The Acid-Catalyzed Hydration of Styrenes

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Abstract: First-order rate constants for hydration of para substituted styrenes and equilibrium styrene: 1-phenylethanol ratios have been determined, covering a wide range of $HClO_4$ molarity. The solvent deuterium isotope effect on hydration also has been extensively investigated. General catalysis has been found for the hydration of p-methoxy-α-methylstyrene in dilute aqueous solution. Based on these results, coupled with earlier ones, the most probable rate-controlling step is simple proton transfer to the β carbon of the styrene, though rate-controlling rearrangement of a styrene–H_3O^+ complex to α-methylbenzyl cation cannot be excluded. A number of other mechanisms, including rearrangement of a styrene–proton complex, are inconsistent with observation. Medium and substituent effects on hydration rate constants and the solvent isotope effects indicate that proton transfer in the activated complex lies between "half-way" and far advanced.
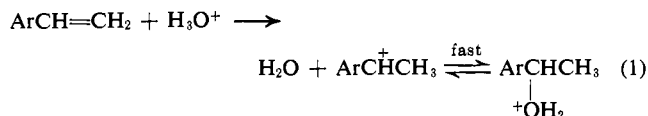
This paper deals with the influence of perchloric acid media, deuterioperchloric acid media, and para substituents on the reversible hydration of styrene.[1] The possibility of general acid catalysis also has been investigated with p-methoxy-α-methylstyrene. A preliminary report of this work has been published,[1a] as has prior work on styrene itself.[1b]

Most of the earlier mechanistic investigations of olefin hydration had been carried out by Lucas and by Taft, who used aliphatic olefins.[2,3] Largely on the basis of the acidity dependence of the hydrations, *i.e.* application of the Zucker–Hammett hypothesis, Taft first postulated that the rate-controlling step involved rearrangement of a π complex between alkene and H+, later suggesting that reaction *via* a complex between alkene and H_3O^+ also was possible.[3e] In recent years, it has been amply demonstrated by a number of workers, including Taft and the senior author of this paper, that the acidity dependence of an observed rate constant is an insufficient criterion of mechanism. In light of this, Professor Taft now feels that the available data on aliphatic olefins do not require rate-controlling π-complex rearrangement.[4]

In the preliminary report of the work described here in full,[1a] Schubert, Lamm, and Keeffe concluded that the activated complex of the rate-controlling step of the hydration of styrenes contained the elements of the styrene, a proton *and* a molecule of water, the most likely rate-controlling step being direct proton transfer to the β carbon of the styrene, eq 1. Direct proton transfer to carbon is favored by Deno, based on studies with α-methylstyrenes in sulfuric acid.[5]

Whalley has concluded that the transition states in the hydration of propylene and isobutylene contain a molecule of water, on the basis of the values of the

volumes of activation.[6] In a study of the hydration of isobutylene, Gold has found that direct proton transfer from lyonium ion, L_3O^+, satisfactorily accounts for the product ratios $(CH_3)_3COH/DCH_2C(CH_3)_2OH$ in various D_2O–H_2O mixtures, as related to the kinetic solvent isotope effect.[7]

$$ArCH=CH_2 + H_3O^+ \longrightarrow$$
$$H_2O + Ar\overset{+}{C}HCH_3 \overset{fast}{\rightleftharpoons} ArCHCH_3 \quad (1)$$
$$\underset{\overset{|}{+}OH_2}{}$$

Experimental Section[8]

Compounds. All of the styrenes used, except p-methoxy-α-methylstyrene, were obtained from commercial sources. The latter was prepared from p-methoxyacetophenone and methylmagnesium iodide, followed by dehydration of the carbinol with a little p-toluenesulfonic acid at 200°.

The 1-phenylethanols were prepared from the corresponding acetophenones by treatment with sodium borohydride in ethanol until a 2,4-dinitrophenylhydrazine test was negative or only faintly positive. It was established that the amount of acetophenone impurity necessary to just discernibly influence the spectrum of the alcohol also gave a strongly positive 2,4-dinitrophenylhydrazine test. Final purification of the styrenes and 1-phenylethanols was accomplished by fractional distillation at reduced pressure under nitrogen, except for p-nitrostyrene and p-methoxy-α-methylstyrene, which were recrystallized from methanol.

