Mechanism of Hydration of Simple Olefins in Aqueous Solution. *cis-* and *trans-*Cyclooctene

Y. Chiang and A. J. Kresge*

Contribution from the Department of Chemistry, University of Toronto, Scarborough College, Scarborough, Ontario M1C 1A4, Canada. Received March 18, 1985

Abstract: Rates of hydration of *cis-* and *trans-*cyclooctene and 2,3-dimethyl-2-butene to the corresponding alcohols have been measured in concentrated and dilute aqueous perchloric acid, and those of the latter two olefins in bisulfate ion and phosphoric acid buffer solutions as well. The systems examined in buffers show general-acid catalysis. The reaction of *trans-*cyclooctene is not reversible, but those of *cis-*cyclooctene and 2,3-dimethyl-2-butene are; for *cis-*cyclooctene, K = [alcohol]/[olefin] = 1.8 and for 2,3-dimethyl-2-butene, $K \simeq 4$. For the hydration of *trans-*cyclooctene, $\Delta H^{\ddagger}$ = 22 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 1 cal K^{-1} mol^{-1}, and k_{H^+}(25 °C) = 5.2 × 10^{-4} M^{-1} s^{-1}; for the hydration of *cis-*cyclooctene, $\Delta H^{\ddagger}$ = 24 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −10 cal K^{-1} mol^{-1}, and k_{H^+}(25 °C) = 2.1 × 10^{-7} M^{-1} s^{-1}; and for the rate of approach to equilibrium in the 2,3-dimethyl-2-butene system, k_{H^+}(25 °C) = 2.9 × 10^{-4} M^{-1} s^{-1}. The lifetime of tertiary carbocations such as that formed by protonation of 2,3-dimethyl-2-butene is estimated to be $\tau \simeq 10^{-10}$ s in dilute aqueous solution, which allows this ion to be a viable, solvationally equilibrated intermediate in the hydration reaction. The secondary cyclooctyl cation is likewise judged to be a solvationally equilibrated species in concentrated aqueous acids, with $\tau \simeq 5 \times 10^{-8}$ to 5×10^{-9} s in the 45–55 wt % HClO$_4$ solutions used for the hydration of *cis-*cyclooctene. In dilute aqueous solution, however, carbocation lifetimes are shorter, and $\tau \simeq 5 \times 10^{-12}$ s is estimated for the cyclooctyl cation in dilute acids such as those used for the hydration of *trans-*cyclooctene. Species as short-lived as this can probably still be reaction intermediates, but they are not solvationally equilibrated and may have to react by preassociation mechanisms; an argument is presented that shows that such a mechanism is likely not to be required in the hydration of *trans-*cyclooctene.

Incorporation of a trans double bond into a small carbocyclic ring produces strain that markedly increases the reactivity of this unsaturated center to electrophilic addition. For example, Inoue and co-workers have recently found that *trans-*cycloheptene undergoes acid-catalyzed addition of methanol 10^9 times faster than does *cis-*cycloheptene.[1] *trans-*Cycloheptene is in fact so strained that it cannot be stored at room temperature: it isomerizes spontaneously to *cis-*cycloheptene in a process whose lifetime at 25 °C is of the order of 1 min. The smallest *trans-*cycloalkene that will persist for reasonable lengths of time at room temperature is *trans-*cyclooctene,[2] but this substance also shows increased reactivity; e.g., it undergoes acid-catalyzed addition of methanol in methanol solution 3 × 10^3 times faster than does its cis isomer.[3]

In earlier publications we reported that bicyclo[3.3.1]non-1-ene (**1**) and bicyclo[4.2.1]non-1(8)-ene (**2**), each of which contains a *trans-*cyclooctene ring, are 1 × 10^5 and 1 × 10^3 times more
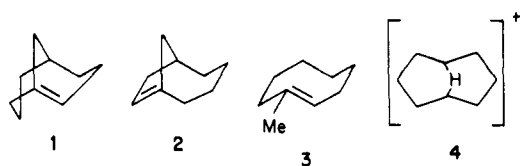
reactive, respectively, to acid-catalyzed hydration in aqueous solution than appropriate unstrained acyclic models[4] and that 1-methyl-*trans-*cyclooctene (**3**) undergoes the same reaction 2 × 10^4 times faster than its cis isomer.[5] In this paper we describe our study of the parent system itself, *cis-* and *trans-*cyclooctene, and consider our results in connection with the mechanism of hydration of simple olefins in general, especially the stability and lifetime of possible carbocationic intermediates. Our results also have a bearing on whether the transannular hydride shift[6] and

formation of a hydrido-bridged cycloalkyl cation **4**,[7] which have been implicated in the addition of acids to *cis-*cyclooctene by recent stereochemical studies,[8] produce a rate acceleration.

Parts of this work were published in preliminary form.[9]

Experimental Section

Materials. *trans-*Cyclooctene was a gift from Dr. P. H. Fitzgerald, who prepared it from *trans-*cyclooctane-1,2-diol by the method of Witham.[10] *cis-*Cyclooctene, cyclooctanol, and 2,3-dimethyl-2-butene were obtained commercially. Samples of these materials for kinetic measurement were purified by gas chromatography. All other materials were best available commercial grades and were used as received.

Solutions were prepared from deionized water purified further by distillation.

