organic Functional Group Preparations," Organic Chemistry, Vol. 12, Academic Press, New York, N. Y., 1968, p 208.

(22) (a) L. S. Silbert, E. S. Siegel, and D. Swern, *J. Org. Chem.*, **27**, 1336 (1962); (b) *cf.* ref 7o, Vol. 1, p 492.

(23) This absorption overlaps the *p*-nitrobenzoyl absorption in the region above δ 8.00.

(24) J. I. G. Cadogan and W. R. Foster, *J. Chem. Soc.*, 3071 (1961).

(25) A. Dodonov and W. A. Waters, *J. Chem. Soc.*, 2459 (1965).

(26) Although we are aware of the fact that acetone reacts slowly with iodine, because of the excellence with which most of our data fit the first-order law, we assume that this error is scalar, and perhaps kept small by the fact that the solutions were kept cold. *Cf.* R. D. Mair and R. T. Hall in ref 7o, p 587.

Kinetics and Mechanisms of Reactions of 3-Buten-2-one and Related Compounds in Aqueous Perchloric Acid

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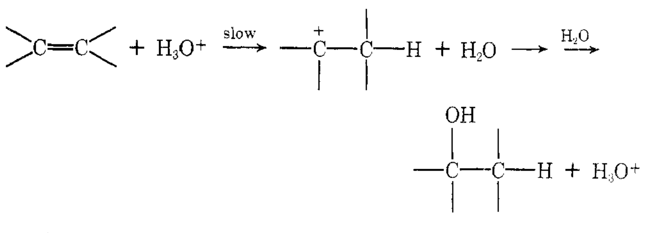
A detailed study of the hydration of homologs of 3-buten-2-one is reported. Rate constants for the hydration and dehydration reactions have been separated and activation parameters, precise solvent isotope effects, and acidity dependences have been measured over a wide range of acidity, 1–10 *M* perchloric acid. These mechanistic criteria are discussed in view of other olefin hydrations.

Hydration of olefins in aqueous acidic media has been studied extensively and the reaction mechanisms for several classes of olefins have been established.[1–5] For simple aliphatic olefins, dienes, and substituted styrenes, the mechanism of hydration has been shown to involve rate-determining proton transfer from hydronium ion to olefinic carbon, followed by addition of water to the carbonium ion thus formed[1–4] (Scheme I).

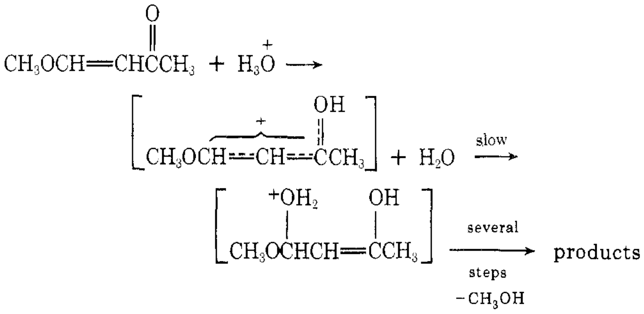
Scheme I



These reactions are characterized by solvent isotope effects, $k(H_2O)/k(D_2O)$, of 1.4–5 and entropies of activation of −5 to 0 eu. 3-Buten-2-one and its homologs are a special class of olefins having a carbonyl group conjugated with a double bond. Hydration of some α,β-unsaturated ketones has been reported previously.[6–9] The compounds studied do not appear to hydrate by the type of mechanism accepted for hydration of aliphatic olefins, dienes, and styrenes.

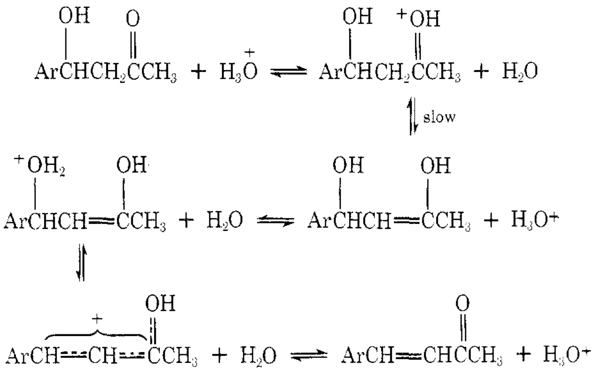
The alkoxy-substituted α,β-unsaturated ketone 4-methoxy-3-buten-2-one undergoes a vinyl ether hydrolysis which proceeds *via* a 1,4 addition of water to the conjugated system followed by loss of methanol[6] (Scheme II). This reaction proceeds faster in deuterio solvent and exhibits an entropy of activation of −26 eu. It is significant that the rate-controlling step in this hydrolysis is attack by water on the conjugate acid of 4-methoxy-3-buten-2-one.

