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Acid-Catalyzed Hydration of *anti*-Sesquinorbornene

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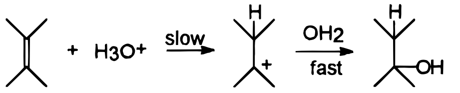
The acid-catalyzed hydration of *anti*-sesquinorbornene (**1**) has been studied at 25 °C in 20% DME/H_2O from $0.001\ M < [HC1] < 0.05\ M$. The second-order rate constant for hydration is $5.35 \pm 0.07\ M^{-1}\ s^{-1}$ which can be compared with a value of $1.38 \pm 0.06\ M^{-1}\ s^{-1}$ for ethyl vinyl ether determined under the same conditions. The solvent deuterium kinetic isotope effect for hydration of **1** is 2.7, and a plot of the observed second-order rate constant for the hydration in a mixed solvent system of H_2O/D_2O against the atom fraction of deuterium (n) is bowed upward. The reaction also shows marked buffer catalysis by formic, chloroacetic, and dichloroacetic acids, the Brønsted α being 1 for these three carboxylic acids: H_3O^+ does not fit on this Brønsted line. A mechanism for the reaction is presented which is consistent with the generally accepted one for acid-catalyzed hydration of an alkene in which the rate-limiting step involves proton transfer from H_3O^+ to the double bond. Whether attack of a second water on the developing carbocation occurs simultaneously with protonation cannot be ascertained from the data for **1**, but if so, the extent of its $C-OH_2$ bond formation must be small enough that there is little change in the bonding of these O−H bonds.

Introduction

Acid-catalyzed addition of H_2O to alkenes is a well-understood process which, in general, adheres to the Ad_E2 mechanism as illustrated in eq 1.[1] The evidence upon



(1)

which this mechanism is founded consists of the following: (1) structure/activity relationships that show that the reaction is strongly accelerated by electron-releasing substituents, the rates correlating well with σ^+ over many orders of magnitude;[2] (2) solvent deuterium kinetic isotope effects (Dkie's) that indicate that the rate-limiting step involves proton-transfer from the acid catalyst to the olefin,[2,3] and; (3) observations that the reaction is subject to general acid catalysis as would be expected if protonation of the alkene were rate-limiting.[3b,d,4] Certain exceptions to the generalized process in eq 1 are known[5] but these involve systems where the first-formed carbocation is highly stabilized or sterically hindered so that reversal of the protonation step is favored over water attack.

anti-Sesquinorbornene (**1**) is an unusual olefin for study of the mechanism of electrophilic additions because its structure precludes any trans solvent-assisted additions since the structure will only tolerate cis adducts.[6,7] This, and the fact that it is highly reactive toward electrophiles and has a convenient chromophore at 230−250 nm in the UV spectrum, makes it convenient to study without recourse to the more drastic conditions of high acidity usually employed to study the hydration of less reactive alkenes. The reactivity appears to result from a large ground state strain around the double bond which is relieved by pyramidalization of one or both of the central carbons.[6d] In a recent study[7] we have shown that **1** reacts rapidly with acetic acid to generate the monoacetate derivative. The reaction exhibits a primary solvent Dkie of $k_{HOAc}/k_{DOAc} = 3.3$, and proton inventory analysis[8] indicated that the mechanism for the addition involved two or more protons in flight or undergoing significant change in their overall bonding in the transition state. The results of that study were interpreted in terms of kinetically indistinguishable mechanisms where two or more HOAc molecules underwent concerted cis addition to the olefin, or a stepwise process with the rate-liming step being protonation of **1** by HOAc . Given the possibility that the addition of HOAc was concerted, it seemed reasonable that in a more polar medium, any cationic forms resulting from stepwise electrophilic addition would be more stable so that stepwise additions might be favored. Herein we report a study of the addition of water in H_2O and D_2O in the presence of H_3O^+ and some general acids which shows that **1** has roughly a 3-fold greater reactivity toward H_3O^+-catalyzed hydration than does ethyl vinyl ether, but similar general reaction characteristics.[3d,9]