Kinetics. Rates of reaction were determined spectroscopically by monitoring the UV absorption of the olefin substrates at λ = 200 nm (ϵ = 3 × 10^3 M^{-1} cm^{-1} for *cis-*cyclooctene). Absorbance measurements were made with a Cary Model 118C spectrophotometer with thermostated cell compartment; initial substrate concentrations were of the order of 10^{-4} M. "Infinite-time" readings, A_∞, were made after 8–10 half-lives, and rate constants were evaluated as slopes of plots of ln $(A - A_\infty)$ [or ln $(A_\infty - A)$ when cyclooctanol was the starting substrate] vs. time. The data so obtained conformed to the first-order rate law well in all cases.

Results

*trans-*Cyclooctene. Rates of disappearance of this olefin were measured at 25 °C in aqueous perchloric acid solutions over the concentration range 2–17 wt % acid. The data are summarized in Table S1.[11] Observed first-order rate constants so obtained were found to increase with acidity considerably more strongly than in direct proportion to molar acid concentration, and an acidity function was therefore used to correlate the data. The X_0 function[12] appears to be the best currently available quantity for this purpose,[13] and this measure of acidity did in fact give a

(1) Inoue, Y.; Ueoka, T.; Kuroda, T.; Hakushi, T. *J. Chem. Soc., Perkin Trans. 2* **1983**, 983–988.

(2) Ziegler, K.; Wilms, H. *Justus Leibigs Ann. Chem.* **1950**, *567*, 1–43. Cope, A. C.; Pike, R. A.; Spencer, C. F. *J. Am. Chem. Soc.* **1953**, *75*, 3212–3215.

(3) Inoue, Y.; Ueoka, T.; Hakushi, T. *J. Chem. Soc., Chem. Commun.* **1982**, 1076–1077.

(4) Chiang, Y.; Kresge, A. J.; Wiseman, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 1564–1566.

(5) Chiang, Y.; Chwang, W. K.; Kresge, A. J.; Powell, M. F.; Szilagyi, S. *J. Org. Chem.* **1984**, *49*, 5218–5224.

(6) Prelog, V.; Traynham, J. G. In "Molecular Rearrangements"; de Mayo, P., Ed., Interscience: New York, 1963; Vol 1, p 593. Cope, A. C.; Martin, M. M.; McKervey, M. A. *Q. Rev., Chem. Soc.* **1966**, *20*, 119–152.

(7) Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1979**, *101*, 3240–3243.

(8) Nordlander, J. E.; Kotian, K. D.; Raff, D. E., II; Njoroge, F. G.; Winemiller, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 1427–1432.

(9) (a) Kresge, A. J.; Chiang, Y.; Fitzgerald, P. H.; McDonald, R. S.; Schmid, G. H. *J. Am. Chem. Soc.* **1971**, *93*, 4907–4908. (b) Kresge, A. J.; Chen, H. J.; Chiang, Y. *J. Chem. Soc., Chem. Commun.* **1972**, 969–970.

(10) Hines, J. N.; Peagram, M. J.; Witham, G. H.; Wright, M. *Chem. Commun.* **1968**, 1593–1594.

(11) Supplementary material; see paragraph at end of this paper.

(12) Cox, R. A.; Yates, K. *Can. J. Chem.* **1981**, *59*, 2116–2124.

6364 *J. Am. Chem. Soc., Vol. 107, No. 22, 1985*

Chiang and Kresge

Table I. Summary of Acid-Catalyzed Rate Constants[a]

$T/°C$	catalyst	$10^3 k/(M^{-1}\ s^{-1})$
trans-Cyclooctene		
25.0	H⁺	0.522
28.7	H⁺	1.29
32.0	H⁺	1.84
38.3	H⁺	4.31
38.9	H⁺	4.34
45.2	H⁺	8.02
52.4	H⁺	17.6
52.4	HSO₄⁻	2.16
52.4	H₃PO₄	0.627
cis-Cyclooctene		
16.1	H⁺	0.000 065 1
20.7	H⁺	0.000 102
25.0	H⁺	0.000 204
29.6	H⁺	0.000 382
34.2	H⁺	0.000 717
39.1	H⁺	0.001 33
43.6	H⁺	0.002 29
2,3-Dimethyl-2-butene		
25.0	H⁺	0.286
52.4	H⁺	9.34
52.4	H₃PO₄	0.243

[a] Rate constants for *cis*- and *trans*-cyclooctene are for the forward (hydration) direction; those for 2,3-dimethyl-2-butene are sums of forward and reverse rate constants.

good linear relationship in this case: log $(k_{obsd}/[H^+] = -3.283 \pm 0.009 + (1.96 \pm 0.03)X_0$. Extrapolation of this expression to zero acid concentration gives $k_{H^+} = (5.22 \pm 0.10) \times 10^{-4}\ M^{-1}\ s^{-1}$ as the bimolecular rate constant for the disappearance of *trans*-cyclooctene in dilute aqueous solution catalyzed by the hydronium ion.

Rates of disappearance of *trans*-cyclooctene were also measured at higher temperatures (six values over the range $T = 29–52\ °C$) directly in dilute perchloric acid solutions ($[H^+] = 0.04–0.10\ M$). These data are summarized in Table S2.[11] Observed first-order rate constants were transformed into specific bimolecular rates by division by acid concentration. The results, listed in Table I, gave a good linear plot of log (k_{H^+}/T) vs. T^{-1}, from which the following activation parameters were obtained: $\Delta H^\ddagger = 22.0 \pm 0.7$ kcal mol⁻¹ and $\Delta S^\ddagger = 0.9 \pm 2.3$ cal K⁻¹ mol⁻¹.