Scheme II



β-Aryl-β-hydroxy ketones are dehydrated reversibly by two mechanisms, the reverse of Scheme I and Scheme III.[7] Reactions occurring *via* Scheme III are characterized by entropies of activation of −20 eu and a nonlinear dependence of log k on $-H_0$. Substitution of carbonium ion stabilizing groups on the carbon β to the carbonyl favor reaction *via* Scheme I.

Scheme III



These facts, taken in conjunction with the considerable discussion surrounding the mechanism of hydration of simple aliphatic alkenes *vs.* substituted styrenes, demonstrate the importance of precisely elucidating the mechanism of hydration of simple aliphatic α,β-unsaturated ketones *vs.* aryl-substituted α,β-unsaturated ketones. In view of the conclusions regarding hydrolysis of 4-methoxy-3-buten-2-one, it is critical to establish not only whether a 1,2 or 1,4 addition of water occurs, but also whether attack by water or proton transfer from hydronium ion to carbon is rate controlling.

Hydration of 4-methyl-3-penten-2-one has been reported recently[8,9] but the results thus far are consistent with several interpretations.[9] Consequently, a complete detailed study of the hydration of homologs of 3-buten-2-one is now reported. Rate constants for the hydration and dehydration reactions have been separated and acidity dependences, activation parameters, and precise solvent isotope effects have been measured over a wide range of acidity, 1–10 M perchloric acid. These mechanistic criteria are particularly useful when considered in light of results from other olefin hydrations.

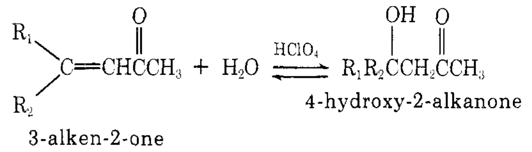
Experimental Section

Materials and Kinetic Method. All substrates were obtained from Aldrich Chemical Co. and were molecularly distilled just prior to each kinetic run. The kinetic method employed was that described previously.[1] Deuterioperchloric acid solutions were made from deuterium oxide (99.8% D_2O, Stohler Isotope Chemicals) and concentrated deuterioperchloric acid, as described previously.[1]

Product Analysis. It was suspected that acetone was being formed from 4-methyl-3-penten-2-one in perchloric acid solutions greater than 8 M. Consequently, 1.0 g (0.01 mol) of 4-methyl-3-penten-2-one was dissolved in 5 ml of ethanol and this solution was added slowly to 1 l. of 10 M perchloric acid accompanied by vigorous stirring. After about 10 half-lives of reaction time (100 hr at 25°), 300 mg (0.0015 mol) of 2,4-dinitrophenylhydrazine was added to a 100-ml aliquot of the 10 M acid–ketone solution. Back-titration with 2 N NaOH to about 80% neutralization yielded yellow-orange crystals which were recrystallized from ethanol–water and dried under vacuum. The yield of bright yellow dinitrophenylhydrazone was 195 mg (80%), mp 123–125° (lit.[10] mp 126°). Pmr spectra of this dinitrophenylhydrazone and authenic acetone dinitrophenylhydrazone were superimposable.

Results

The reactions investigated are reversible and at equilibrium the product concentration is greater than the reactant concentration.



(1)

1, $R_1 = R_2 = H$
2, $R_1 = H$; $R_2 = CH_3$
3, $R_1 = R_2 = CH_3$

Observed Rate Constants, k_{obsd}. Pseudo-first-order rate constants were determined in the traditional way[1] and are tabulated in Table I. In order to measure the solvent isotope effect, k_{obsd} was determined in $DClO_4$–D_2O solutions. However, since the reaction is overall reversible, exchange of hydrogen for deuterium occurred on the substrate. To ensure that $k_{obsd}(D_2O)$ was measured prior to exchange becoming important, a computer program was developed[11] similar to the iterative type provided by Wiberg.[12] The pseudo-first-order rate constants in Table II are those calculated by computer and are true constants over at least 2 half-lives of reaction.