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Table 1. Pseudo-First-Order (k_{obs}) and Second-Order (k_2) Rate Constants for Acid-Catalyzed Hydration of 1 by Hydrochloric Acid in H_2O Containing 20% v/v DME, (μ = 0.1 ($LiClO_4$), 25.0 °C)

[HCl] (M)	k_{obs} (s^{-1})	k_2(M^{-1} s^{-1})
0.10 (μ=0.2)	0.470 ± 0.003	4.7
0.05	0.270 ± 0.002	5.4
0.025	0.132 ± 0.002	5.2
0.012	0.0642 ± 0.0005	5.35
0.006	0.032 ± 0.001	5.38
0.003	0.016 ± 0.001	5.22
0.001	0.0053 ± 0.0002	5.3

Table 2. Temperature Dependence of the Observed Rate Constants of Acid-Catalyzed Hydration of 1 by Hydrochloric Acid in H_2O and D_2O Containing 20% v/v DME ([HCl] = [DCl] = 0.012 M, μ = 0.1 ($LiClO_4$))

	k_{obs} (s^{-1})	
t (°C)	HCl/H_2O	DCl/D_2O
35	0.109	0.050
	0.116	0.049
		0.051
30	0.078	0.036
	0.079	0.036
25	0.066	0.023
	0.064	0.024
	0.063	0.024
15	0.034	0.013
	0.032	0.012
	0.034	
11	0.027	0.0082
	0.025	0.0083
	0.023	0.0082

[a] Error limits ± 3–5% of the quoted number.

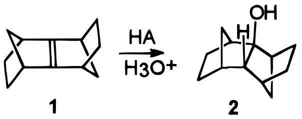
Table 3. Activation Parameters for Acid-Catalyzed Hydration of 1 by Hydrochloric Acid in H_2O and D_2O Containing 20% v/v DME ([HCl] = [DCl] = 0.012 M, μ = 0.1 ($LiClO_4$))

	HCl/H_2O	DCl/D_2O
$\Delta H^{\ddagger}$ (kcal/ mol)	10.1 ± 0.3	12.1 ± 0.3
$\Delta S^{\ddagger}$ (cal/K/mol)	−22.0 ± 1.1	−17.0 ± 0.9
E_a (kcal/ mol)	10.6 ± 0.3	12.7 ± 0.3
log A	8.4 ± 0.3	9.5 ± 0.2

Table 4. Rate Constants of Acid-Catalyzed hydration of 1 in H_2O, D_2O, and H_2O/D_2O Mixtures at 25.0 °C ([HCl] = [DCl] = 0.012 M, μ = 0.1 ($LiClO_4$))

solvent composition (%)			
H_2O	D_2O	k_{obs} (s^{-1})	k_2 (M^{-1} s^{-1})
100	0	0.064 ± 0.001	5.35 ± 0.07
75	25	0.064 ± 0.003	5.35 ± 0.22
50	50	0.580 ± 0.003	4.57 ± 0.19
25	75	0.043 ± 0.001	3.55 ± 0.09
0	100	0.024 ± 0.001	1.98 ± 0.05

[a] Values of k_{obs} are averages of 3–4 determinations.



1 2

Results

anti-Sesquinorbornene (**1**) has an intense ultraviolet absorption band below 240 nm, and the course of its reaction can be conveniently followed by observing the rate of decrease in absorbance in the 230–250 nm range. Since **1** has only very limited solubility in water, a 20% DME (by volume)/H_2O mixture was used as the reaction medium. In dilute solutions of hydrochloric acid (μ = 0.1 ($LiClO_4$)) the reaction follows excellent pseudo-first-order kinetics, the observed first-order rate constants being directly proportional to [HCl]. The bimolecular rate constant for catalysis by the hydronium ion at 25.0 °C is 5.35 ± 0.07 M^{-1} s^{-1} in the range 0.001 < [HCl] < 0.05 M.