Reagents. All inorganic chemicals used were reagent grade. Perchloric acid solutions were prepared by suitable dilution of concentrated perchloric acid (Mallinckrodt), and were titrated against standard sodium hydroxide. A stock solution of deuterioperchloric acid (52% $DClO_4$) was prepared by slow simultaneous continuous addition of D_2O below the surface and distillation of water. The procedure was carried out in an all-glass, grease-free apparatus, and required several days to perform. Chlorine oxides were removed by entrainment with nitrogen. The stock solution contained at least 97.5% deuterium, by nmr analysis. More concentrated $DClO_4$ solutions were prepared by further distillation of D_2O from the stock solution (careful!). More dilute $DClO_4$ solutions were prepared by appropriate dilution with D_2O (99.7% D, General Dynamics Corporation). All $HClO_4$ and $DClO_4$ solutions were virtually transparent in the uv above 210 mμ.

Spectral Measurements. Ultraviolet spectra for styrene–alcohol equilibrium measurements, alcohol basicity measurements, and location of optimum wavelengths to carry out rate measurements were determined in 1- and 10-cm stoppered silica cells with a Cary Model 14 recording spectrophotometer.

(1) (a) W. M. Schubert, B. Lamm, and J. R. Keeffe, *J. Amer. Chem. Soc.*, **86**, 4727 (1964); (b) W. M. Schubert and B. Lamm, *ibid.*, **88**, 120 (1966); (c) W. M. Schubert and G. W. Barfknecht, *ibid.*, **92**, 207 (1970).

(2) H. J. Lucas and W. F. Ebertz, *ibid.*, **56**, 460 (1934); H. J. Lucas and Y-P. Liu, *ibid.*, **56**, 2138 (1934).

(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) R. W. Taft, Jr., private communication.

(5) N. C. Deno, A. Kish, and H. J. Peterson, *J. Amer. Chem. Soc.*, **87**, 2157 (1965).

(6) B. T. Baliga and E. Whalley, *Can. J. Chem.*, **42**, 1019 (1964).

(7) V. Gold and M. A. Kessick, *J. Chem. Soc.*, 6718 (1965).

(8) Experimental procedures and properties of the styrenes and carbinols are described in detail in the Ph.D. Thesis of J. R. Keeffe, University of Washington, 1964.

Table I. First-Order Hydration Rate Constants and Per Cent Styrene at Equilibrium[a]