The rate of this reaction was also measured at 52.4 °C in series of bisulfate and phosphoric acid buffer solutions under conditions of constant stoichiometric buffer ratio and constant ionic strength (0.10 M); these data are summarized in Table S3.[11] In experiments of this kind, the first term in the rate law, eq 1, which applies

$$k_{obsd} = k_{H^+}[H^+] + k_{HA}[HA] \tag{1}$$

to such a system[9a] is usually held constant by an invariant hydrogen ion concentration, and the second term can then be evaluated by analyzing the relationship between k_{obsd} and [HA]. In the present case, however, because the buffer acids were moderately strong, their extents of dissociation changed as their concentrations varied, and [H⁺] consequently did not remain sufficiently constant. This "buffer failure" was compensated for by adjusting observed rate constants to values expected at the hydrogen ion concentration of the most concentrated buffer solution of a given series, i.e., by adding to k_{obsd} the increment $\delta[H^+]k_{H^+}$, where $\delta[H^+]$ is the difference in [H⁺] between the most concentrated and a given buffer, and k_{H^+} is the hydrogen ion catalytic coefficient measured in perchloric acid solutions. Values of [H⁺] for this purpose were obtained by calculation by using the activity coefficients estimated by the Debye–Hückel equation with ion-size parameters of 9.0 Å for H⁺, 4.5 Å for HSO₄⁻ and H₂PO₄⁻, and 4.0 Å for SO₄²⁻,[14] plus literature values of the required acid dissociation constants: that for HSO₄⁻ at 52.4 °C was obtained by interpolating between values listed for 10 °C temperature intervals in Table 15-6-1A

of the book by Harned and Owen,[15a] and that for H₃PO₄ was obtained by calculation using Harned and Owen's eq 15-6-9[15b] with constants given in their Table 15-6-4A.[15c] The relationship between rate constants adjusted in this way and general-acid concentrations, [HA], were determined by linear least-squares analysis, and the general-acid catalytic coefficients so obtained are listed in Table I.

Kinetic data analyzed in this way can be examined for internal consistency by using the intercepts from the least-squares analyses, which are equal to $k_H[H^+]$ (see eq 1), to evaluate k_{H^+}. The results obtained here, $k_{H^+} = 1.86 \times 10^{-2}$ and $1.88 \times 10^{-2}\ M^{-1}\ s^{-1}$ from the HSO₄⁻ and H₃PO₄ buffers, respectively, are in excellent agreement with $k_{H^+} = 1.85 \times 10^{-2}\ M^{-1}\ s^{-1}$ predicted for 52.4 °C from the temperature dependence of this rate constant measured in perchloric acid solutions.

***cis*-Cyclooctene.** This olefin was considerably less reactive than *trans*-cyclooctene, and its hydration proceeded at conveniently measurable rates only in concentrated perchloric acid solutions. Rate determinations were carried out over the range 40–55 wt % acid at temperatures from 16 to 44 °C. These data are summarized in Table S4.[11]

The absorbance whose changes were used to make these rate determinations did not fall to zero at the end of the reactions but rather reached steady final values some 10–20% of initial readings. Since the reaction product, cyclooctanol, does not absorb light at the wavelength used, this suggests that hydration did not go to completion and that some unreacted olefin remained in equilibrium with alcohol product. This suggestion was verified by NMR and gas chromatographic examination of final reaction mixtures: both methods showed the presence of significant amounts of cyclooctene. Gas chromatography, moreover, also indicated that 1-methylcycloheptene was being formed; this, however, occurred at a rate 350 times slower than the cyclooctene–cyclooctanol equilibration, and the immediate product of cyclooctene hydration is therefore only cyclooctanol.

Specific rates of interconversion of two substances such as this should be the same for approach to equilibrium from the product as from the reactant side,[16] and this proved to be the case here. Initially transparent solutions of cyclooctanol in perchloric acid developed absorbance characteristic of cyclooctene, and this absorbance change followed the first-order rate law well and gave rate constants identical with those obtained starting with *cis*-cyclooctene at the same acid concentration. For example, at 34.2 °C rate constants determined with *cis*-cyclooctene as the starting substrate gave the correlation log $(k/[H^+]) = -6.13 \pm 0.10 + (1.45 \pm 0.04)X_0$, and those with cyclooctanol as the substrate gave log $(k/[H^+]) = -6.08 \pm 0.04 + (1.44 \pm 0.02)X_0$. Kinetic measurements starting with cyclooctanol were made at two temperatures, 34.2 and 43.6 °C; these data are listed in Table S4.[11]

Specific rates of approach to equilibrium such as this are sums of forward and reverse rate constants, $k_{obsd} = k_f + k_r$,[16] and they may be separated into their components by using equilibrium constants, K $(=k_f/k_r)$; e.g., $k_f = k_{obsd}/(1 + K^{-1})$. Values of K (=[cyclooctanol]/[*cis*-cyclooctene]) were obtained for this purpose from data gathered during the kinetic runs themselves, from initial and final absorbance readings when *cis*-cyclooctene was the starting substrate, and from known initial concentrations and final absorbance readings plus measured cyclooctene extinction coefficients in the case of runs beginning with cyclooctanol.

This method of measuring K did not produce highly accurate results: the uncertainties are probably of the order of ±10%. But this is sufficient for the present purpose inasmuch as values of K ranged from 5 to 10 and the magnitude of the factor $(1 + K^{-1})^{-1}$ used to convert observed to forward rate constants therefore did not depend strongly on K. This experimental scatter in K obscured any variation this constant may have with temperature, but it was

(13) Kresge, A. J.; Chen, H. J.; Capen, G. L.; Powell, M. F. *Can. J. Chem.* **1983**, *61*, 249–256.

