The Acid-Catalyzed Hydration of Styrene

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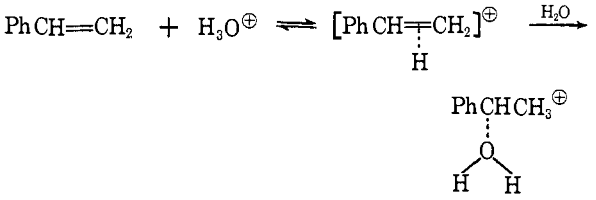
Abstract: First-order rate constants for the hydration of styrene in 36–50% perchloric acid at 25° and in 47–54% perchloric acid at 10° have been determined by an ultraviolet spectrophotometric method. About 2% of styrene remains in equilibrium with 1-phenylethanol. The equilibrium constant is relatively insensitive to a change in mineral acid molarity or temperature. The acidity dependence of the hydration rate constant is intermediate between H_0 and $H_{R'}$. No detectable isotope effect was observed in the hydration rates of styrene-*α*-*d* and styrene-*β*,*β*-d_2. Neither deuterio compound suffers hydrogen exchange during the forward reaction. The results are consistent with a rate-controlling formation of carbonium ion by proton transfer from solvent acid to styrene.

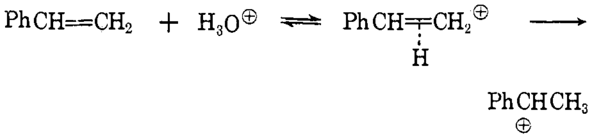
In a preliminary communication on the hydration of styrene and substituted styrenes, evidence was presented that the reaction is general acid catalyzed and that a carbonium ion intermediate cannot be formed reversibly.[2] The simplest mechanism fulfilling these requirements is rate-controlling proton transfer from $H_3O^{\oplus}$ to styrene, giving directly the carbonium ion (eq. 1).

$$\mathrm{PhCH{=}CH_2} + \mathrm{H_3O^{\ominus}} \longrightarrow \mathrm{H_2O} + \mathrm{Ph}\overset{\oplus}{\mathrm{C}}\mathrm{HCH_3} \xrightarrow{\text{fast}} \mathrm{PhCHOHCH_3} \quad (1)$$

Not excluded by the experimental findings is rate-controlling formation of an "encumbered" carbonium ion, as in the mechanism of eq. 2, suggested by Taft.[3e] Ruled out, however, are mechanisms in which the transition state contains the elements of the styrene and a proton *only*, such as rate-controlling rearrangement of an olefin–proton complex, proposed earlier by Taft[3a–d] for the hydration of aliphatic olefins (eq. 3). Deno, Kish, and Peterson recently have published results consistent with the mechanism of eq. 1.[4]



$$\mathrm{PhCH{=}CH_2} + \mathrm{H_3O^{\oplus}} \rightleftharpoons [\mathrm{PhCH{=}CH_2}]^{\oplus} \xrightarrow{\mathrm{H_2O}} \mathrm{PhCHCH_3}^{\oplus}\cdots\mathrm{OH_2} \quad (2)$$



$$\mathrm{PhCH{=}CH_2} + \mathrm{H_3O^{\oplus}} \rightleftharpoons \mathrm{PhCH{=}CH_2}^{\oplus}\cdots\mathrm{H} \longrightarrow \mathrm{PhCH}\underset{\oplus}{\mathrm{C}}\mathrm{H_3} \quad (3)$$

In this paper, the details of the work on styrene, styrene-*α*-*d*, and styrene-*β*,*β*-d_2 are presented.[2] Styrene was chosen for study because the first-order rate constant for its hydration in perchloric acid medium could be measured with convenience, as well as accuracy, by an ultraviolet spectrophotometric method. The initial concentration of styrene could be kept low enough (10^{-4} to 10^{-5} *M*) to completely suppress polymerization.[5]