Substituent	HClO₄, M	−H_0'[b]	a_{H_2O}[c]	−H_R'[d]	Equil % styrene[e]	$10^4 k_{hyd}$[f]
Para CH₃O, α-CH₃	0.102	−0.89	0.999	−0.89	6.3[g]	9.06 ± 0.02
Para CH₃O	0.102	−0.89	0.999	−0.89		0.089 ± 0.015
	1.26	0.47	0.939	1.27	2.6, 2.7	2.00 ± 0.02
	1.96	0.86	0.909	2.08		5.58 ± 0.06
	2.33	1.03	0.869	2.45	2.5, 2.2	9.34 ± 0.04
	2.71	1.20	0.846	2.83		15.7 ± 0.15
	3.11	1.38	0.819	3.22	3.1, 2.6	27.7 ± 0.2
	3.53	1.57	0.778	3.63	3.4, 3.1	48.8 ± 0.7
Para CH₃	3.53	1.57	0.778	3.63	2.1, 2.1	1.64 ± 0.01
	3.98	1.77	0.728	4.09	2.6, 2.8	3.26 ± 0.08
	4.46	2.02	0.670	4.60		6.54 ± 0.08
	5.12	2.38	0.584	5.29	2.3, 2.4	18.6 ± 0.15
	5.33	2.48	0.556	5.51		24.6 ± 0.4
	5.50	2.58	0.532	5.70	2.5, 2.5	35.8 ± 0.5
Para H[h]	4.57	2.08	0.656	4.73	2.3 ± 0.1[i]	0.553 ± 0.01
	5.08	2.36	0.589	5.25	2.3 ± 0.1	1.24 ± 0.02
	5.76	2.71	0.500	5.94	2.4 ± 0.1	3.95 ± 0.01
	6.44[j]	3.16	0.393	6.72	2.5 ± 0.2	15.2 ± 0.6[l]
	6.85[k]	3.41	0.332	7.22	2.5 ± 0.2	34.0 ± 0.1[l]
	7.40	3.78	0.267	7.93	2.6 ± 0.1	83.4 ± 0.3
Para Cl	4.59	2.09	0.653	4.74	2.6, 2.4	0.195 ± 0.001
	5.51	2.58	0.529	5.71	2.7, 2.9	0.880 ± 0.002
	6.56	3.23	0.382	6.85	2.8	5.58 ± 0.04
	6.93	3.45	0.328	7.33	2.5, 2.6	11.4 ± 0.04
	7.40	3.78	0.267	7.93		28.8 ± 0.15
Para NO₂	8.96	5.08	0.108	9.87		0.464 ± 0.01
	9.90	6.01	m	m	9.9, 10.5[n]	3.86 ± 0.01
	10.2	6.34				8.35 ± 0.03
	10.5	6.66				18.4 ± 0.1[l]
	10.9	7.07				44.5 ± 0.04
	11.3	7.37				77.1 ± 2.4
Para NO₂ at 50°[p]	6.93	3.45	0.328	7.33	7.8, 7.9	0.148[o]
	7.63	3.95	0.238	8.21	9.1, 9.1	0.574 ± 0.003
	8.13	4.36	0.182	8.81		1.63 ± 0.001
	8.59[p]	4.78	0.138	9.40	10.3, 10.7	3.82 ± 0.07
	9.05[p]	5.11	0.105	9.94	10.4, 9.8	8.49 ± 0.03
	9.37[p]	5.51	0.079	m	10.6, 10.4[q]	19.4 ± 0.1

[a] Values at 25° unless noted. [b] Values of ref 12. [c] Values of R. A. Robinson and O. J. Baker, *Trans. Roy. Soc. N. Z.*, **76**, 250 (1946). [d] Calculated using H_R' = H_R − log a_{H_2O};[13a] H_R data of ref 13b. [e] Mole per cent styrene at equilibrium. [f] In sec⁻¹; average of at least three runs, except where noted; average deviation given. [g] Value of ref 5. [h] Values of ref 1b, except in highest molarities. [i] Maximum deviations from average, four determinations. [j] $\Delta H^{\ddagger}$ = 19.9 ± 5 kcal, $\Delta S^{\ddagger}$ = −5 ± 2 eu.[1b] [k] $\Delta H^{\ddagger}$ = 19.2 ± 0.5 kcal, $\Delta S^{\ddagger}$ = −5 ± 2 eu.[1b] [l] Two runs only. [m] Values not known in higher molarities. [n] Value at 40°. [o] One determination. [p] Activation parameters (data at 40, 50, 60°): 8.59 M, $\Delta H^{\ddagger}$ = 23.2 ± 0.8, $\Delta S^{\ddagger}$ = −2.8 ± 2.4; 9.05 M, $\Delta H^{\ddagger}$ = 21.8 ± 0.7, $\Delta S^{\ddagger}$ = −5.5 ± 2.1; 9.37 M, $\Delta H^{\ddagger}$ = 20.7 ± 1.2, $\Delta S^{\ddagger}$ = −7.3 ± 3.6. [q] Value at 40° is 10.3; at 60°, 10.4.

Kinetic Measurements. The previously described ultraviolet spectrophotometric method was used.[1a] To avoid polymerization of the styrene during its introduction into the solution, the vapor injection method[1a] was used except for *p*-nitrostyrene and *p*-methoxy-α-methylstyrene, which were too involatile.[9] The latter styrenes did not polymerize when introduced in liquid form.

Results

The acid-catalyzed hydration of the styrenes, or dehydration of the corresponding carbinols, produced an equilibrium mixture of styrene and alcohol containing a small percentage of styrene. Both first-order rate constants for reversible hydration (k_{obsd} = k_{hyd} + k_{dehyd}) and equilibrium ratios, [styrene]$_e$/[alcohol]$_e$ = k_{dehyd}/k_{hyd}, were determined.