(14) Bates, R. G. "Determination of pH"; Wiley-Interscience: New York, 1973; p 49.

(15) Harned, H. S.; Owen, B. B. "The Physical Chemistry of Electrolytic Solutions"; Reinhold: New York, 1958; (a) p 755, (b) p 665, (c) p 758.

(16) Moore, J. W.; Pearson, R. G. "Kinetics and Mechanism"; Wiley-Interscience: New York, 1981; p 304.
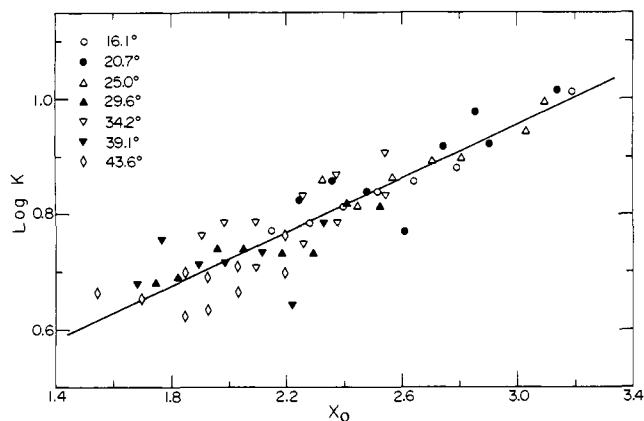
Mechanism of Hydration of Simple Olefins

J. Am. Chem. Soc., Vol. 107, No. 22, 1985 6365

Figure 1. Equilibrium constants for the *cis*-cyclooctene/cyclooctanol system in aqueous perchloric acid.

not enough to hide a tendency for K to increase with increasing acid concentration. Because K is the ratio of rate constants for two acid-catalyzed processes, each of which should give a linear correlation of log $(k/[H^+])$ with X_0, log K might be expected to be related linearly to X_0 as well. As Figure 1 shows, this proved to be the case, and least-squares fitting of the data at all temperatures to a single expression gave log $K = 0.260 \pm 0.035 + (0.232 \pm 0.015)X_0$. Extrapolation of this relationship to $X_0 = 0$ gives $K = 1.82 \pm 0.15$ for dilute aqueous solution.

Observed rate constants for the approach to an equilibrium mixture of *cis*-cyclooctene and cyclooctanol were converted to rate constants for the forward reaction with values of K averaged over all determinations (usually 3–4) at a given temperature and acid concentration. The results (25–30 rate constants for each temperature) were then correlated with X_0 values for 25 °C multiplied by the absolute temperature ratio as recommended by Cox and Yates.[17] This gave good linear relationships in all cases. These correlations were then extrapolated to $X_0 = 0$, and the dilute-solution hydrogen ion catalytic coefficients so obtained are listed in Table I. These rate constants in turn gave a linear plot of log (k_{H^+}/T) vs. T^{-1} from which the following activation parameters were derived: $\Delta H^{\ddagger} = 23.6 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -9.9 \pm 1.7$ cal K^{-1} mol^{-1}. The best value of the hydronium ion catalytic coefficient for the hydration of *cis*-cyclooctene at 25.0 °C based on all of these data is $k_{H^+} = (2.07 \pm 0.06) \times 10^{-7}$ M^{-1} s^{-1}.

2,3-Dimethyl-2-butene. This olefin does not belong to the cyclooctene–cyclooctanol system, but rate measurements made with it were used in one of our preliminary communications on *trans*-cyclooctene,[9a] and these are therefore now reported here in full. Rate constants were determined at 25.0 °C in concentrated perchloric acid over the range 3–26 wt % acid; these data are summarized in Table S5.[11] Additional measurements were also made at 52.4 °C in dilute perchloric acid and in phosphoric acid–sodium dihydrogen phosphate buffer solutions; these data are listed in Table S6.[11]

Final absorbances in these systems also did not go to zero but remained fixed at ca. 20% of initial values. Equilibrium constants, however, were not evaluated, and observed rate constants were not separated into their constituent forward and reverse components. But, inasmuch as the equilibrium constants in this system are of the order of 4, the specific rates of approach to equilibrium consist largely of rate constants for the forward, hydration, direction.

The rates of reaction at 25 °C in concentrated perchloric acid were again correlated by using the X_0 function. This treatment gave the hydrogen ion catalytic coefficient $k_{H^+} = (2.86 \pm 0.08) \times 10^{-4}$ M^{-1} s^{-1}, which is consistent with the value $k_{H^+} = 2.3 \times 10^{-4}$ M^{-1} s^{-1} we obtained by an X_0 correlation of some older, literature data for this reaction, also measured in concentrated perchloric acid.[18]
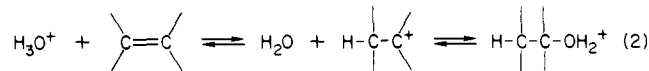
The rate constants determined in dilute perchloric acid solutions

at 52.4 °C were proportional to acid concentration, and linear least-squares analysis gave a zero intercept and the hydrogen ion catalytic coefficient $k_{H^+} = (9.34 \pm 0.76) \times 10^{-3}$ M^{-1} s^{-1}.