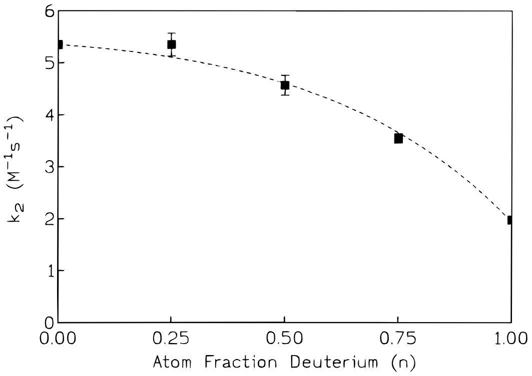


Figure 1. Plot of the second-order rate constant for the acid-catalyzed hydrolysis of **1** at 25 °C in 20% DME/L_2O (L = H, D) containing 0.012 M LCl vs atom fraction of deuterium in the L_2O. Dashed line through the data computed from fit to eq 2 where ϕ_1, referring to the proton in flight, is 0.15, and ϕ_2 is 0.90.

As the hydration of alkenes is known to be susceptible to general acid catalysis, the reaction of **1** in H_2O with vaying concentrations of formate, chloroacetate, and dichloroacetate buffers (1:1 ratio of Na salt and acid) was investigated. The second-order rate constants for these buffers, evaluated[10] as 2 × the gradient of the $[buffer]_{total}$ vs k_{obs} plots are 0.0125, 0.05, and 2.45 M^{-1} s^{-1}, respectively.

Rate constants of acid-catalyzed hydration in H_2O and D_2O of identical hydrochloric acid concentration (1.2 × 10^{-2} M) were also measured as a function of temperature (Table 2). Activation parameters in both solvents were calculated using the Eyring equation and the standard Arrhenius equation to give E_a and A. The values of the various activation parameters are summarized in Table 3. The solvent deuterium kinetic isotope effect on acid-catalyzed hydration of **1** was determined by measuring the rates of reaction of **1** in H_2O, D_2O, and in mixtures of these two solvents containing 20% v/v DME at 25 °C. The experimental data are given in Table 4. The relationship between the mole fraction of D in the solvent (n) and k_{obs} is shown in Figure 1.

Finally, since the solvent system here is slightly different than what has been used before to measure the acid-catalyzed hydration of alkenes, the rate of hydration of ethyl vinyl ether in 20% DME/H_2O was determined in order to tie the present results to previous ones. The second-order rate constant determined in 20% DME/H_2O at 25 °C is 1.38 ± 0.06 M^{-1} s^{-1}, while that determined previously[3d] in H_2O was 2.13 ± 0.01 M^{-1} s^{-1} at 26.7 °C (Table 5).

Discussion

All the above results point to a mechanism for acid-catalyzed hydration of **1** being similar to that generally accepted for other alkenes. The data in Table 1 indicate

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(10) The factor of 2 arises from the fact that 1/2 the buffer is in the active acid form at the pK_a.

(11) (a) Kwart, H. *Acc. Chem. Res.* **1982**, *15*, 401. (b) Lewis, E. S. In *Proton Transfer Reactions*; Caldin, E., Gold, V., Eds.; Chapman and Hall: London, 1975; p 317.