In the extensive investigations of Taft and coworkers on the hydration of gaseous olefins,[3] rate constants were determined by measuring the decrease in pressure of gaseous olefin when it was shaken with aqueous mineral acid. This method caused some complication in the interpretation of the medium dependence of the specific rates since the pressure of gaseous olefin measures its activity in solution rather than its concentration. To correlate properly the observed rate constants with the Hammett acidity function, Taft had to obtain values for the activity coefficients of the olefins, f_0, in the different media employed. Values of f_0 in 0.1 to 1 *M* nitric acid were obtained from k_c/k_p, where k_p is the observed rate constant for hydration of gaseous olefin and k_c is the concentration rate constant as obtained earlier by Lucas.[6] Values of f_0 in up to 5 *M* nitric acid were then obtained by an extrapolation procedure using the Setschenow equation.[3a]

In the present work, *concentration* rate constants for hydration were obtained directly. The reaction was found to lead to an equilibrium mixture of 1-phenylethanol and a small proportion of styrene. The position of equilibrium as a function of perchloric acid molarity and of temperature was determined separately, approaching the equilibrium from the alcohol side.

Experimental Section

Styrene. In the kinetic runs, Eastman Kodak White Label styrene was used without further treatment. It was later revealed by mass spectroscopy that this material contained a compound having two units higher mass, most probably ethylbenzene. Therefore, styrene was also prepared from 2-phenylethanol.[7] A sample of this styrene, b.p. 72–73° (67 mm.), stabilized with a trace of 4-*t*-butylcatechol, was used for determination of extinction coefficients. The amount of ethylbenzene in the commercial styrene was estimated at less than 2% and does not affect the accuracy of the kinetic runs since it does not react under the conditions employed.

Styrene-*α*-*d*. Acetophenone (Eastman Kodak White Label) was redistilled under reduced pressure and reduced with lithium alumi-

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[1] The work was done while B. L. was on leave from the Nobel Institute of Chemistry, Stockholm, Sweden.

[2] W. M. Schubert, B. Lamm, and J. R. Keeffe, *J. Am. Chem. Soc.*, 86, 4727 (1964).

[3] (a) R. W. Taft, Jr., *ibid.*, 74, 5372 (1952); (b) R. W. Taft, Jr., E. L. Purlee, P. Riesz, and C. A. DeFazio, *ibid.*, 77, 1584 (1955); (c) E. L. Purlee and R. W. Taft, Jr., *ibid.*, **78**, 5807, 5811 (1956); (d) P. Riesz, R. W. Taft, Jr., and R. H. Boyd, *ibid.*, **79**, 3724 (1957); (e) R. H. Boyd, R. W. Taft, Jr., A. P. Wolf, and D. R. Christman, *ibid.*, 82, 4729 (1960).

[4] N. C. Deno, F. A. Kish, and H. J. Peterson, *ibid.*, 87, 2157 (1965).

[5] Acid-catalyzed polymerization, which depends on a higher power of the concentration of styrene than does hydration, became noticeable when the styrene concentration was greater than 10^{-3} *M*.

[6] H. J. Lucas and W. F. Eberz, *J. Am. Chem. Soc.*, **56**, 460 (1934); H. J. Lucas and Yun-Pu Liu, *ibid.*, **56**, 2138 (1934).

[7] S. Sabetay, *Bull. soc. chim. France*, [4] **45**, 69 (1929).

num deuteride (Metal Hydrides Inc., Beverly, Mass., minimum isotopic purity 97.8%) to 1-phenylethanol-1-*d* in 89% yield. This alcohol then was dehydrated with a trace of *p*-toluenesulfonic acid[8] to give a 50% yield of styrene-α-*d*, b.p. 67.5–70.5° (60 mm.). No detectable absorption by α-hydrogen could be seen in the 60-Mc.p.s. n.m.r. spectrum, and a mass spectral analysis carried out on a Consolidated Engineering Corp. Model 21-103 instrument, ionization potential 8 v., indicated an isotopic purity of 98.5 ± 0.1 atom % D. The styrene was stabilized with a trace of 4-*t*-butylcatechol.

Styrene-β,β-d_2. Ethyl phenylacetate (Eastman Kodak White Label) was redistilled under vacuum and reduced with lithium aluminum deuteride to 2-phenylethanol-1,1-d_2 in 75% yield. This alcohol was dehydrated with potassium hydroxide.[7] Styrene-β,β-d_2, b.p. 69–71° (60 mm.), was obtained in 64% yield. Inhibitor was added as above. The 60-Mc.p.s. n.m.r.spectrum showed no evidence of H in the β-positions (*cis* and *trans*) and a mass spectral analysis indicated an isotopic purity of 98.5 ± 0.1 mole % D.

