The Reversible Hydration of 1,3-Cyclohexadiene in Aqueous Perchloric Acid

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The reversible hydration of 1,3-cyclohexadiene in aqueous perchloric acid has been investigated. The reaction is acid catalyzed; $k_{HClO_4}/k_{DClO_4} = 1.19$, $d(\log k_{obsd})/d(-H_0) = 1.33$, $\Delta H^{\ddagger} = 22.8$ kcal/mol, and $\Delta S^{\ddagger} = -5.4$ eu. These mechanistic criteria are consistent with data for the analogous hydrations of 1-phenyl-1,3-butadiene, styrenes, and aliphatic alkenes.

The hydration of alkenes in aqueous acidic media has been investigated by numerous workers during the previous two decades.[1-16] To date, the hydration of alkenes containing no additional functional groups may be classified by one of the three following descriptive types.

(1) The addition of water across an isolated carbon-carbon double bond.[1-7]

$$\text{\Large $\diagdown$} C = C \text{\Large $\diagup$} + H_2O \xrightarrow{H_3O^+} H - C - C - OH$$
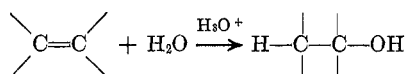
(2) The addition of water across a carbon-carbon double bond which is conjugated with a benzene ring.[8-13]

$$Ph - C = C \text{\Large $\diagup$} + H_2O \xrightarrow{H_3O^+} Ph - C - C - H \;(\overset{OH}{\vphantom{x}})$$
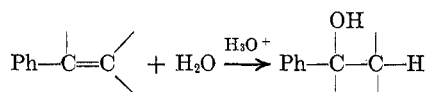
(3) The addition of water across a carbon-carbon double bond conjugated with a benzene ring and another carbon-carbon double bond.[14-16]

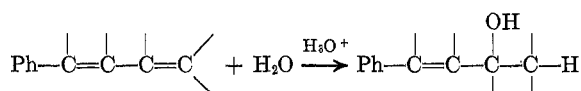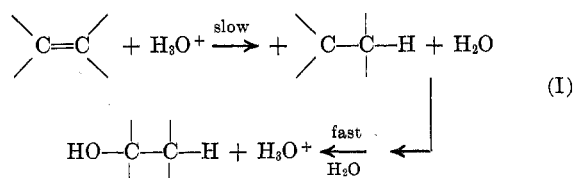$$Ph - C = C - C = C \text{\Large $\diagup$} + H_2O \xrightarrow{H_3O^+} Ph - C = C - C - C - H$$

Table I presents a comparative compilation of mechanistic criteria for these three reactant types. Much work of major importance to the delination of each of the individual classes is not included in Table I, since such mechanistic criteria has only been reported for one of the categories (*e.g.*, Hammett ρ for styrenes[8,10,11] and volume of activation for aliphatic alkenes[7]). From the comparative mechanistic criteria available, classes 2 and 3 appear to react by a very similar reaction pathway (*i.e.*, the PhC=C– group apparently acts very much like Ar in its substituent
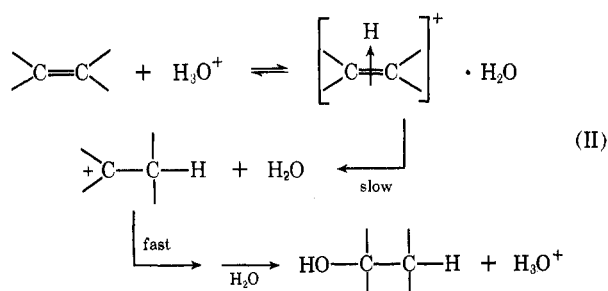
TABLE I

DATA FOR THE HYDRATION OF 1-PHENYL-1,3-BUTADIENE, STYRENES, AND ALIPHATIC ALKENES IN AQUEOUS ACID

Mechanistic criteria	1-Phenyl-1,3-buta-diene[a] (3)	Styrenes (2)	Aliphatic alkenes (1)
$d(\log k_{obsd})/d(-H_0)$	1.2	1.1–1.3[b]	1.0–1.2[c]
Solvent–isotope effect, $k_{H_3O^+}/k_{D_3O^+}$	3.0	2–4[d]	1.4[e]
General acid catalysis		Yes[d]	No[f]
$\Delta H^{\ddagger}$, kcal/mol	20.3	17.3–21.4[g]	23.2[h]
$\Delta S^{\ddagger}$, eu		–5 to –13.6[g]	–3[i]
Bronsted α		0.74, 0.78[i]	0.85[e]