Rate Constants. First-order rate constants were determined by following the change in ultraviolet absorbance of solutions of the styrene (approximately

(9) During introduction of a liquid sample, the local concentration of styrene is often sufficiently great to bring about polymerization. Styrene polymerization in these solutions evidently depends on a higher power of the styrene concentration than does hydration. Thus, polymerization becomes a problem with some of the styrenes when the concentration of styrene is greater than 10⁻³ M, but is indetectable at the concentration used for rate and equilibrium measurements (5 × 10⁻⁵ M and less).

5 × 10⁻⁵ M) in 1-cm stoppered silica cells at wavelengths at or near λ_max of the styrene. The initial absorbance was generally around 0.6 and the final readings were near zero. First-order plots of log (A − A_∞) against time were linear for at least two to three half-lives. Values of the first-order rate constants, k_{obsd}, were extracted from the visual slopes of the first-order plots and generally were reproducible to ±1%.

Styrene-Alcohol Equilibria. The ratio of stoichiometric alcohol to styrene at equilibrium was determined by application of eq 2 at three wavelengths, corresponding to maximum absorption by styrene, and a relatively flat region of absorption by alcohol. In this equation, ϵ_S and ϵ_A represent molar absorptivities of pure styrene and alcohol, respectively, and ϵ_∞ is the absorption at equilibrium per stoichiometric mole of substrate.

Since solutions of accurately known molarity of styrene could not be prepared by the vapor injection method required for dissolving most of the styrenes,[1a,9] the equilibrium was approached from the alcohol side.[9] Also, 10-cm cells were usually used. In the case of *p*-
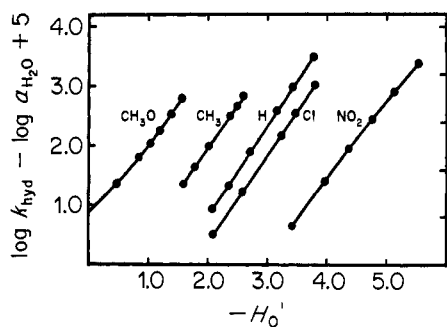
Figure 1. Plots of $\log k_{hyd} - \log a_{H_2O}$ against $-H_0'$.

Figure 2. Plots of $\log k_{hyd} - \log a_{H_2O}$ against $-H_R' = -H_R + \log a_{H_2O}$.

nitrostyrene, relative inertness to polymerization allowed the equilibrium also to be approached from the styrene side. The same observed equilibrium mixture was obtained as from the alcohol side.

$$\frac{k_{hyd}}{k_{dehyd}} = \frac{[A]_e}{[S]_e} = \frac{\epsilon_S - \epsilon_\infty}{\epsilon_\infty - \epsilon_A} \qquad (2)$$

Values of mole per cent styrene at equilibrium are listed in Table I. Except for p-nitrostyrene at 50°, there is no experimentally significant variation in the equilibrium percentage with perchloric acid molarity, and the average value for the acid range was used in calculating values of k_{hyd}. The inherent *percentage* error in determining $[A]_e/[S]_e$ is fairly large due to the small fraction of styrene at equilibrium. However, this introduces only a fraction of a per cent error in k_{hyd}, but gives a large uncertainty to k_{dehyd}.

Equilibrium values were not determined in $DClO_4$ solutions, due to the fact that the measurements require large volumes of solution and the tediously prepared $DClO_4$ was in short supply. However, from a comparison of initial and final absorbancies at one wavelength, obtained in hydration rate studies in $HClO_4$ and $DClO_4$, it can be concluded that the per cent styrene at equilibrium is much the same in $DClO_4$ as in $HClO_4$ solutions. Furthermore, in an independent study on p-dimethylaminostyrene, Jensen has found little solvent isotope effect on the equilibrium styrene percentage (about 10%) in 0.01–2.8 M perchloric acid.[10] In any event, since k_{dehyd} contributes little to the sum $k_{obsd} = k_{hyd} + k_{dehyd}$, the k_{hyd} values are insensitive to small solvent isotope effects on the equilibrium.