1-Phenylethanol. The Eastman Kodak White Label product gave a carbonyl reaction with 2,4-dinitrophenylhydrazine reagent and was entirely unsuitable for ultraviolet spectroscopy. Through treatment with Girard P reagent according to the standard procedure,[9] a pure material was obtained, b.p. 64–64.5° (less than 2 mm.), suitable for determining the extinction coefficient and the equilibrium with styrene. A sample of 1-phenylethanol-1-*d* was purified similarly.

Perchloric Acid. Stock solutions were prepared by dilution of 70% perchloric acid (Baker C.P. grade) and assayed by titration of weighed portions with 0.2 *M* sodium hydroxide which had been standardized against both constant boiling point hydrochloric acid and potassium hydrogen phthalate.

Kinetic Procedure. First-order rate constants for the hydration of styrene (*ca.* 5 × 10^{-5} *M*) in perchloric acid solutions were determined by the ultraviolet spectrophotometric method previously described.[10] To avoid a local high concentration of styrene,[5] it was introduced into the Beckman cell as a gas with the aid of a syringe. The decrease in absorbance with time was recorded, the measurements being made in the region 240–250 mμ, where styrene has a high extinction coefficient. As a check that truly first-order conditions prevailed, some runs were made at 282 mμ with about 15-fold higher concentrations of styrene.

Check Experiments for Deuterium Exchange. In a 2-l. flask, 1.0 l. of 43.43% perchloric acid and 0.1 ml. of styrene-α-*d* were shaken for 15 min. at 20°. The time had been calculated to allow about 15% of the styrene to react. Then air was aspirated through the solution, which was dried over KOH pellets and led through a Dry Ice trap, in which the styrene was condensed. After 5 min., when it was judged that the styrene had been entrained from the perchloric acid solution, a mass spectral analysis (see above) was made. The trap had been designed so that it could be connected to the inlet system of the mass spectrometer, and the styrene was analyzed immediately after it had been collected. An analogous experiment was carried out on styrene-β,β-d_2. No change in isotopic composition was observed in either case.

Equilibrium Measurements. Solutions of *ca.* 10^{-4} *M* 1-phenylethanol (or 1-phenylethanol-1-*d*) in various strengths of perchloric acid were introduced into a 10-cm. Cary cell and thermostated for 7 half-lives. The spectrum of the resulting 1-phenylethanol–styrene equilibrium mixture was then recorded on a Cary Model 14 spectrometer. The spectra of pure styrene in 95% ethanol and pure 1-phenylethanol in water also were recorded.

Results

Observed Rate Constants. The first-order rate constants listed in Table I were obtained from visual slopes of plots of log ($D - D_\infty$) against time, where D denotes optical density. The plots were linear for at least 3 half-lives. Values of D_∞ were obtained at about 9 half-lives and remained constant for at least 3 additional half-lives. After that the optical density increased and a turbidity set in, presumably because of styrene polymerization.

Table I. Values of k_{obsd}[a] for the Reversible Hydration of Styrene in $HClO_4$

$HClO_4$, wt. %	10^4k_{obsd}, sec.$^{-1}$
	Runs at 25°
36.59	0.565, 0.566, 0.568
39.68	1.26, 1.26, 1.27
43.35[b]	3.97, 4.05, 4.06
47.27	15.2, 16.0
49.40	34.8, 35.0
	Runs at 10°
47.22	2.39, 2.40, 2.42
49.33	5.55, 5.56, 5.61
51.49	14.2, 14.2, 14.4
53.26	33.5, 33.7, 34.2

[a] Sum of forward and reverse reaction rate constants. [b] Three runs at 282 mμ, with initial styrene concentration 15 times higher than usual, gave 4.02 ± 0.02.