The measurements in phosphoric acid buffer solutions were made at constant stoichiometric buffer ratio and constant ionic strength, but buffer failure occurred again. This was handled as described above for *trans*-cyclooctene. Linear least-squares analysis gave the general-acid catalytic coefficient $k_{H_3PO_4} = (2.43 \pm 0.17) \times 10^{-4}$ and a hydronium ion catalytic coefficient $k_{H^+} = 8.5 \times 10^{-3}$ M^{-1} s^{-1}, in good agreement with that measured in dilute perchloric acid at this temperature, $k_{H^+} = 9.34 \times 10^{-3}$ M^{-1} s^{-1}.

Discussion

Carbocation Lifetimes. The conventional reaction mechanism for acid-catalyzed interconversion of simple olefins and alcohols in aqueous solution involves a carbocationic intermediate (eq 2).[19]

$$H_3O^+ + \underset{/}{\overset{\backslash}{C}}{=}\underset{\backslash}{\overset{/}{C}} \rightleftharpoons H_2O + H{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{}^+ \rightleftharpoons H{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{-}OH_2{}^+ \quad (2)$$

This intermediate, however, must have a certain minimum stability for this mechanism to operate.[20] If its lifetime in the medium in which it is generated is less than the period of a molecular vibration, $\tau \simeq 10^{-13}$ s, then it does not exist in a minimum on the energy surface for the reaction and it cannot be a reaction intermediate; the process will then have to occur by a concerted mechanism. If, on the other hand, the lifetime of the carbocation is greater than 10^{-13} s but less than the time required for proper reorientation of the water molecule with which it must react, which should be on the order of the rotational correlation time of liquid water, $\tau = 10^{-11}$ s,[21] then the process will occur by a preassociation mechanism in which the water molecule gets into reaction position before the carbocation is formed. Since simple aliphatic carbocations are believed to be quite unstable in nucleophilic solvents such as water,[22] it is important to inquire whether the conventional stepwise mechanism of eq 2 involving a stable solvationally equilibrated intermediate can in fact operate in the presently investigated systems.

No direct information on the lifetimes of simple aliphatic carbocations in aqueous solution is available, but indirect, order-of-magnitude estimates can be made. We have done this in connection with our study of the 1-methylcyclooctyl system and have obtained $\tau \simeq 10^{-10}$ s for a model tertiary aliphatic carbocation,[5] which implies that such an ion is just barely stable enough to be a solvationally equilibrated reaction intermediate in dilute aqueous solution. This suggests that the presently examined hydration of 2,3-dimethyl-2-butene, which would give a tertiary carbocation, can occur by the conventional stepwise mechanism of eq 2.

The ions formed in the hydration of *cis*- and *trans*-cyclooctene, on the other hand, would be formally secondary species, which can be expected to be less stable than tertiary carbocations. *cis*-Cyclooctene should actually give the μ-hydrido-bridged species **4**,[7,8] and *trans*-cyclooctene is likely to produce a conformationally different cyclooctyl ion that may or may not be a hydrido-bridged species. But hydrido bridging is believed not to affect the stability of carbocations very much,[7,24] and a simple secondary ion such as isopropyl might be a reasonable model for the carbocation formed from *cis*- and *trans*-cyclooctene.

The rate constant for the reaction of isopropyl cation with water in aqueous solution can be estimated by extrapolating a σ-constant correlation[5] of rate data for this reaction obtained with more stable

(17) Cox, R. A.; Goldman, M. F.; Yates, K. *Can. J. Chem.* **1979**, *57*, 2960–2966. Cox, R. A.; Yates, K. *Can. J. Chem.* **1984**, *62*, 2155–2160.
(18) Jensen, J. L.; Carré, D. J. *J. Org. Chem.* **1971**, *36*, 3180–3183.

(19) Nowlan, V. J.; Tidwell, T. T. *Acc. Chem. Res.* **1977**, *10*, 252–258.
(20) Jencks, W. P. *Chem. Rev.* **1972**, *72*, 705–718. *Acc. Chem. Res.* **1976**, *9*, 425–432; **1980**, *13*, 161–169. *Chem. Soc. Rev.* **1981**, *10*, 345–375.
(21) Eisenberg, D.; Kauzmann, W. "The Structure and Properties of Water"; Oxford University Press: New York, 1969; pp 206–214.
(22) (a) Bethell, D.; Gold, V. "Carbonium Ions"; Academic Press: New York, 1967; p 196. Knier, B. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6789–6798. (b) Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 2889–2895.
(23) (a) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 8238–8248. (b) McClelland, R. A.; Ahmad, M. *J. Am. Chem. Soc.* **1978**, *100*, 7031–7036.
(24) Kirchen, R. P.; Okazawa, N.; Ranaganayakulu, K.; Rauk, A.; Sorensen, T. S. *J. Am. Chem. Soc.* **1981**, *103*, 597–604.

alkoxy-substituted cations.[23] This gives $k_{H_2O} = 2 \times 10^{11}$ s^{-1}, which corresponds to the lifetime $\tau = 5 \times 10^{-12}$ s, and that puts the isopropyl cation into the category of being a stable but certainly not a fully solvationally equilibrated intermediate. This result refers to dilute aqueous media such as the solutions in which *trans*-cyclooctene was studied. *cis*-Cyclooctene, on the other hand, was investigated only in concentrated acids where the reaction of carbocations with water is known to be slower.[23b] An estimate of the slowing can be made with the acidity function established for the reactions of alkoxy-substituted carbocations with water.[23b] This gives factors of the order of 10^3–10^4 for the solutions used here, and that raises the lifetime to $\tau \simeq 5 \times 10^{-8}$ to 5×10^{-9} s, putting this intermediate into the stable *and* solvationally equilibrated category.