Equilibrium Ratios, [4-Hydroxy-2-alkanone]/[3-Alken-2-one]. Since the reactant, 3-alken-2-one, is the only specie absorbing significantly at the wavelengths used, calculation of the equilibrium ratio (eq 2) is considerably simplified (data in Table III).

$$\frac{[\text{4-hydroxy-2-alkanone}]}{[\text{3-alken-2-one}]} = \frac{A_0 - A_e}{A_e} \qquad (2)$$

[4-hydroxy-2-alkanone] = molarity of the product at equilibrium

[3-alken-2-one] = molarity of the reactant at equilibrium

A_0 = absorbance at time zero (*i.e.*, upon mixing)

A_e = absorbance at equilibrium (*i.e.*, at time "infinity")

The value of A_e was not directly measurable in $DClO_4$–D_2O solutions (owing to exchange of hydrogen for deuterium on the substrate); consequently, the value of A_e calculated by the iterative computer program (see previous section) was used to calculate the equilibrium ratios in Table IV.

Table I
Values of k_{obsd} in Aqueous $HClO_4$[a]

		$10^4 k_{obsd}$		
M_{HClO_4}	$-H_A$[b]	3-Buten-2-one[c]	3-Penten-2-one[d]	4-Methyl-3-penten-2-one[e]
		15°		
4.03	1.64	5.87		
6.28	2.42	15.4		
8.26	3.24	32.3		
9.30	3.59	42.9		
9.96	3.83	46.9		
11.10	4.20	36.1		
		20°		
2.57	1.09	4.91		
		25°		
9.30	3.59	97.6		
		30°		
2.57	1.09	12.5	2.89	4.54
6.28	2.42			14.0
8.26	3.24	114		
9.30	3.59	147		
9.96	3.83			0.187[f]
		40°		
1.05	0.31	9.72	2.85	3.90
2.57	1.09	27.8	6.95	10.3
4.03	1.64	55.0	12.5	19.1
6.28	2.42	144	21.7	31.8
7.48	2.92		31.0	26.6[f]
8.26	3.24	284	30.5	0.96[f]
9.30	3.59			0.702[f]
9.96	3.83			0.666[f]
		50°		
2.57	1.09		15.5	22.2
6.28	2.42			61.1
9.96	3.83			1.54[f]

[a] Means of replicate determinations; average deviations from mean values were $< \pm 2\%$. [b] Reference 14. [c] Followed at 210 nm. [d] Followed at 226 nm. [e] Followed at 243 nm. [f] Followed at 278 nm.

Table II
Values of k_{obsd} in $DClO_4$–D_2O Solution at 40° [a]

	$10^4 k_{obsd}$		
M_{DClO_4}	3-Buten-2-one[b]	3-Penten-2-one[c]	4-Methyl-3-penten-2-one[d]
1.05	4.71	0.979	1.33
4.70	28.9	6.88	8.51
9.39	63.8		0.537

[a] Means of replicate determinations; average deviation from mean value were $< \pm 2\%$. [b] Followed at 210 nm. [c] Followed at 226 nm. [d] Followed at 243 nm. [e] Measured at 30° rather than 40°.

Table III
Equilibrium Measurements, [4-Hydroxy-2-alkanone]/[3-Alken-2-one[a]]

M_{HClO_4}	[4-hydroxy-2-butanone]/[3-buten-2-one][b]	[4-hydroxy-2-pentanone]/[3-penten-2-one][c]	[4-hydroxy-4-methyl-2-pentanone]/[4-methyl-3-penten-2-one][d]
	15°		
4.03	22.7		
6.28	20.4		
	20°		
2.57	22.2		
	30°		
2.57	19.0	3.90	9.02
6.28			4.08
	40°		
1.05		3.35	8.49
2.57	13.0	3.14	6.75
4.03		2.46	5.21
6.28		1.96	3.92
7.48		1.06	1.36
8.26		0.912	
	50°		
2.57		2.67	5.15
6.28			2.52

[a] Means of replicate determinations; average deviations from mean values were $< \pm 2\%$. [b] Measured at 210 nm. [c] Measured at 226 nm. [d] Measured at 243 nm.