Rate constants for styrene-α-*d* and styrene-β,β-d_2 are given in Table II. In the case of the latter compound, the D_∞ reading is that for an equilibrium mixture of natural styrene and 1-phenylethanol. However, as the equilibrium mixture consists of only about 2% styrene and the spectrum of styrene-β,β-d_2 is shifted only slightly from that of styrene,[11] the error introduced into k_{obsd} is negligible.

Table II. Values of k_{obsd}[a] for the Reversible Hydration of Light and Deuterated Styrenes in $HClO_4$

	10^4k_{obsd}, sec.$^{-1}$	
Compd.	43.35% $HClO_4$ at 25°	49.33% $HClO_4$ at 10°
Styrene	4.06	5.56, 5.61, 5.64
Styrene-α-*d*	4.15	5.68, 5.82
Styrene-β,β-d_2	3.95	5.44, 5.57

[a] Sum of forward and reverse reaction rate constants.

Equilibrium Determinations. Equation 4 was applied to the determination of the ratio of 1-phenylethanol to styrene concentration at equilibrium in a number of perchloric acid percentages. The equilibrium was approached by dehydration of the alcohol in a 10-cm. Cary cell so as to keep the styrene concentration low at all times.

$$\frac{[\mathrm{ROH}]}{[\mathrm{sty}]} = \frac{\epsilon_{\text{sty}} - \epsilon}{\epsilon - \epsilon_{\text{ROH}}} \tag{4}$$

In eq. 4, ϵ_{sty}, ϵ_{ROH}, and ϵ are the extinction coefficients of pure styrene, pure 1-phenylethanol, and the equilibrium mixture of the two, respectively. Values of ϵ_{sty} were determined in 95% ethanol at four wave lengths between 247 and 257 mμ; values of ϵ_{ROH} were determined in water at the same wave lengths. Application of eq. 4 assumes that ϵ_{sty} and ϵ_{ROH} are insignificantly affected by medium change. This was confirmed for styrene, which was found to have its principal $\lambda_{\max}$ at 248 mμ (ϵ 14,800 ± 200) in isooctane, 95% ethanol, or 25% perchloric acid (compare with

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[8] I. A. Berstein, W. Bennett, and M. Fields, *J. Am. Chem. Soc.*, 74, 5763 (1952).

[9] Houben-Weyl, "Methoden der Organischen Chemie," Vol. 7, Part 1, 4th Ed., Georg Thieme Verlag, Stuttgart, 1954, p. 479.

[10] W. M. Schubert and R. E. Zahler, *J. Am. Chem. Soc.*, 76, 1 (1954).

[11] The $\lambda_{\max}$ of styrene-β,β-d_2 is shifted 0.5 mμ to shorter wave length.

Table III. Mole Per Cent Styrene in the Styrene–1-Phenylethanol Equilibrium in $HClO_4$

	PhCH=CH$_2$			PhCD=CH$_2$	
	Values at 25°				
Acid, %	36.5	40.0	45.3	52.1	40.0
Styrene,[a] %	2.3 ± 0.2	2.4 ± 0.1	2.4 ± 0.1	2.6 ± 0.4	1.8 ± 0.1
	Values at 10°				
Acid, %	45.3		52.1	45.3	52.1
Styrene,[a] %	1.5 ± 0.1		1.7 ± 0.3	1.2 ± 0.3	1.2 ± 0.2

[a] Average of eight values, two at each of the wave lengths: 247, 248, 251.5, and 257.0 mμ. The ± deviation given is the maximum deviation of any of the eight values.

ref. 12 and 13). Table III lists the mole percentages of styrene at equilibrium for both normal styrene and styrene-α-*d*.

Discussion

The values of k_{obsd} listed in Table I for the hydration of styrene are sums of the specific rates for hydration of styrene and dehydration of 1-phenylethanol. Measurement of the concentration of styrene to alcohol at equilibrium (Table III) gives the ratio of dehydration to hydration rates. This enables calculation of both k_{hydr} and k_{dehydr}. Since the equilibrium showed little dependence on acidity, values of k_{hydr} and k_{dehydr} (Table IV) were easily obtained by interpolation for the media in which the kinetic runs were made.