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Table 5. Rate Constants of Acid-Catalyzed Hydration of Ethyl Vinyl Ether by Hydrochloric Acid in H_2O Containing 20% v/v DME (μ = 0.1 ($LiClO_4$), 25 °C)

[HCl] (M)	k_{obs} (s^{-1})[a]	k_2 (M^{-1} s^{-1})[b]
0.012	0.017 ± 0.001	1.39 ± 0.07
0.024	0.033 ± 0.001	1.36 ± 0.05
0.036	0.050 ± 0.002	1.38 ± 0.06

[a] Values of k_{obs} are averages of 2−3 determinations. [b] k_2 (M^{-1} s^{-1}) = 2.14 (H_2O, $HClO_4$, 26.6 °C).[3d]

that the reaction is first order in [H_3O^+], and the fact that the carboxylic acids HCOOH, $ClCH_2COOH$, and $Cl_2CHCOOH$ strongly promote the reaction indicates that the process must be general acid catalyzed. From the second-order rate constants obtained for the three carboxylic acids and H_3O^+ can be derived a poor Brønsted plot having a slope of 0.5 ± 0.2. Using only the data for the three carboxylic acids, a Brønsted plot can be constructed having a slope of 1.0 ± 0.2. H_3O^+ does not fall on this line, the observed catalytic coefficient being too small by $\sim 10^3$ which may suggest a fundamentally different process for its catalysis. A similar observation that H_3O^+ does not fit a Brønsted line for carboxylic acids was made by Kresge and Chiang for the acid-catalyzed hydration of ethyl vinyl ether.[3d]

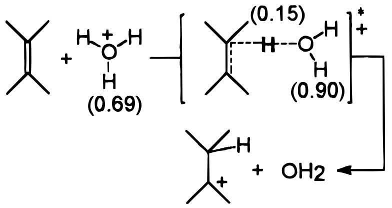
Nevertheless, the observed Dkie of 2.7 is in the range anticipated for a process having a primary kinetic isotope effect resulting from a proton in flight in the rate-limiting step. The activation parameters given in Table 3 for the L_3O^+-catalyzed reaction (L = H, D) give no indication for tunneling as contributing to the Dkie for this system since the ratio of the Arrhenius *A* values is 0.88, and there is no evidence of curvature in the Arrhenius or Eyring plots.[11] By way of comparison, the $\Delta H^\ddagger$ for the reaction of **1** with H_3O^+ is lower than that for the hydration of ethyl vinyl ether[3d] by some 3.6 kcal/mol and the $\Delta S^\ddagger$ is −22 ± 1.1 cal/K/mol relative to −11.1 ± 0.5 cal/K/mol. The lower entropy could relate to greater restriction of solvent in the transition state for hydration of **1** relative to the situation for ethyl vinyl ether.

Further information concerning the nature of the transition state for hydration of **1** can be gleaned from the data given in Table 4 that show the dependence of the reaction rate on the atom fraction of deuterium in the solvent. Equation 2 expresses the relationship between the rate constant observed in mixtures of L_2O (L = H, D) with known isotopic composition and the fractionation factors (ϕ) for the exchangeable protons undergoing change in their bonding; *n* is the atom fraction of D in the medium, and *i* and *j* represent the sites undergoing exchange in the transition and reactant states, respectively.[8]

$$k_n = k_o \prod_i^{TS} (1 - n + n\Phi_i) / \prod_j^{RS} (1 - n + n\Phi_j) \qquad (2)$$

The fractionation factors for the various hydrogens relate to the tightness of their bonding and are significantly less than unity if the overall bonding is weak as is the case for H's being transferred or in flight in the transition state, or for H's involved in hydrogen bonds where the overall bonding is loose.[12] The former case relates to primary kinetic isotope effects, while the latter relates to secondary kie's, and these can contribute significantly to the overall effect.

Scheme 1[a]



[a] Numbers in parentheses refer to fractionation factors.