Table IV
Equilibrium Measurements in $DClO_4$–D_2O Solutions at 40° [a]

M_{DClO_4}	[4-hydroxy-2-butanone]/[3-buten-2-one][b]	[4-hydroxy-2-pentanone]/[3-penten-2-one][c]	[4-hydroxy-4-methyl-2-pentanone]/[4-methyl-3-penten-2-one][d]
1.05	6.55	1.67	2.92
4.70	3.91	0.96	2.07
9.39	3.25[e]		

[a] Means of replicate determinations; average deviations from mean values were $< \pm 5\%$. [b] Measured at 210 nm. [c] Measured at 226 nm. [d] Measured at 243 nm. [e] Measured at 30° rather than 40°.

Separation of k_{hyd} and k_{dehyd}. These rate constants were calculated from k_{obsd} and the equilibrium ratios using the following relationships.[13]

$$k_{obsd} = k_{hyd} + k_{dehyd} \tag{3}$$

$$\frac{[\text{4-hydroxy-2-alkanone}]}{[\text{3-alken-2-one}]} = \frac{k_{hyd}}{k_{dehyd}} \tag{4}$$

k_{hyd}, the rate constant for the forward reaction in eq 1

k_{dehyd}, the rate constant for the reverse reaction in eq 1

Figure 1 shows the acidity dependence of k_{hyd}. H_A[14] is used as the measure of medium acidity, since it has been shown that α,β-unsaturated ketones behave as Hammett bases when the extent of protonation is measured using H_A.[15,16]

At 15°, the equilibrium ratio for the hydration of 3-buten-2-one is sufficiently large (>20) so as to make calculation of k_{hyd} from k_{obsd} unnecessary (*i.e.*, k_{obsd} essentially equals k_{hyd}); consequently the rate constants plotted for 3-buten-2-one are k_{obsd}. Two of these, at $H_A = -0.31$ and -1.09, are extrapolated from studies at higher temperatures (Table I).

Plots of log k_{hyd} *vs.* $-H_A$ (Figure 1) for 3-buten-2-one, 3-penten-2-one, and 4-methyl-3-penten-2-one are linear through $H_A = -1.64$ (4.03 M $HClO_4$) with slopes of 0.58, 0.48, and 0.51, respectively. Though the significance of these slopes is discussed later, it is interesting to note that similar plots *vs.* $-H_0$ are nonlinear even in this moderate acid concentration range. The curvature in Figure 1 at greater acid concentrations is due to protonation of the substrate (discussion to follow and ref 16).

Solvent Isotope Effects, $k_{hyd}(H_2O)/k_{hyd}(D_2O)$. Calculation of solvent isotope effects given in Table V required interpolation of $k_{hyd}(H_2O)$ in 4.70 M $HClO_4$ at 40° from

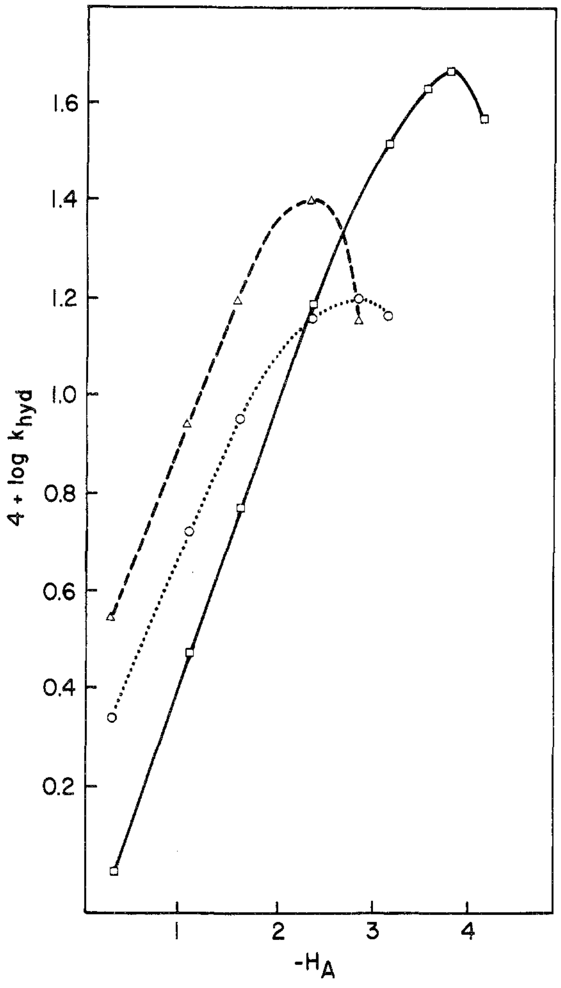


Figure 1. Acidity dependence of the hydration of 3-buten-2-one (□ ——, 0.58), 3-penten-2-one (○ · · · ·, 0.48), and 4-methyl-3-penten-2-one (△ - - - -, 0.51). The number in parentheses gives the slope of the straight line established by the first three points. Data for 3-buten-2-one are at 15°; other data are at 40°.