Table IV. Average Values of Equilibrium Amounts of Styrene, Observed Rate Constants, and Specific Rates of Hydration and Dehydration

$HClO_4$, %	$-H_0$[a]	Styrene at eq.,[b] %	10^4 k_{obsd}, sec.$^{-1}$	10^4 k_{hydr}, sec.$^{-1}$	10^6 k_{dehydr}, sec.$^{-1}$
		Runs at 25°			
36.59	2.05	2.3	0.566	0.553	1.3
39.68	2.36	2.3	1.27	1.24	2.9
43.35	2.71	2.4	4.04	3.94	9.7
47.27[c]	3.16	2.5	15.6	15.2	39.0
49.40[c]	3.41	2.5	34.9	34.0	87.0
		Runs at 10°			
47.22	3.16	1.6	2.40	2.36	3.9
49.33	3.40	1.6	5.60	5.51	9.0
51.49	3.70	1.7	14.3	14.0	24.0
53.26	3.95	1.8	33.8	33.2	61.0

[a] Taken from data of Yates and Wai,[14] which differs only slightly from that of Paul and Long.[15] [b] Same definition as in Table III. [c] For the hydration reaction, ΔH^* is 19.9 ± 0.5 kcal./mole in 47.27% acid and 19.2 ± 0.5 kcal./mole in 49.40% acid; the quantity ΔS^* is −5 ± 2 e.u. at 25° in both these acids.

The errors in k_{hydr} are small owing to the fact that the relative amount of styrene at equilibrium is small, approximately 2%. However, the accuracy in k_{dehydr} is considerably less owing to the large percentage error possible in measuring the small ratio of styrene to alcohol concentration at equilibrium. With one exception, the individual values of k_{obsd} are within ±2% of the average values. A conservative estimate of the accuracy of the measurement of [sty]/[ROH] at equilibrium is ±20%. This would lead to a maximum relative error in k_{hydr} of ±2.5%, and in k_{dehydr} of ±20%.

Isotope Effects. Styrene-α-*d*. The ratio of k_{obsd} values for styrene and styrene-α-*d* in 43.4% perchloric acid at 25° is 0.98 ± 0.03; in 49.3% perchloric acid at 10° it is 0.97 ± 0.03. Thus there is no detectable isotope effect in the observed first-order rate constants. Since the relative amount of styrene at equilibrium is quite small, this means that the isotope effect in k_{hydr} also is indetectably small, having the value of 0.97 ± 0.03 at 25° and 0.97 ± 0.03 at 10°. Substitution of α-deuterium significantly decreases the equilibrium concentration of styrene to alcohol, indicating an isotope effect of greater than unity in the dehydration rates. In view of the large inherent percentage error in determining [sty]/[ROH], we refrain from assigning any specific numbers to the isotope effect in the dehydration.

Several workers have shown that solvolysis reactions of the SN1 type are retarded significantly by α-deuterium substitution.[16–18] For example, k_H/k_D is 1.15 for the solvolysis of $C_6H_5CDClCH_3$.[19] Thus the fact that k_{dehydr} is smaller for 1-phenylethanol-1-*d* than for the normal alcohol is not surprising. However, the lack of a detectable α-deuterium isotope effect in k_{hydr} is of some interest. It appears that changes in the zero-point energy are minimized by the fact that the α carbon is trigonal in the transition state as well as the ground state. By contrast the solvolysis reactions referenced above, as well as the dehydration of α-phenylethanol, involve a change of the α carbon from a tetrahedral toward a trigonal state.

The fact that α-deuterium substitution reduces the concentration of styrene in the styrene–1-phenylethanol equilibrium is consistent with the expectation voiced in ref. 18. This is based on the larger frequency for tertiary C–H bending (~1340 cm.$^{-1}$)[20] as compared to out-of-plane olefinic C–H bending (~990 cm.$^{-1}$).[20] The difference in stretching frequency between the α-CH of the styrene and that of the 1-phenylethanol is probably small.[18,20,21]

Isotope Effects. Styrene-β,β-*d*$_2$. There is no exchange of the β-deuterium atoms during the forward reaction of hydration of styrene-β,β-*d*$_2$. Of course,

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(12) American Petroleum Institute, Research Project 44, Catalogue of Ultraviolet Spectral Data, Carnegie Institute of Technology, Pittsburgh, Pa., 1955, Serial No. 168.