Some further support for a lifetime of this order of magnitude comes from our observation that 1-methylcycloheptene is formed slowly from an equilibrating mixture of *cis*-cyclooctene and cyclooctanol. A plausible route for the formation of this secondary product is through isomerization of the hydrido-bridged cyclooctyl cation to the 1-methylcycloheptyl ion (eq 3), which is known to

$$\left[\begin{array}{c} \text{(bicyclic)} \end{array} \right]^+ \longrightarrow \text{(cycloheptyl cation)} \qquad (3)$$
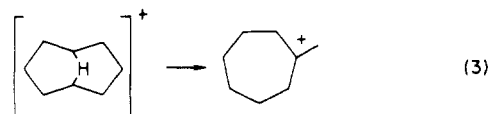
occur readily when the cyclooctyl ion is generated in superacids under stable ion conditions;[7] expulsion of a proton from the rearranged ion would then give 1-methyl-1-cycloheptene. We found that 1-methylcycloheptene is produced 350 times more slowly than the *cis*-cyclooctene/cyclooctanol equilibration occurs. This means that, if 1-methylcycloheptene is indeed being produced in our media through the isomerization of eq 3, the lifetime of the hydrido-bridged cyclooctyl ion under our conditions is 350 times shorter than the average time required for the ion isomerization. The rate of the isomerization has been measured at -142 °C; extrapolation of this value to 25 °C on the assumption that $\Delta S^{\ddagger} = 0$ gives $\tau = 3 \times 10^{-9}$ s for the lifetime of the cyclooctyl ion under our conditions, and taking $\Delta S^{\ddagger} = 10$ cal K^{-1} mol^{-1} gives $\tau = 2 \times 10^{-10}$ s. Both of these results are in reasonably good agreement with the estimates made from the rate correlation discussed above.

Reaction Mechanism. These estimates of carbocation lifetimes suggest that the hydration of two of the olefins studied here, *cis*-cyclooctene and 2,3-dimethyl-2-butene, occur by the conventional mechanism of eq 2 but that the hydration of *trans*-cyclooctene might require a preassociation mechanism. The conditions for preassociation can be specified more precisely than we have done so far with the aid of the reaction scheme shown in eq 4.

$$\text{(reaction scheme)} \qquad (4)$$

$$\text{I}$$
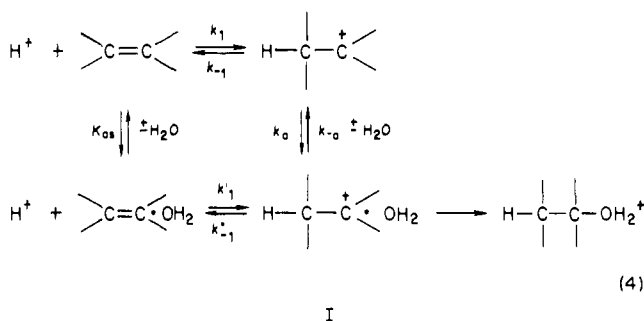
The conventional mechanism with a solvationally equilibrated carbocationic intermediate follows the sequence of reaction steps across the top and down the right side of this scheme. The olefin is protonated to give a carbocation, a water molecule then gets into correct position for making a carbon–oxygen bond to the positively charged carbon atom of the carbocation, thus forming the intermediate I, and finally the bond is made and the product is generated. The intermediate I may also be formed by preassociation of a water molecule with the olefin before the carbocation is produced by the sequence of steps down the left side and across the bottom of this scheme. If the barrier to removal of the water

molecule from reaction position in the intermediate I is greater than the barrier for return of this intermediate to reactants, i.e., if $k_{-a} < k'_{-1}$, then the lowest energy pathway to and from I will be by the preassociation route. For preassociation to occur, the lifetime of I must therefore be limited by its rate of return to reactants. Since the most rapid process by which formation of I from the carbocation can take place is probably the rotation into position of a water molecule originally in the solvation shell of the olefin, which will require a time of the order of magnitude of the rotational correlation time of water, $\tau_R \simeq 10^{-11}$ s, k'_{-1} will have to be greater than $\tau_R^{-1} = 10^{11}$ s^{-1} for the preassociation mechanism to operate.

An important feature of this argument is that occurrence of the preassociation mechanism is determined by a limitation put upon the lifetime of the critical intermediate I by the speed of its *return to reactants*. However, the lifetime of $\tau = 5 \times 10^{-12}$ s estimated above for a secondary aliphatic carbocation in dilute aqueous solution, such as the ion which might be generated from *trans*-cyclooctene under the conditions of the present study, is based upon its combination with water to give reaction products. It is likely that the barrier for return of the carbocation to reactants in the *trans*-cyclooctene case will be much higher than the 2 kcal mol^{-1} that corresponds to $\tau = 5 \times 10^{-12}$ s and that hydration in this case will not occur by a preassociation mechanism. This follows from the following considerations.