[a] References 14 and 15. The solvent is aqueous sulfuric acid. [b] References 8–12. The data are for variously substituted styrenes covering a wide range of acidity (0.1–9.4 M HClO₄). [c] References 1 and 2. The data are for various alkenes in nitric and sulfuric acids. [d] References 8 and 11. The data are for variously substituted styrenes covering a wide range of acidity (0.1–9.4 M HClO₄). [e] Reference 6. The data is for isobutene in perchloric acid (α is calculated from data in mixed H₂O–D₂O solvents). [f] References 4 and 5. [g] References 9 and 10. The data are for styrenes in perchloric and sulfuric acids (6–8 M). [h] Reference 3. The data is for isobutene in nitric acid. [i] Reference 2. The data is for isobutene in nitric acid. [j] Reference 12.

$$\text{\Large $\diagdown$} C = C \text{\Large $\diagup$} + H_3O^+ \xrightarrow{\text{slow}} \text{\Large $\diagdown$} C - C - H + H_2O$$
$$HO - C - C - H + H_3O^+ \underset{H_2O}{\overset{\text{fast}}{\longleftarrow}} \qquad (I)$$

effect on >C=C<). Taft and coworkers[1] have proposed mechanism II for the hydration of aliphatic alkenes [largely on the basis of $d(\log k)/d(-H_0)$].

$$\text{\Large $\diagdown$} C = C \text{\Large $\diagup$} + H_3O^+ \rightleftharpoons \left[\text{\Large $\diagdown$} C \overset{H}{\underset{\vphantom{x}}{=}} C \text{\Large $\diagup$} \right]^+ \cdot H_2O$$
$$+ C - C - H + H_2O \xleftarrow{\text{slow}} \qquad (II)$$
$$\xrightarrow[H_2O]{\text{fast}} HO - C - C - H + H_3O^+$$

More recently, several workers have proposed that aliphatic alkenes are hydrated by a pathway similar to that proposed for styrenes (mechanism I).[5-7]

Hydration of styrenes is a general acid catalyzed reaction exhibiting a solvent-isotope effect of 2–4[8-13] (Table I). Hydration of aliphatic alkenes (*e.g.*, isobutene) is a specific acid catalyzed reaction[4,5] exhibiting a solvent isotope effect of 1.4[6] (Table I).

(1) R. H. Boyd, R. W. Taft, A. P. Wolf, and D. R. Christman, *J. Amer. Chem. Soc.*, **82**, 4729 (1960), and references therein.
(2) R. W. Taft, E. L. Purlee, P. Riesz, and C. A. DeFazio, *ibid.*, **77**, 1584 (1955).
(3) J. B. Levy, R. W. Taft, D. Aaron, and L. P. Hammett, *ibid.*, **73**, 3792 (1951).
(4) F. G. Ciapetta and M. Kilpatrick, *ibid.*, **70**, 639 (1948).
(5) J. L. Jensen, *Tetrahedron Lett.*, 7 (1971).
(6) V. Gold and M. A. Kessick, *J. Chem. Soc.*, 6718 (1965).
(7) B. T. Baliga and E. Whalley, *Can. J. Chem.*, **43**, 2453 (1965).
(8) W. M. Schubert, B. Lamm, and J. R. Keefe, *J. Amer. Chem. Soc.*, **86**, 4727 (1964).
(9) W. M. Schubert and B. Lamm, *ibid.*, **88**, 120 (1966).
(10) J. P. Durand, J. Davidson, M. Hellin, and F. Coussemant, *Bull. Soc. Chim. Fr.*, **43**, 52 (1966).
(11) W. M. Schubert and J. R. Keefe, *J. Amer. Chem. Soc.*, in press.
(12) W. M. Schubert and J. L. Jensen, *ibid.*, in press.
(13) N. C. Deno, F. A. Kish, and H. J. Peterson, *ibid.*, **87**, 2157 (1965).
(14) Y. Pocker and M. J. Hill, *ibid.*, **91**, 3243 (1969).
(15) Y. Pocker and M. J. Hill, *ibid.*, **91**, 7154 (1969).
(16) Y. Pocker and M. J. Hill, *ibid.*, **93**, 691 (1971).