(13) J. H. Elliot and E. V. Cook, *Ind. Eng. Chem. Anal. Ed.*, **16**, 20 (1944).

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

(15) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(16) V. J. Shiner, Jr., *Tetrahedron*, **5**, 243 (1959), and references therein.

(17) E. S. Lewis, *ibid.*, **5**, 143 (1959).

(18) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

(19) B. L. Murr, Jr., "Precise Conductometric Determination of Solvolysis Rate Constants and Deuterium Isotope Effects," Ph.D. Thesis, University of Indiana, 1961.

(20) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, Tables 2 and 3.

(21) A. Pozefsky and N. G. Coggeshall, *Anal. Chem.*, **23**, 1611 (1951).

once equilibrium between alcohol and styrene is attained, exchange has taken place. The lack of exchange of β-deuterium atoms in the forward reaction was first indicated spectrally. The intense principal band of styrene-β,β-d_2 is 0.5 mμ lower in position than that of normal styrene. During the hydration of the deuterium compound, manifest in a decline in the intensity of the principal band, the band retained its slightly lower wave length position during a goodly portion of the reaction. The conclusion that no deuterium exchange took place in the forward reaction was verified by actual isolation of styrene-β,β-d_2 after 15% reaction.

The absence of hydrogen exchange at the β-carbon atom in the forward hydration reaction shows that any species in which the β hydrogens are equivalent, *e.g.*, the carbonium ion, cannot be reversibly formed.[2-4] In other words, if the carbonium ion is an intermediate, nucleophilic attack by water on it is more rapid than abstraction of a β-deuteron. This is in agreement with Taft's results for simple aliphatic olefins,[3] and Deno's results for 2-phenylpropene.[4] It also is consistent with the observation of Grunwald, Heller, and Klein, who found that both O^{18} exchange and racemization of optically active 1-phenylethanol in perchloric acid is about 100-fold faster than dehydration to styrene.[22] In other words, in the dehydration an intermediate is formed which combines much more rapidly with water than it loses a proton. By the principle of microscopic reversibility, this same intermediate with the same properties is a stage in the hydration of styrene.[23]

It is of considerable interest to note that there is no detectable isotope effect in the forward reaction of hydration of styrene-β,β-d_2. The ratio of observed first-order rate constants for normal and β-deuterated styrene is 1.03 ± 0.03 in 43.4% perchloric acid at 25° and 1.01 ± 0.03 in 49.3% perchloric acid at 10°. Since the β-deuteriums are exchanged by the time complete equilibrium between alcohol and styrene is attained, the extent to which k_{dehydr} contributes to k_{obsd} for styrene-β,β-d_2 could not be measured. However, one may consider two extremes for the isotope effect on k_{dehydr}: $k^{D}_{\text{dehydr}} = k^{H}_{\text{dehydr}}$, and $k^{D}_{\text{dehydr}} = 0.4\ k^{H}_{\text{dehydr}}$.[24,25a] In the first instance $k^{H}_{\text{hydr}}/k^{D}_{\text{hydr}} = 1.03 \pm 0.03$ at 25° and 1.02 ± 0.03 at 10°. The second instance gives $k^{H}_{\text{hydr}}/k^{D}_{\text{hydr}} = 1.02 \pm 0.03$ at 25° and 1.01 ± 0.03 at 10°. The corrections are quite small in either case and it is clear that within experimental error there is no β-deuterium isotope effect on k_{hydr}.

The lack of a β-deuterium isotope effect in the hydration of PhCH=CD_2 contrasts with an appreciable β-deuterium isotope effect in a number of solvolysis reactions,[16-18] including a k_H/k_D of 1.22 for C_6H_5-$CHClCD_3$.[19] Insofar as the transition state for styrene hydration resembles that of the solvolysis, the difference between the isotope effects in the two cases is attributable to the ground states, the one having a trigonal β carbon and the other a tetrahedral one. The change in hybridization that occurs in proceeding from styrene to the highest energy transition state in the hydration process may resemble that occurring in the formation of the σ complex in aromatic substitution. Secondary isotope effects in the latter reaction also are absent or very small (see, *e.g.*, ref. 25b).