Discussion

In what follows it will be shown that all the available facts concerning the styrene-1-phenylethanol system are consistent with the rate-controlling step of hydration being simple β carbon protonation of the styrene. Rate-controlling rearrangement of a styrene-H_3O^+ complex to α-methylbenzyl cation cannot be excluded. Other conceivable mechanisms will be found wanting. A conclusion as to the qualitative degree of proton transfer in the activated complex will be made, and medium effects on k_{hyd} will be discussed briefly.

The restrictions and requirements placed on the mechanism are as follows. (1) The activated complex of the rate-controlling step contains a proton. This is inferred from the acidity dependencies of the k_{hyd}

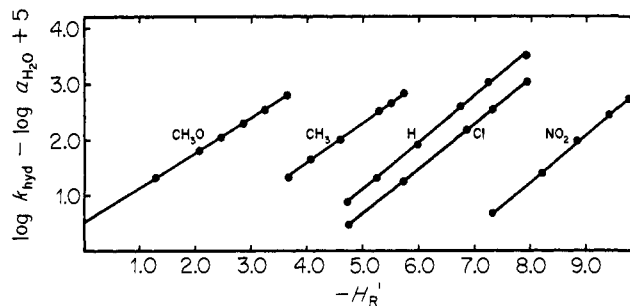(10) J. L. Jensen, Ph.D. Thesis, University of Washington, 1967.

values. (2) The activated complex also contains a base, inferred from general catalysis results. (3) A proton, one originally in the medium, is undergoing covalency change in the activated complex (primary isotope effect). (4) The activated complex develops substantial positive character in conjugation with the aromatic moiety, inferred from para substituent effects. (5) A symmetrical intermediate, *i.e.* one capable of equivalence of three hydrogens on the β carbon, is formed *after* the transition state of the rate-controlling step of hydration. This conclusion is based on experiments with styrene-β,β-d_2 and work of Grunwald, *et al.*, on the relative rates of dehydration, racemization, and oxygen change on 1-phenylethanol.[11] (6) Specific hydrogen-bonding solvation of the activated complex is probably weak, according to the steepness of the acidity dependence of k_{hyd} values.

Composition of Activated Complex. Hydration rates increase steeply with acidity of the medium. Because of the widely different reactivities of the styrenes used, the k_{hyd} values of Table I were perforce obtained over a different range of perchloric acid strength for each styrene, although the ranges overlap somewhat. The usual acidity dependence plots were made. Plots of $\log k_{hyd}$ against $-H_0'$, the acidity function based on primary aromatic amine indicators,[12] were approximately linear. Depending on the substituent, slopes ranged from 1.1 to 1.3. Plots of $\log k_{hyd}$ against $-H_R'$, the acidity function based on 1,1-diarylolefin indicators,[13] showed better linearity, with slopes 0.59–0.68. Still better, but with no clear-cut choice, were plots of $\log k_{hyd} - \log a_{H_2O}$ against $-H_0'$ and $-H_R'$ (Figures 1 and 2), based on the assumption of a molecule of water in the transition state. The slopes of the latter plots are listed in Table II.

No more can be deduced from the appearance of these plots than that the activated complex of the rate-controlling step contains one more proton than the styrene. Whether or not it also contains a molecule of water (Zucker–Hammett hypothesis) cannot be deduced. This was first demonstrated in the proteodeformylation of 2,4,6-trimethylbenzaldehyde, which obeys the Hammett criterion for a unimolecular mechanism ($SH^+ \rightarrow$ products), yet was shown by necessarily indirect means to be general acid catalyzed in very strong sul-

(11) E. Grunwald, A. Heller, and F. S. Klein, *J. Chem. Soc.*, 2604 (1957).
(12) K. Yates and H. Wai, *J. Amer. Chem. Soc.*, **86**, 5408 (1964).
(13) (a) N. C. Deno, P. T. Groves, and G. Saines, *ibid.*, **81**, 5790 (1959); (b) N. C. Deno, W. L. Evans, and H. J. Peterson, *ibid.*, **81**, 2344 (1959).