These two mechanistic criteria are a measure of the extent of proton transfer attained in the transition state of the first step of mechanism I. Recent reports have focused on accumulating evidence that the transition state occurs earlier in the course of proton transfer from hydronium ion to a styrene than from a hydronium ion to an aliphatic alkene.[5-12]

In this paper, we wish to formally report the characterization of a fourth class of simple alkene hydration[17] and a comparative investigation of classes 1, 2, and 4.

(4) The addition of water across a carbon–carbon double bond conjugated with another carbon–carbon double bond.

$$\ce{\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{|}{C} + H2O ->[H3O+] \overset{|}{C}=\overset{|}{C}-\overset{\overset{OH}{|}}{C}-\overset{|}{C}-H}$$
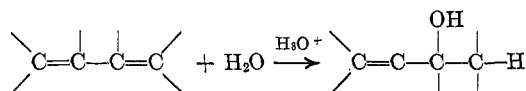
Experimental Section

Materials.—1,3-Cyclohexadiene, 2,3-dimethyl-2-butene, styrene, and 2-phenylpropene were obtained from Aldrich Chemical Co. and were molecularly distilled just prior to each kinetic run. This was conveniently accomplished by introducing alkene into the solvent as a gas, with the aid of a syringe. This procedure avoids local high concentration of alkene and serves to retard polymerization.[8,9,11]

Solutions.—The deuterioperchloric acid solutions were made by diluting concentrated deuterioperchloric acid with deuterium oxide (99.8% D_2O, Stohler Isotope Chemicals). Concentrated deuterioperchloric acid was made from concentrated perchloric acid by a continuous exchange method.[18] The concentrated deuterioperchloric acid was titrated with standard sodium hydroxide. Amounts required to make up appropriately more dilute concentrations were calculated, carefully weighed out, and diluted with deuterium oxide. The concentration of each solution made was checked by titration with standard sodium hydroxide. In this manner solutions of deuterioperchloric acid could be made that were equal in molarity to solutions of perchloric acid.

Kinetic Method.—The reversible hydration of 1,3-cyclohexadiene was followed spectrophotometrically at 257 mμ (λ_{max}). The reaction was monitored by one/both of the following ways. (1) A Beckman recording DU spectrophotometer was modified by placing a specially constructed constant temperature water bath between the monochrometer and the phototube housing. This unit maintains the temperature of the quartz uv cells to within ±0.02° of the desired temperature. Absorbance measurements were taken directly from a Beckman 10-in. linear-log recorder operating in the logarithmic mode. (2) Absorbance measurements were taken from the 10-in. recorder of a Beckman Kintrac VII spectrophotometric system. A Forma constant temperature circulating water bath was used to maintain the desired temperature. Kinetic data obtained *via* these two monitoring systems were interchangeable.

A quartz spectral cell was filled with the appropriate perchloric acid solution and thermostated in the spectrophotometer. When thermal equilibrium was attained, 1,3-cyclohexadiene was introduced, using a 2-cc ground glass syringe to introduce approximately 1 cc of air saturated with 1,3-cyclohexadiene at room temperature. The change of absorbance with time was followed continuously *via* a Beckman 10-in. recorder. In all instances, the absorbance decreased in a first-order fashion and remained constant over the period of time representing 8–12 reaction half-lives.