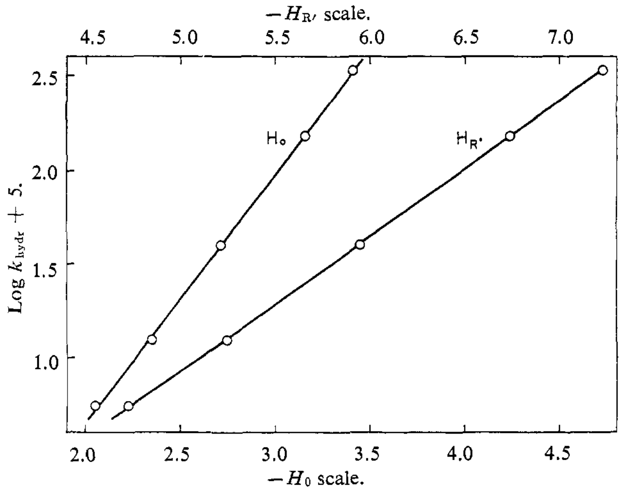

Figure 1. Plot of log k_{hydr} against $-H_0$ and against $-H_{R'}$.

The Acidity Dependence and Mechanism of the Hydration. A plot of log k_{hydr} at 25° against $-H_0$ is approximately linear. The line drawn in Figure 1 has a slope of 1.26. The linear plot of log k_{hydr} at 10° against $-H_0$ (at 25°) has a slope of 1.39. A plot of log k_{hydr} at 25° against $-H_{R'}$, the acidity function that had been applied to the reversible protonation of 1,1-diarylolefins,[26] is linear with slope 0.72 (Figure 1). In other words, the acidity dependence of the hydration rate lies roughly halfway between that of the equilibrium protonation of a primary aromatic amine and that of a 1,1-diarylolefin. The implication of this result is that the transition state is more weakly solvated (through hydrogen bonding to water) than a primary anilinium ion but more strongly solvated than a carbonium ion (*cf.* ref. 4, 27, and 28, and references therein). It is probably reasonable to conclude that the transition state possesses considerable carbonium ion character.

That the highest energy transition state corresponds to a step in which a carbonium ion is being produced also is supported by the lack of exchange of β-deuteriums in the hydration of PhCH=CD_2 and is consistent with the lack of an isotope effect in the hydration of PhCD=CH_2 and PhCH=CD_2. The simplest mechanism that can accommodate the known facts presented here is that of eq. 1.

It is of interest to note that the rate constant for styrene hydration has an appreciably steeper acidity dependence ($-$d log k_{hydr}/dH_0 = 1.26) than do the rate constants for hydration of simple aliphatic olefins ($-$d log k_{hydr}/dH_0 close to unity[3]). This would be perfectly consistent with the assumption that the transition state for hydration of styrene resembles that for the

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[22] E. Grunwald, A. Heller, and F. S. Klein, *J. Chem. Soc.*, 2604 (1957).

[23] It is assumed here that dehydration, O^{18} exchange, and racemization proceed *via* a common intermediate.

[24] These cases represent either no primary isotope effect or a "full" primary isotope effect of 10 for the abstraction of a hydrogen in the reverse reaction; see ref. 25a.

[25] L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York, N. Y., 1960: (a) p. 22; (b) p. 110.

[26] N. C. Deno, P. T. Groves, and G. Saines, *J. Am. Chem. Soc.*, **81**, 5790 (1959).

[27] W. M. Schubert and R. H. Quacchia, *ibid.*, **84**, 3778 (1962); *ibid.*, **85**, 1278 (1963).

[28] W. M. Schubert, H. Burkett, and A. L. Schy, *ibid.*, **86**, 2540 (1964).

hydration of an aliphatic olefin. It is reasonable to suppose that the positive charge in the transition state is better dispersed in the styrene than in the aliphatic olefin case. This would imply that, in any particular medium, the former transition state is less strongly solvated (by water) than the latter. Consequently, as mineral acid molarity is increased (*i.e.*, a_{H_2O} decreased) the free energy of solvation of the former transition state should suffer less of a decrease. This then would lead to the steeper acidity dependence of the rate constants for hydration of styrene.[27,28] It is assumed that the medium effects on the differences in the free energy of solvation of the nonspecifically solvated olefins are of no great consequence.