Shown in Figure 1 is the plot of the observed rate constant for L_3O^+-catalyzed hydration of **1** as a function of the atom fraction (*n*) of D in the medium. That the plot is bowed upward is consistent with the process shown in Scheme 1 where the rate-limiting step for the reaction involves proton transfer from the hydronium ion to alkene. Nonlinear least squares fitting of the data to eq 3 generates the line through the data and the values for the fractionation factors of the hydrogen being transferred (ϕ_1 = 0.15) and the two nonreacting ones (ϕ_2 = 0.90).

$$k_D/k_H = (1 - n + n\phi_1)(1 - n + n\phi_2)^2 / (1 - n + n0.69)^3 \qquad (3)$$

These correspond to a $k_H/k_D = 0.69/0.15 = 4.6$ for the proton in flight, and $k_H/k_D = 0.69^2/0.90^2 = 0.59$ for the two nonreacting hydrogens when the transition state is referenced to a ground state consisting of alkene and H_3O^+. As summarized by Kresge, More O'Ferral, and Powell,[8c] these ϕ values are typical for rate-limiting proton transfer from H_3O^+ to a substrate, the compiled values for roughly 25 reactions being ϕ_1 = 0.12−0.4, and ϕ_2 = 0.66−0.9.[9,13]

In an earlier report,[7] we have indicated that the β-bromocarbocation of **1** must have a lifetime of less than 10^{-11} s in methanol. This was based on our inability to detect changes in the dibromide/methoxy bromide product ratio (~10/90) as a function of added LiBr up to a concentration of 0.3 M. Although the solvent system here is different, it might be expected that the lifetime of a protonated **1** (**1**-H^+), in an aqueous medium, might be similar or slightly less than this. Kresge and co-workers have suggested on the basis of a σ-correlation for cation hydration that a simple tertiary cation has a lifetime of $\sim 10^{-10}$ s in water, while that of a secondary cation is 5×10^{-12} s.[4,14] Such short lifetimes are at the limit of what is considered stable enough to exist as a solvationally equilibrated cationic intermediate. Thus it is possible that the protonation of **1** does not lead to a fully developed cation, but rather is concerted with the asynchronous addition of a second H_2O as in Scheme 2. This might be evidenced by the observed $\Delta S^\ddagger$ of −22 cal/K/mol for the hydration reaction of **1** which is some 11 cal/K/mol more negative than that for hydration of ethyl vinyl ether.[9] In an effort to cast light on this we applied fractionation factor analysis of the hypothetical process shown in Scheme 2 using nonlinear least squares fits of the data

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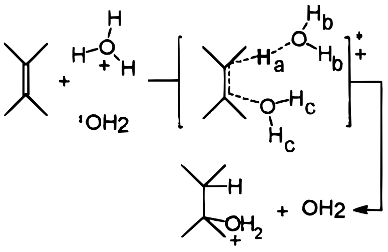
(13) (a) Bui-Nguyen, M.- H., Dahn, H.; McGarrity, J. F. *Helv. Chim. Acta* **1980**, *63*, 63. (b) McGarrity, J. F. *Helv. Chim. Acta* **1980**, *63*, 1767. (c) More O'Ferrall, R. A.; Koeppl, G. W.; Kresge, A. J. *J. Am. Chem. Soc.* **1971**, *93*, 9. (d) Toullec, J.; Dubois, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 3524.

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

(15) Kopecky, K. R.; Miller, A. J. *Can. J. Chem.* **1984**, *62*, 1840.

(16) *Handbook of Chemistry and Physics*, 50th ed.; The Chemical Rubber Co.: Cleveland, 1969−70, D-118.

Scheme 2



to an appropriate form of eq 2. Setting the ϕ values for the hydronium ion as 0.69 (constant) and solving for the ϕ's of $H_{a,b,c}$ gave computed values of 0.47 ± 0.44, 0.33 ± 0.13, and 1.53 ± 0.14, the latter two values clearly being beyond acceptable ranges since both must assume values somewhere between 0.69 and 1.0. In fact, the data are not good enough to define the values of $\phi_{b,c}$ well since these are heavily correlated. To gain some idea of the variation in $\phi_{a,b}$ as a function of ϕ_c, the latter value was varied from 1.0 to 0.94. The computed values of ϕ_a being unchanged, while those for ϕ_b rose from 0.9 to 0.96. Although one cannot on the basis of the available information determine which of Scheme 1 or 2 is more appropriate to explain the data, if the latter is followed the fractionation factor analysis indicates that the association of the second H_2O in Scheme 2 must be weak with little perturbation of the bonding in the O−H_b bonds.