The reversible hydration of styrene, 2-phenylpropene, and 2,3-dimethyl-2-butene was followed spectrophotometrically at 248, 245, and 197 mμ, respectively. The hydrations of styrene and 2-phenylpropene have been described in detail previously.[8-13] The spectrophotometric method described by Gold[6] for following the hydration of isobutene was applied to 2,3-dimethyl-2-butene.
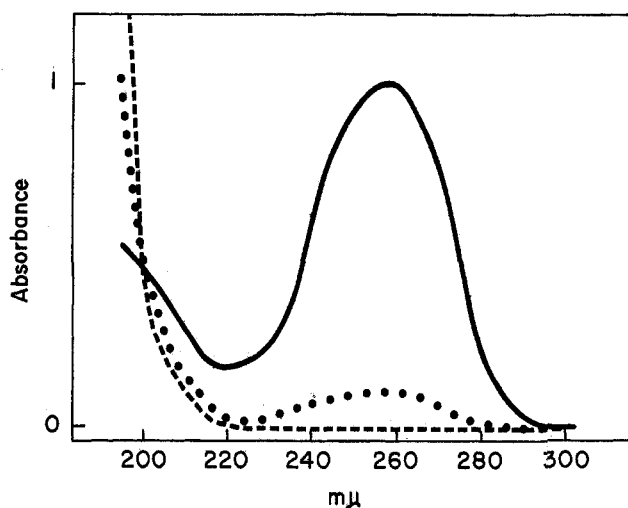
Figure 1.—The ultraviolet spectrum of 1,3-cyclohexadiene in 2.57 *M* $HClO_4$ (—), the same solution after 8 half-lives at 40° (· · · ·), and 2-cyclohexenol in 2.57 *M* $HClO_4$ (- - -).

In all other respects the kinetic method was analagous to that outlined above for 1,3-cyclohexadiene.

Results and Discussion

The hydration of aliphatic alkenes and styrenes have been described in detail previously by other workers[1-13] and our results for these reactions are subsequently discussed in comparison with our characterization of the hydration of 1,3-cyclohexadiene.

Reaction.—The molar absorptivity of 1,3-cyclohexadiene is about 4000 at λ_{max} 257 mμ.[19] A regular decrease of this strong absorption band was observed, until at equilibrium the absorbance was 15% that of the initial (Figure 1). This equilibrium spectrum remained unchanged for several half-lives of reaction time at any given acid concentration.

$$\ce{<benzene ring> + H2O ->[H3O+][<=>] <cyclohexene ring>-OH}$$
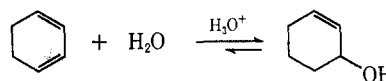
The ultraviolet spectrum of 2-cyclohexenol exhibits a maximum at 192 mμ (ϵ 5200). The change in the ultraviolet spectrum seen in Figure 1 is entirely consistent with the reversible hydration of 1,3-cyclohexadiene to produce 2-cyclohexenol. It is significant that cyclohexene is not hydrated under these conditions;[20] *i.e.*, cyclohexadiene is truly in equilibrium with 2-cyclohexenol and not with 1,2-cyclohexanediol or 1,3-cyclohexanediol. The equilibrium spectrum may be obtained by placing either 1,3-cyclohexadiene or 2-cyclohexenol in 2.57 *M* $HClO_4$ and thermostating the solution for 8 half-lives of reaction time.

The investigation of this reaction at spectral concentrations ($<10^{-3}$ *M*) has the advantage that reactions which are higher order in organic substrate (*e.g.*, polymerization, Diels–Alder, etc.) are suppressed, a situation analogous to that found for the hydration of styrenes.[9,11]

Rate Constants.—When 1,3-cyclohexadiene is hydrated at spectral concentrations ($<10^{-4}$ *M*) in

(17) J. L. Jensen, Abstracts, Fifth Western Regional Meeting of the American Chemical Society, Anaheim, Calif., 1969, No. 195.

(18) J. L. Jensen, Ph.D. Thesis, University of Washington, Seattle, Wash., 1967, p 27.

(19) O. H. Wheeler and L. A. Kaplan, Ed., "Organic Electronic Spectral Data," Vol. I–IV, Interscience, New York, N. Y.

(20) J. L. Jensen, unpublished results, 1970.