data reported in Tables I and III. The ratio $k_{hyd}(H_2O)/k_{hyd}(D_2O)$ thus represents the rate of hydration of a 3-alken-2-one in $HClO_4$–H_2O solution divided by the rate of hydration of a 3-alken-2-one in a $DClO_4$–D_2O solution of equal molarity.

Activation Parameters. Enthalpy and entropy of activation were calculated in the usual fashion[1] for the hydration of 3-alken-2-ones (*i.e.*, data in Table VI is based on k_{hyd} values).

Discussion

The mechanism by which hydration of simple aliphatic α,β-unsaturated ketones proceeds is given in Scheme IV.

Scheme IV

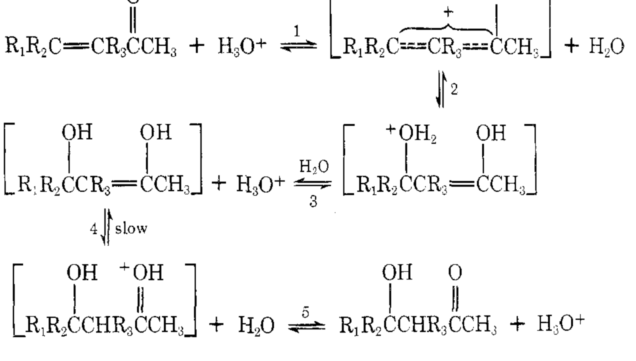


Table V
Solvent Isotope Effects for the Hydration of 3-Alken-2-one at 40°

	$k_{hyd}(H_2O)/k_{hyd}(D_2O)$		
M_{acid}	3-Buten-2-one	3-Penten-2-one	4-Methyl-3-penten-2-one
1.05	2.38	3.56	3.51
4.70	3.46	3.12	3.31
9.39	3.08[a]		1.28

[a] At 30°.

Below about 6 M perchloric acid, equilibrium 1 lies far to the left and step 4 is rate controlling, as shown by (a) the very large solvent isotope effect (Table V), (b) the very large negative entropy of activation (Table VI), and (c) the fact that 3-buten-2-one hydrates three times faster than 4-methyl-3-penten-2-one (Table I). The primary solvent isotope effect indicates that proton transfer to carbon is rate controlling. The large negative entropy is consistent with incorporation of a molecule of water into the transition state in addition to the hydronium ion. The somewhat greater reactivity of 3-buten-2-one over 4-methyl-3-penten-2-one demonstrates that reaction cannot occur *via* Scheme I (*e.g.*, isobutene hydrates 10^3–10^4 times faster than propene).[17]

Above 6 M perchloric acid, some of the substrates are *present increasingly as the conjugate acid* (*i.e.*, equilibrium 1 lies to the right). The kinetic expression differs significantly from that of the reaction in dilute acid. Allowing S = substrate and SH^+ = protonated substrate

$$\text{when } [S] \gg [SH^+] \; v = \frac{k_1k_2k_3k_4}{k_{-1}k_{-2}k_{-3}}[S]A_{H_3O^+}A_{H_2O}\frac{f_s}{f_{tr^+}}$$

$$\text{when } [SH^+] \gg [S] \; v = \frac{k_2k_3k_4}{k_{-2}k_{-3}}[SH^+](A_{H_2O})^2\frac{f_{SH^+}}{f_{tr^-}}$$