Experimental Section

(a) Materials. *anti*-Sesquinorbornene (**1**, tetracyclo-[6.2.1.1^{3,6}.0^{2,7}]dodec-2(7)-ene, or 1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanonaphthalene) was prepared by the proceedure of Miller and Kopecky[15] and had physical constants identical to those reported. Ethyl vinyl ether (Aldrich, 99%) was heated under reflux over sodium for 4 h and then distilled at atmospheric pressure.[3d] D_2O (Isotech. Inc., A Matheson USA Co., 99.9 atom %D) was used as supplied as was DCl (Aldrich, 37 wt % solution in D_2O, 99.5 atom %D) and HCl (Aldrich, hydrochloric acid volumetric standard, 0.5027 N or 0.985 N).

Ethylene glycol dimethyl ether (DME, Aldrich, 99.9%, HPLC grade) was used with no further purification. $LiClO_4$ was purified as described previously.[7]

(b) Kinetics. The kinetics of acid-catalyzed hydration of **1** were determined under pseudo-first-order conditions of excess acid (0.001−0.1 M, $\mu = 0.1$ ($LiClO_4$) by observing the rate of decrease of absorbance at 230 or 250 nm using an Applied Photophysics SX-17MV stopped-flow spectrophotometer for the faster reactions where [HCl] = 0.1, 0.05 M, or an OLIS modified Cary 17 UV-vis spectrophotometer for the slower reactions. Solutions containing 20% DME (for reason of solubility) and H_2O (or D_2O) at various concentrations of HCl (or DCl) were placed into 3 mL cuvettes which were then equilibrated at 25 °C in the spectrophotometer for 15 min prior to the initiation of the kinetics. The reactions were initiated by adding a small amount (5−8 μL) of stock solution (1×10^{-2} M) of **1** in pure DME. Pseudo-first-order rate constants (k_{obs}) were evaluated by fitting the absorbance vs time data to a standard exponential model via NLLSQ treatment. The second-order rate constants for the reaction were evaluated as $k_2 = k_{obs/}[HCl]$. The rate constants, k_{obs} and k_2, are presented in Table 1, the reported values being the averages of 3−5 runs.

For the hydration reaction in the presence of the general acids HCOOH, $ClCH_2COOH$, and $Cl_2CHCOOH$, a 0.1 M 1:1 solution of the acid and its sodium salt in 20%DME/water was prepared. While the aqueous pK_a values for these are 3.75, 2.85, and 1.48,[16] the measured pH values were 0.3 units lower, this being attributable to the presence of the cosolvent. This is verified by the fact that for the completely dissociated acid HCl, the pH readings were 0.3 units lower than those calculated on the basis of concentrations. The [buffer] was varied by dilution of the above stock solution with 0.1 M KCl. For the higher buffer concentrations it was not necessary to adjust the pH readings, but for the more dilute ones, the pH was adjusted to 0.3 units less than the aqueous pK_a by the addition of tiny amounts of concentrated acid or base as needed.. The buffer catalytic constants were evaluated as 2 times the gradient of the $[buffer]_{total}$ vs k_{obs} plots.[10]

(c) Product Studies. A 30 μL amount of the above stock solution of **1** in pure DME was added to 25 mL of HCl solution (1.2×10^{-2} M, $\mu = 0.1$ ($LiClO_4$)) in 20% DME−water, and the reaction mixture was stirred for 10 min. The solution was extracted with purified (by distillation) CH_2Cl_2, the organic phase being dried ($MgSO_4$) and evaporated to yield a residue that was analyzed by GC-mass spectrometry. The identity of the material corresponding to the major peak (hydrate **2**) was made by comparison of its mass spectral data to that reported by Bartlett et al.[6a]

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