TABLE II

OBSERVED RATE CONSTANTS FOR THE REVERSIBLE HYDRATION OF ALKENES IN AQUEOUS PERCHLORIC ACID[a]

Molarity of HClO4	$-H_0$[b]	2,3-Dimethyl-2-butene Temp, °C	$10^4 k_{obsd}$	2-Phenylpropene Temp, °C	$10^4 k_{obsd}$	1,3-Cyclohexadiene Temp, °C	$10^4 k_{obsd}$	Styrene Temp, °C	$10^4 k_{obsd}$
1.05	0.34	25	9.26	25	2.04	40	0.535		
1.44	0.54	25	19.1	25	4.58	40	0.930		
2.57	1.16	20	65.1	20	14.6	30	1.72	30	0.0614
2.57	1.16	25	119	25	28.0	40	6.06	40	0.198
2.57	1.16	30	209	30	48.1	50	19.1	50	0.674
2.57	1.16			40	140			60	2.18
4.03	1.80			25	200	40	47.0		
Molarity of DClO4									
1.05						40	0.451		

[a] The rate constants were determined spectrophotometrically using a Beckman Kintrac VII and/or a Beckman recording DU. The reactions were monitored at the following wavelengths: 2,3-dimethyl-2-butene, 197 mμ; 2-phenylpropene, 245 mμ; 1,3-cyclohexadiene, 257 mμ; styrene, 248 mμ. The rate constants above are an average of replicate determinations. In all cases the average deviation was less than ±3%. [b] Reference 23.

perchloric acid solutions, the reaction is pseudo-first-order. The reaction thus fits the general equation[21]

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$$
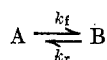
$$k_{obsd} = k_f + k_r$$

$$\text{rate} = k_{obsd}[A]; \quad \ln([A] - [A_\infty]) = k_{obsd}t + \text{constant}$$

The reaction was monitored by measuring the decrease in concentration (*via* absorbances) with time of 1,3-cyclohexadiene. A conventional plot of ln ([A] − [A_∞]) *vs.* time yields a straight line with a slope equal to k_{obsd}. The ratio of k_f to k_r is about 85 to 15; *i.e.*, $k_f/k_r = [B]/[A] = 85/15$, where A is 1, 3-cyclohexadiene and B is 2-cyclohexenol. It was observed that this ratio, k_f/k_r, was rather insensitive to acid concentration (as reflected in roughly equal per cent changes in absorbance in all rate measurements). Since k_{obsd} is largely k_f and since the ratio k_f/k_r is reasonably constant, none of the interpretations to follow are affected by treating k_{obsd} directly and stating that changes in k_f are accurately represented by changes in k_{obsd}. Table II lists the experimentally observed rate constants. In all instances, experimental "infinity" absorbance values were obtained and the rate plots were linear for at least three half-lives.

Activation Parameters.—The change in rate constant with temperature was analyzed for the usual terms of entropy and enthalpy of activation.[22] Log (k_{obsd}) was plotted *vs.* the reciprocal of the absolute temperature. The slope and intercept were obtained by the method of least squares. All calculations were carried out with the aid of a CDC 3300 computer. The general equations used were

$$\ln k_{obsd} = \frac{-E_a}{RT} + \ln A$$

$$\Delta H^{\ddagger} = E_a - RT$$

$$\ln k_{obsd} = \ln\left(\frac{kT}{h}\right) + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}$$

Table III presents data for the enthalpy and entropy of activation. The magnitudes of these quantities are typical for alkene hydration.[2,3,7,9,10,15]

Solvent–Isotope Effect.—The hydration of 1,3-cyclohexadiene in deuterioperchloric acid–deuterium oxide

(21) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 186.
(22) Reference 21, pp 99–100.