Thus as long as the substrate is present as S (equilibrium 1 lies to the left), k_{obsd} will increase with increasing acidity according to the term $A_{H_3O^+}A_{H_2O}$ (f_s/f_{tr^+}) above. However, when the substrate is present as SH^+ (equilibrium 1 lies to the right), k_{obsd} will decrease with increasing acidity according to the term $(A_{H_2O})^2$ (f_{SH^+}/f_{H_2O}). This becomes of great significance when the kinetic expressions for dehydration are examined (*i.e.*, the reverse of Scheme IV). No matter whether the α,β-unsaturated ketone is present as S or SH^+, k_{obsd} for dehydration increases with increasing acidity according to the term $A_{H_3O^+}$ (f_{ROH}/f_{tr^+}), where ROH denotes the β-hydroxy ketone product of Scheme IV. Consequently as the acidity increases beyond 6 M $HClO_4$, a marked *decrease* in equilibrium constant (Table III) indicates that the substrate S is becoming increasingly SH^+ by equilibrium 1 shifting to the right. For 4-methyl-3-penten-2-one this occurs at about 6 M $HClO_4$; for 3-penten-2-one it occurs at *ca.* 7 M $HClO_4$. A forthcoming paper will discuss the basicities of these ketones in detail.[16] The only matter of consequence to Scheme IV is that as protonation of the α,β-unsaturated ketone becomes significant, the rate of hydration will decrease with increasing acidity *and* the equilibrium constant will *decrease*, favoring the α,β-unsaturated ketone over the β-hydroxy ketone. The curves in Figure 1 are in quantitative agreement with the reported pK_b of α,β-unsaturated ketones in aqueous perchloric acid; *i.e.*, the maxima in Figure 1 coincide with those expected based on pK_b data[16] and the preceding discussion.

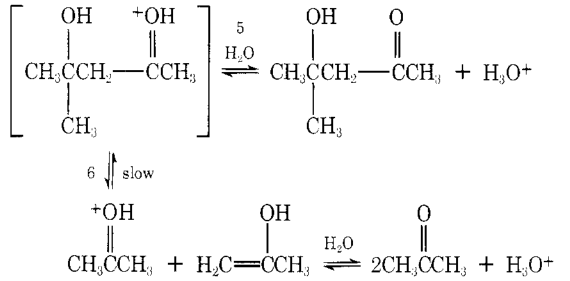
The reaction of 4-methyl-3-penten-2-one in acidities greater than 8 M $HClO_4$ is suprising. As previously discussed, the equilibrium constant is changing since k_{dehyd} is becoming greater than k_{hyd} and consequently in acidities much greater than 8 M there is no *apparent* hydration

Table VI
Activation Parameters for the Hydration of 3-Alken-2-ones in Aqueous Perchloric Acid[a]

Compd	$M_{\mathrm{HClO_4}}$	ΔH^*, kcal/mol[b]	ΔS^*, eu[b]
3-Buten-2-one	2.57	15.2 ± 0.4	−21.7 ± 1.4
3-Buten-2-one	8.26	14.9 ± 0.7	−18.2 ± 2.3
3-Buten-2-one	9.30	13.6 ± 0.2	−22.0 ± 0.6
3-Penten-2-one	2.57	15.7 ± 0.4	−22.8 ± 1.4
4-Methyl-3-penten-2-one	2.57	14.8 ± 0.0	−25.0 ± 0.1
4-Methyl-3-penten-2-one	6.28	13.7 ± 0.7	−26.3 ± 2.2
4-Methyl-3-penten-2-one	9.96	20.1 ± 1.8	−13.7 ± 5.9

[a] Calculated at 40°. [b] Enthalpy, entropy, and standard deviations were calculated using least-squares method, carried out on a CDC 3300 computer.

since the equilibrium constant strongly favors α,β-unsaturated ketone. *However,* a slow reaction incurs at about this acidity which results in total destruction of α,β-unsaturated ketone. This reaction is characterized by irreversibility (for practical purposes), small solvent isotope effect [$k(H_2O)/k(D_2O) = 1.3$], a very slight inverse acidity dependence [$d(\log k)/d(-HA) = -0.1$], a negative entropy (−13 eu) significantly more positive than that for hydration (−25 eu), and acetone being the product (isolated as dinitrophenylhydrazone). These data all support the incursion of a retro aldol condensation as outlined below.



Recalling that at these acidities the reactant state is protonated α,β-unsaturated ketone (>90% SH^+) and merging the above scheme with Scheme IV we have

$$v = \frac{k_2k_3k_4k_6}{k_{-2}k_{-3}k_{-4}}\,A_{H_2O}[SH^+]\,\frac{f_{SH^+}}{f_{tr^+}}$$