The difference in enthalpy between *cis*- and *trans*-cyclooctene has been determined to be $\Delta H° = 9.2$ kcal mol^{-1},[25] and most of this difference is believed to be due to strain imposed by twisting about the olefinic double bond in the trans isomer.[26] This strain will be relieved when this bond becomes single in the carbocationic intermediate of the *trans*-cyclooctene hydration reaction, but our study shows that only a small part of the strain relief is realized at this reaction's transition state: the difference in $\Delta H^{\ddagger}$ for *cis*- and *trans*-cyclooctene hydration determined here is only 1.6 kcal mol^{-1}. This implies that the transition state still has appreciable double-bond character and that there is still much strain enthalpy to be lost in going from the transition state to the carbocation. This enthalpy loss, plus some accompanying entropy gain, will put the transition state above the carbocation by a considerable amount of free energy, thus producing a barrier for return of the carbocation to reactants that should easily be greater than the 2 kcal mol^{-1} limit ($\Delta G^{\ddagger}$ for a process with $\tau = 10^{-11}$ s) beyond which a preassociation mechanism would be inoperative.

It follows from these arguments that, despite the very short lifetime estimated for the carbocation formed in the hydration of *trans*-cyclooctene in dilute aqueous solution, this reaction does not occur by a preassociation mechanism. It takes place rather by rate-determining carbocation formation from an olefin molecule in a normal state of solvation followed by solvent-reorganization-controlled reaction of the carbocation with water. Preassociation mechanisms might operate for the hydration in dilute aqueous solution of simple unstrained olefins that give secondary carbocation intermediates, for in such cases the barriers to return from the carbocation to reactants would be expected to be much smaller than for *trans*-cyclooctene. Such olefins, however, would be fairly unreactive in dilute aqueous acids; in the more concentrated acid media more likely to be employed for these reactions, the carbocationic intermediates should be sufficiently long lived not to equire a preassociation mechanism.

This assignment of rate-determining carbocation formation, through proton transfer from the catalyzing acid to olefinic carbon, as the mechanism for the hydration of *trans*-cyclooctene is consistent with our observation of general-acid catalysis for this reaction. We also found general-acid catalysis in the hydration of 2,3-dimethyl-2-butene, but it is likely that in this case, and in the hydration of *cis*-cyclooctene as well, carbon protonation and

(25) Turner, R. B.; Meador, W. R. *J. Am. Chem. Soc.* **1957**, *79*, 4133–4136.
(26) (a) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; p 112. Ermer, O. *Struct. Bonding (Berlin)* **1976**, *27*, 161–211. (b) Traetteberg, M.; Bakken, P. *J. Mol. Struct.* **1981**, *74*, 321–330.

the subsequent reaction of carbocation with water occur at closely similar rates; these two steps are therefore very probably each partly rate determining in these two cases. This follows from the following reasoning and the fact that overall equilibrium constants for both of these reactions are near unity. For the *cis*-cyclooctene/cyclooctanol system, $K = 7$–10 in the acid concentration range used, and for 2,3-dimethyl-2-butene/2,3-dimethyl-2-butanol, for which equilibrium constants were not observed directly, the residual absorbances left at the end of kinetic runs imply $K \simeq 4$. In the somewhat more exergonic isobutene/*tert*-butyl alcohol system, for which $K = 7500$,[27] comparison of rates of oxygen-18 exchange of the alcohol with rates of its dehydration to olefin indicate that the carbocationic intermediate reacts with water only 29 times faster than it ejects a proton to give isobutene.[28] This ratio drops from 29 to 9 in the 2-methyl-2-butene/2-methyl-2-butanol system,[28] for which $K = 200$,[28,29] and in the 1-methyl-*cis*-cyclooctene/1-methylcyclooctanol system, where $K = 1.3$, the ratio is 0.44.[5] This pattern suggests that this ratio will pass through unity, and the two reaction steps will consequently occur at the same rate, when K is only slightly greater than 1, as is the case with *cis*-cyclooctene and 2,3-dimethyl-2-butene.

In both eq 2 and 4, the reaction product is shown to be protonated alcohol. Even in the most concentrated acid solutions used in this study, however, the alcohols generated will exist largely in their unprotonated forms and deprotonation will therefore have to occur. There is no direct evidence bearing upon the question of whether in the present cases this deprotonation will occur in a separate step or whether it will be concerted with carbon–oxygen bond making, but a case can be made out for a stepwise process. The pK_a's of the protonated alcohols are likely to be about -2,[30] and the free energies of these species will therefore be only some 3 kcal mol^{-1} above those of the free alcohols. This is well below the free energy levels of the transition states for reaction of the carbocations with water inasmuch as free energies of activation for the dehydration reactions are of the order of 25 kcal mol^{-1}, and the protonated alcohols are therefore far from being high-energy intermediates; there would therefore seem to be little mechanistic advantage to avoiding them through a concerted reaction path.[20,31] This conclusion is supported by the fact that concerted reactions seem to occur only in the case of relatively stable carbocations;[32] the moderately unstable 1-phenylethyl cation, for example, reacts by a stepwise mechanism.[33]

Relative Reactivities and Anchimeric Assistance. Since μ-hydrido bridging is believed not to improve the stability of the cyclooctyl ion very much,[7,24] formation of this ion during the hydration of *cis*-cyclooctene should provide little if any rate acceleration or anchimeric assistance of the reaction. In an early investigation of this matter, a modestly exalted reaction rate was in fact found: *cis*-cyclooctene was observed to undergo addition of trifluoroacetic acid in trifluoroacetic acid solution 11 and 14 times faster than the acyclic models *cis*-3-hexene and *cis*-2-hexene, respectively.[34] The presently determined rate constant for the hydration of *cis*-cyclooctene in aqueous solution gives somewhat smaller rate ratios: it is only 1.2 times the specific rate of hydration of *cis*-3-hexene in this medium[35] and only 2.5 times that of *cis*-2-butene.[35]