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The Acid Cleavage of Allylmercuric Iodide

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Abstract: The rate-determining step in allylmercuric iodide cleavage by aqueous acid is proton transfer to carbon. The reaction shows a primary kinetic isotope effect, $\varkappa_H/\varkappa_D$, of 7.3 (measured competitively at 35°) and an over-all solvent isotope effect of 3.1 at the same temperature. From these values the rate constant at intermediate deuterium concentrations can be successfully calculated with no additional parameters. The temperature coefficient of $\varkappa_H/\varkappa_D$ leads to a $\Delta S°$ of -2.9 ± 0.3 cal. mole^{-1} deg.$^{-1}$, which suggests a certain amount of tunneling. The reaction shows general acid catalysis by molecular acetic acid and by methyldi(2-cyanoethyl)ammonium ion. For catalysis by the latter ΔH^* is 15.0 ± 0.4 kcal. mole^{-1} and ΔS^* is -27.7 ± 0.8 cal. mole^{-1} deg.$^{-1}$. For hydronium ion the comparable values are 16.21 ± 0.07 kcal. mole^{-1} and -12.6 ± 0.2 cal. mole^{-1} deg.$^{-1}$. In the absence of added iodide ion the original reaction is followed by complicating side reactions but these can be eliminated, without altering the rate constants, by adding small concentrations of sodium iodide.

In previous papers[2-4] the mechanism by which aqueous, nonhalogen acid cleaves the carbon–mercury bond has been examined. The present paper extends this study to allylmercuric iodide. The reaction products have been determined both for allyl- and crotylmercuric iodide. The form of the rate law has been studied both in the presence and in the absence of small amounts of iodide ion. General acid catalysis has been observed. Isotope effects, k_H/k_D, have been observed both by direct kinetic measurement and by competition experiments. The thermodynamic properties of activation, ΔH^* and ΔS^*, have been evaluated for both hydronium ion and methydi(2-cyanoethyl)-ammonium ion acting as acids. It is concluded from these that proton transfer is rate determining. Subsequent papers will explore the details of transition state structure more fully.

Results

Products. When allylmercuric iodide was treated with aqueous perchloric acid, 0.5 mole of propene, identified by its infrared spectrum, was produced per mole of allylmercuric iodide; the amount of product gas was determined manometrically. If the reacting solution contained sufficient sodium iodide to provide 1 mole of iodide ion per mole of allylmercuric iodide, 1 mole of propene per mole of starting material, identified both by its infrared and mass spectra, was produced. The quantity was determined manometrically. When the reaction was carried out in highly deuterated solvent, in the presence of 1 equiv. of iodide, the hydrocarbon product was mostly monodeuteriopropene with *no* dideuteriopropene. This was determined mass spectroscopically, and the precision is such that a few tenths of 1% of dideuteriopropene would have been detected.

In the presence of the iodide ion, 1 mole of mercuric iodide per mole of starting material is produced, identified by its ultraviolet spectrum and melting point. If no iodide is added, the ultraviolet spectrum of the reacting solution changes sequentially from that of the starting material to that of some unknown intermediate to a spectrum corresponding roughly to that of 0.5 mole of mercuric iodide per mole of starting material. Figure 1 shows a series of such spectra.

The reactions shown in eq. 1–4 are consistent with

$$CH_2{=}CH{-}CH_2HgI + H^+ \longrightarrow CH_3CH{=}CH_2 + HgI^+ \quad (1)$$

$$CH_2{=}CH{-}CH_2{-}HgI + HgI^+ \rightleftharpoons HgI_2 + A^+ \quad (2)$$

$$I^- + HgI^+ \rightleftharpoons HgI_2 \quad (3)$$

$$A^+ + H^+ \longrightarrow \text{other products} \quad (4)$$

these observations and others that will be cited.

Attempts to determine the other products obtained in the absence of free iodide ion by means of vapor phase chromatography were unsuccessful. A number of low-intensity peaks were obtained, none of which could be positively identified. It was established that allyl alcohol was not among the products.

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