Tabulated values of A_{H_2O} in $HClO_4$ solutions[18] give $d(\log A_{H_2O})/d(-H_A) = -1.0$ in the region of acidity studied here. Consequently, for $d(\log k)/d(-H_A)$ to equal −0.1 requires f_{SH^+}/f_{tr^+} to increase significantly, compensating largely for the change in A_{H_2O}. This is very significant, since it demonstrates that in rather concentrated perchloric acid solution, activity coefficient *ratios* of similarly structured ions charge drastically with acid molarity (in this case, about as much as the activity of water changes). This is yet another example of the failure of the premise of the Zucker–Hammett hypothesis; previous reports have been in more dilute solutions.[19] It is also significant that this system is not a very sensitive one to changes in acidity. This is clear since protonation of α,β-unsaturated ketones follows H_A, not H_0, and $d(-H_A)/dM_{\mathrm{HClO}} < d(-H_0)/d_{\mathrm{HClO}}$ by about a factor of 3 in this region of acidity.[14,16]

Although not studied because of the slowness of reaction, 3-penten-2-one exhibits behavior similar to 4-methyl-3-penten-2-one in 10–11 *M* $HClO_4$. That is, acid-catalyzed retro aldol condensation appears to be characteristic of α,β-unsaturated ketones.

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Registry No.—3-Buten-2-one, 78-94-4; 3-penten-2-one, 625-33-2; 4-methyl-3-penten-2-one, 141-79-7.

References and Notes

(1) J. L. Jensen and D. J. Carre, *J. Org. Chem.*, **36**, 3180 (1971), and references cited therein.
(2) (a) W. M. Schubert and J. R. Keefe, *J. Amer. Chem. Soc.*, **94**, 559 (1972); (b) W. M. Schubert and J. L. Jensen, *ibid.*, **94**, 566 (1972), and references cited therein.
(3) A. J. Kresge, Y. Chiang, P. H. Fitzgerald, R. S. McDonald, and G. H. Schmid, *J. Amer. Chem. Soc.*, **93**, 4907 (1971), and references cited therein.
(4) M. B. Hocking, *Can. J. Chem.*, **48**, 3393 (1970).
(5) (a) D. S.Noyce, and E. C. McGoran, *J. Org. Chem.*, **34**, 2558 (1969); (b) D. S. Noyce, S. K. Brauman, and F. B. Kirby, *J. Amer. Chem. Soc.*, **87**, 4335 (1965), and references cited therein.
(6) (a) L. R. Fedor and J. McLaughlin, *J. Amer. Chem. Soc.*, **91**, 3594 (1969); (b) L. R. Fedor, N. C. De, and S. K. Gurwara, *ibid.*, **95**, 2905 (1973).
(7) (a) D. S. Noyce and W. L. Reed, *J. Amer. Chem. Soc.*, **80**, 5539 (1958); (b) D. S. Noyce and M. J. Jorgenson, *J. Org. Chem.*, **28**, 3208 (1963).
(8) R. P. Bell, J. Preston, and R. B. Whitney, *J. Chem. Soc.*, 1166 (1962).
(9) J. J. Scott and K. R. Brower, *J. Amer. Chem. Soc.*, **89**, 2682 (1967).
(10) R. C. Weast, Ed., "Handbook of Tables for Organic Compound Identification," 3rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967.
(11) Time and absorbance (including "infinity" absorbance) were input data. Rate constants for each of the first 3 half-lives were calculated, based on the inputed "infinity" absorbance. The rate constants for each half-life were compared and data from half-lives having rate constants within 5% were used for varying the "infinity" absorbance. The "infinity" absorbance was varied in increments of 0.002 absorbance unit until a minimum RMS deviation was obtained in the k_{obsd} calculation. Rate constants were again calculated for each of the first 3 half-lives, based on the newly calculated infinity absorbance. In this manner it was determined that the exchange process usually did not affect the observed reaction rate until the third or fourth half-life of reaction.
(12) K. Wilberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964.
(13) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1961, p. 186.
(14) K. Yates, H. Wai, G. Welch, and R. A. McClelland, *J. Amer. Chem. Soc.*, **95**, 418 (1973).
(15) R. E. Zalewski and G. E. Dunn, *Can. J. Chem.*, **48**, 2538 (1970).
(16) J. L. Jensen and D. J. Carré, manuscript in preparation.
(17) P. D. Bartlett and G. D. Sargent, *J. Amer. Chem. Soc.*, **87**, 1297 (1965).
(18) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1959.
(19) (a) W. M. Schubert and J. L. Jensen, *J. Amer. Chem. Soc.*, **94**, 566 (1972); (b) W. M. Schubert, H. Burkett, and A. L. Schy, *ibid.*, **86**, 2520 (1964).