These comparisons for aqueous solution, however, use a measured rate constant for *cis*-cyclooctene, k_m, which is very probably a composite of rate constants for two reaction steps, the formation of the carbocation intermediate (k_1, k_{-t}) and reaction of that intermediate with water (k_2): $k_m = k_1/(1 + k_{-1}/k_2)$. It was argued above that, since the equilibrium constant for the *cis*-cyclooctene hydration reaction is near unity, these two steps will occur at comparable rates in this case. The hydration equilibria for *cis*-3-hexene and *cis*-2-butene, on the other hand, are likely to lie on the side of alcohol, as in the case of isobutene whose double bond is also dialkyl substituted and thus of comparable stability, and carbocation formation is consequently likely to be fully rate determining here. The rate ratios given above, therefore, very probably compare $k_1/(1 + k_{-t}/k_2)$ for *cis*-cyclooctene with k_t for the acyclic models. These ratios are consequently smaller by the factor $1/(1 + k_{-1}/k_2)$ than ratios of rate constants for the carbocation-forming steps, which is where anchimeric assistance would of course be expressed. This puts these comparisons for aqueous solutions somewhat closer to the rate ratios found for trifluoroacetic acid.

Evidence from the related 1-methylcyclooctyl system, however, suggests that these modest rate accelerations are not produced by anchimeric assistance through transannular hydrido bridging. Such bridging has also been observed between secondary and tertiary centers in the 1-methylcyclooctyl system,[24] but here it is very much weaker than in the symmetrical disecondary parent cyclooctyl ion. And yet, formation of this weakly bridged ion occurs in the hydration of 1-methyl-*cis*-cyclooctene with a rate constant[5] that is 6.8 times that for generation of the model acyclic isoamyl ion formed in the hydration of 2-methyl-2-butene.[36] This implies that these rate accelerations are not produced by anchimeric assistance through hydrido-bridged ion formation but are rather the result of some other property of eight-membered carbocyclic rings. A similar conclusion has been reached concerning the exalted reactivity often shown by eight-membered-ring substrates in other reactions.[38]

The rate constants determined here show *trans*-cyclooctene to be 2500 times more reactive to acid-catalyzed hydration than its cis isomer. This comparison, however, is once again based upon a measured rate constant for *cis*-cyclooctene that is very likely less than the specific rate of carbocation formation in this system. The ratio of rate constants for the carbocation-forming steps in these two reactions is therefore probably less than 2500, and significantly less than the ratio 18 500 for the same reaction steps of the trans and cis isomers in the 1-methylcyclooctene system.[5] This is consistent with the fact that 1-methyl-*trans*-cyclooctene appears to be slightly more strained than *trans*-cyclooctene, as judged by the extent of twisting about the double bonds.[26b]

Supplementary Material Available: Tables of rate data (Tables S1–S6) for the rate of disappearance of *trans*-cyclooctene in aqueous perchloric acid solution and in buffer solution and for the rate of approach to equilibrium for the *cis*-cyclooctene–cyclooctanol system and the hydration of 2,3-dimethyl-2-butene (9 pages). Ordering information is given on any current masthead page.

(27) Lucas, H. J.; Eberz, W. F. *J. ,Am. Chem. Soc.* **1934**, *56*, 1230–1234.

(28) Boyd, R. H.; Taft, R. W., Jr.; Wolf, A. P.; Christman, D. R. *J. Am. Chem. Soc.* **1960**, *82*, 4729–4736.

(29) Purlee, E. L.; Taft, R. W., Jr.; DeFazio, C. A. *J. Am. Chem. Soc.* **1955**, *77*, 837–842.

(30) Lee, D. G.; Cameron, R. *J. Am. Chem. Soc.* **1971**, *93*, 4724–4728.

(31) Jencks, W. P. *J. Am. Chem. Soc.* **1972**, *94*, 4731–4732.

(32) Ritchie, C. D. *J. Am. Chem. Soc.* **1972**, *94*, 3275–3276. Ritchie, C. D.; Wright, D. J.; Huang, K. S.; Kamego, A. A. *J. Am. Chem. Soc.*, **1975**, *97*, 1163–1170. Bunton, C. D.; Huang, K. S. *J. Am. Chem. Soc.* **1974**, *96*, 515–522. Bunton, C. A.; Davoudazedeh, F., Watts, W. E. *J. Am. Chem. Soc.* **1981**, *103*, 3855–3858. Ride, J. N.; Wyatt, P. A. H.; Zochowski, Z. M. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1188–1189. J. R. Gandler, personal communication.

(33) Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1396–1401.

(34) Peterson, P. E.; Allen, G. *J. Org. Chem.* **1962**, *27*, 1505–1509.

(35) Knittel, P.; Tidwell, T. T. *J. Am. Chem. Soc.* **1977**, *99*, 3408–3414.

(36) This rate ratio is based upon $k_{H^+} = 2.37 \times 10^{-4}$ M^{-1} s^{-1} for the hydration of 2-methyl-2-butene[37] modified by the partitioning ratio $k_1/k_2 = 1/9$.[28]

(37) Lucas, H. J.; Liu, Y.-P. *J. Am. Chem. Soc.* **1934**, *56*, 2138–2140.

(38) Sicher, J. *Prog. Stereochem.* **1962**, *3*, 202–263. Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977; pp 28–31. Scheider, H.-J.; Schmidt, G.; Thomas, F. *J. Am. Chem. Soc.* **1983**, *105*, 3556–3563.