TABLE III

ACTIVATION PARAMETERS FOR THE REVERSIBLE HYDRATION OF STYRENE, 2-PHENYLPROPENE, 1,3-CYCLOHEXADIENE, AND 2,3-DIMETHYL-2-BUTENE IN 2.57 M HClO4 AT AMBIENT TEMPERATURES[a]

Compd	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
Styrene	24.2 ± 0.1	−2.8 ± 0.4
2-Phenylpropene	19.9 ± 0.4	−3.6 ± 1.3
1,3-Cyclohexadiene	22.8 ± 0.2	−5.4 ± 0.6
2,3-Dimethyl-2-butene	20.0 ± 0.2	−0.3 ± 0.7

[a] The enthalpy, entropy, and standard deviations were calculated by a least-squares analysis of the data in Table II, carried out on a CDC 3300 computer.

solutions proceeded in a first-order fashion and the "infinity" absorbance values remained constant for several half-lives of reaction time. The ratio k_f/k_r is approximately the same in the isotopic solvents, $k_f/k_r \simeq$ 85/15 in HClO4 and $k_f/k_r \simeq$ 75/25 in DClO4. Such small changes effect very little change in the overall reported solvent–isotope effect of k_{obsd} and consequently are ignored.

Mechanism.—The hydration of 1,3-cyclohexadiene is clearly a pseudo-first-order acid-catalyzed reaction. A plot of log k_{obsd} *vs.* $-H_0$[23] gives a straight line of slope 1.33 (Figure 2).

The mechanistic criteria reported herein are summarized in Table IV. The media and temperature for all compounds and criteria are closely similar. Comparison of data from Tables I and IV demonstrate the necessity of reporting criteria in closely similar media. For example, $\Delta H^{\ddagger}$ for styrene has been reported as 17.5 and 19.9 kcal mol⁻¹ in 6.5 M ($H_0 = -3$) H2SO4[10] and 6.4 M ($H_0 = -3.2$) HClO4,[9] respectively. Acidity dependence, $d(\log k)/d(-H_0)$, is reported for styrene as 1.17 and 1.26 over comparable ranges of sulfuric[10] and perchloric[9,11] acids, respectively. The solvent–isotope effect, $k_{H_3O^+}/k_{D_3O^+}$, may be dependent not only on alkene structure but also on perchloric acid molarity.[11] Since the data were previously not available, Table IV presents $d(\log k)/d(-H_0)$ over practically identical ranges of acidity (Figure 2), $k_{H_3O^+}/k_{D_3O^+}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ at essentially the same acidities for several types of alkenes. It is significant that $\Delta H^{\ddagger}$ for hydration of styrene is some 4 kcal/mol greater in 2.57 M HClO4 than in 6.5–7 M HClO4.[9] Schubert and Lamm reported values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in 49.4% HClO4 and 47.3%

(23) K. Yates and H. Wai, *J. Amer. Chem. Soc.*, **86**, 5408 (1964).

TABLE IV

DATA FOR THE HYDRATION OF 1,3-CYCLOHEXADIENE, 2,3-DIMETHYL-2-BUTENE, 2-PHENYLPROPENE, AND
1-PHENYL-1,3-BUTADIENE AT COMPARABLE ACID CONCENTRATIONS AND AT AMBIENT TEMPERATURE

Mechanistic criteria	1,3-Cyclohexadiene	2,3-Dimethyl-2-butene	2-Phenylpropene	1-Phenyl-1,3-butadiene[a]
$d(\log k)/d(-H_0)$	1.33	1.32	1.34	1.2
Solvent–isotope effect,				
$k_{H_3O^+}/k_{D_3O^+}$	1.2	1.4[b]		3.0
$\Delta H^{\ddagger}$	22.8	20.0	20.0 (24.2)[c]	20.3
$\Delta S^{\ddagger}$	−5.4	−0.3	−3.2 (−2.8)[c]	

[a] Reference 14 and 15. The solvent is aqueous sulfuric acid (3 M for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$). [b] Reference 6. The data is for isobutene in 0.4 M perchloric acid. [c] Values in parentheses are for styrene in 2.57 M perchloric acid.

HClO$_4$ of 19.2 kcal/mol and −5 eu and 19.9 kcal/mol and −5 eu respectively.[9] Our values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in 22.6% HClO$_4$ are 24.2 kcal/mol and −2.8 eu, respectively. Thus we have confirmed the earlier indication by Schubert and Lamm that $\Delta H^{\ddagger}$ decreases with increasing perchloric acid molarity. The change in $\Delta S^{\ddagger}$ is barely outside experimental error and may not be real. The decrease in $\Delta H^{\ddagger}$ with increasing perchloric acid concentration may be due to (1) the increased activity (destabilization) of H$_3$O$^+$ with increasing acid concentration, (2) salting-in (stabilization) of the charged transition state, and/or (3) salting-out (destabilization) of the uncharged styrene ground state.