Table II. Acidity Dependence of log k_{hyd} — log $a_{\text{H}_2\text{O}}$ and Solvent Isotope Effects at 25° [a]

Styrene	H_0' slope[b]	H_R' slope[c]	M, acid	$k_{\text{H}_3\text{O}^+}/k_{\text{D}_3\text{O}^+}$[d]
Para CH₃O, α-CH₃			0.102	2.23
Para CH₃O	1.42[e]	0.62	3.84	1.93
Para CH₃	1.48	0.70	4.53	2.43
			4.96	2.31
			5.48	2.24
Para H	1.56	0.82	4.91	2.27
			6.79	3.33
			7.32	3.29
Para Cl	1.51	0.80	4.86	2.29
			6.79	3.38
			7.84	4.00
Para NO₂	1.46–1.27[f]	0.86	8.99	1.95
			10.73	2.21

[a] All values at 25° except where noted. [b] Slopes of plots of Figure 1. [c] Slopes of plots of Figure 2. [d] Ratio of hydration rate constants in HClO₄ and DClO₄ of same molarity, $k_{\text{H}_3\text{O}^+}$ interpolated. [e] Slope from 1.96 to 3.53 M HClO₄ only. [f] Initial and final slopes of curved plot, rate constants at 50°.

furic acid, *i.e.* proceeds by the scheme

$$S + HA_i \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{0pt}{0pt}}} SH^+ \xrightarrow{A_i} \text{products}$$
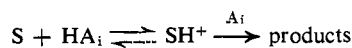
where A_i can be bisulfate ion as well as water.[14] A number of groups have since shown that specific medium effects (as yet not fully systemized) on such activity coefficient ratios as $f_B f_{B'H^+}/f_{BH^+}f_{B'}$[15,16] and f_{SH^+}/f_{tr^+}[17] preclude the use of the dependence of a rate constant upon mineral acid percentage as a sole criterion of detailed mechanism.

The time-honored and unequivocal approach of making rate measurements in dilute aqueous buffer solutions was used in order to establish whether or not the activated complex of the rate-controlling step of hydration also contains a base, as well as a proton.[18] This required the use of a more reactive styrene, *p*-methoxy-α-methylstyrene. At 50°, in formic acid buffer solutions of low and constant ionic strength, the reversible hydration of this styrene was found to be general acid catalyzed (Table III), with $k_{\text{obsd}}^{50°} =$

Table III. Hydration of *p*-Methoxy-α-methylstyrene in Formic Acid Buffer at 50°[a,b]

[HCO₂H], M	[HCO₂Na], M	[NaClO₄], M	$10^5 k_{\text{obsd}}$, sec⁻¹ [c]
0.0200	0.0100	0.0900	6.03 ± 0.04
0.0600	0.0300	0.0700	7.42 ± 0.04
0.1000	0.0500	0.0500	8.24 ± 0.08
0.1400	0.0700	0.0300	9.65 ± 0.07

[a] $[\text{H}_3\text{O}^+] = 3.50 \times 10^{-4} M$, $K_{\text{HA}} = 1.748 \times 10^{-4}$, at 50°, $\mu = 0.1$, from ref 33. [b] $k_{\text{H}_3\text{O}^+} = 1.55 \times 10^{-1}$ l. mol⁻¹ sec⁻¹; $k_{\text{HCO}_2\text{H}} = 3.00 \times 10^{-4}$ l. mol⁻¹.[19] [c] Triplicate runs, average deviation given.

$0.155[\text{H}_3\text{O}^+] + 3.00 \times 10^{-4}[\text{HCO}_2\text{H}]$.[19] General catalysis also has been observed in the hydration of *p*- and *m*-aminostyrenes.[20] By inference the activated complexes in the hydrations of other styrenes also must contain a base. This is supported by the fact that the solvent isotope effects in the hydration of the other styrenes are similar to those of *p*-methoxy-α-methylstyrene.