Of the types of mechanistic criteria investigated, only the solvent–isotope effect differentiates the hydration of 1,3-cyclohexadiene from other hydration reactions. The remaining criteria, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $d(\log k_{obsd})/d(-H_0)$, do not appear to change in any characteristic fashion with alkene type. Following is the simplest mechanism for the hydration of 1,3-cyclohexadiene which is consistent with the data listed in Table IV.
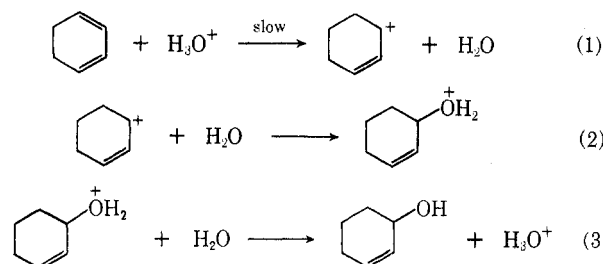
The magnitude of the solvent–isotope effect is not inconsistent with the proposed rate-controlling proton transfer from hydronium ion to olefinic carbon, provided that proton transfer is quite extensive in the transition state [5,6,24] (*i.e.*, the Brønsted α approaches one[25,26]).

(24) J. L. Longridge and F. A. Long, *J. Amer. Chem. Soc.*, **89**, 1287, 1292 (1967).

(25) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 156–159, 241.

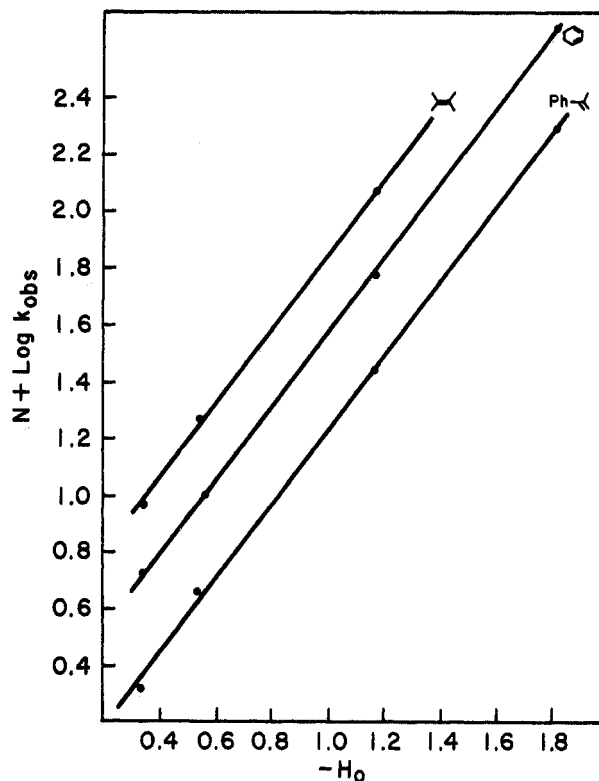(26) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).

Figure 2.—Acidity dependence of the hydration of alkenes in aqueous perchloric acid: 2,3-dimethyl-2-butene and 2-phenylpropene, $N = 4$ at 25°; 1,3-cyclohexadiene, $N = 5$ at 40°. The slopes are 1.32, 1.34, and 1.33, respectively.

The data presented herein do not discount the possibility of the hydration of 1,3-cyclohexadiene proceeding *via* a mechanism similar to II. The intermediacy of a π complex is not disproven for either aliphatic alkenes or 1,3-cyclohexadiene hydration in aqueous acidic media; however, neither is it required.

Registry No.—1,3-Cyclohexadiene, 592-57-4; perchloric acid, 7601-90-3; 2-cyclohexenol, 822-67-3; 2,3-dimethyl-2-butene, 563-79-1; 2-phenylpropene, 98-83-9; styrene, 100-42-5.