Proton in Transit. The solvent deuterium isotope effects, $k_{\text{H}_3\text{O}^+}/k_{\text{D}_3\text{O}^+}$, range in value from 2 to 4, depending on the specific styrene and the perchloric acid molarity (Table II). The effect is large enough to indicate that a proton is in transit (primary effect) in the transition state of the rate-controlling step. Values within the range observed have been shown by a variety of reactions to which rate-controlling carbon protonations have been assigned.[21,22] These include aromatic deformylation,[14] aromatic deboronation,[23] aromatic hydrogen exchange,[24] acid cleavage of allylmercuric iodide,[25] the hydrolysis of vinyl ethers,[26] the isomerization of *cis*-stilbene,[27] and the hydration of phenylacetylene.[28]

Para Substituent Effects on k_{hyd}. The substituent effect on k_{hyd} is considerable, as indicated by the large increase in mineral acid molarity that is required to get comparable rates as one proceeds from the para CH₃O to para NO₂ compound. Because of this wide variation in reactivity of the styrenes, k_{hyd} values could not be directly determined at a common acidity for all. However, by extrapolation of the plots of log k_{hyd} — log $a_{\text{H}_2\text{O}}$ against H_0' (Figure 1), values at a common acidity, 3.53 M HClO₄, were calculated (Table IV).

Table IV. Values of k_{hyd} in 3.53 M HClO₄ at 25°[a]

Styrene	$k_{\text{hyd}} \times 10^8$, sec⁻¹	σ[b]	σ^+[b]
Para CH₃O	488,000	−0.268	−0.788
Para CH₃	16,400	−0.170	−0.311
Para H[a]	811	0	0
Para Cl[a]	318	0.227	0.114
Para NO₂[a]	1.44	0.778	0.790

[a] Values for H, Cl, and NO₂ extrapolated from plots of log k_{hyd} — log $a_{\text{H}_2\text{O}}$ against H_0'. [b] Values of ref 29.

Plots against Hammett σ values and Brown–Okamoto σ^+ values are shown in Figure 3.[29] It is seen that

(14) W. M. Schubert and R. E. Zahler, *J. Amer. Chem. Soc.*, **76**, 1 (1954); W. M. Schubert and H. Burkett, *ibid.*, **78**, 64 (1956); W. M. Schubert and P. C. Myhre, *ibid.*, **80**, 1755 (1958).

(15) R. W. Taft, Jr., *ibid.*, **82**, 2965 (1960).

(16) See, *e.g.*, W. M. Schubert and R. H. Quacchio, *ibid.*, **85**, 1284 (1963), and references cited therein.

(17) W. M. Schubert, H. Burkett, and A. L. Schy, *ibid.*, **86**, 2520 (1964).

(18) R. P. Bell, "Acid-Base Catalysis," Oxford University Press, London, England, 1949, Chapter IV.

(19) Due to an error in computation, the values of $k_{\text{H}_3\text{O}^+}$ and $k_{\text{HCO}_2\text{H}}$ given in ref 1a are in error; the data reported therein, those of Table III here, are not.

(20) W. M. Schubert and J. L. Jensen, *J. Amer. Chem. Soc.*, **94**, 566 (1972).

(21) C. A. Bunton and V. J. Shiner, Jr., *ibid.*, **83**, 42, 3207, 3214 (1961).

(22) C. G. Swain and E. R. Thornton, *ibid.*, **83**, 3884 (1961).

(23) H. G. Kuivala and K. Nahabedian, *ibid.*, **83**, 2159 (1961).

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the correlation is much better with σ^+ values, which were specifically based on reactions leading to benzylic cations. The slope, ρ^+, is -3.58.[30] A similar ρ^+, -3.21, was obtained by Deno for the hydration of α-methylstyrenes.[5] The substantial magnitude of ρ^+ and the better correlation with σ^+ than with σ indicate that considerable positive character in conjugation with the aromatic moiety has developed in the transition state of the rate-controlling step.

The Symmetrical Intermediate. In earlier work, styrene-β,β-d_2 in 43.4% $HClO_4$ was recovered isotopically unchanged at the time of 15% conversion to carbinol.[1b] This shows that equivalence of the β hydrogens with the proton being introduced cannot occur *prior* to the rate-controlling step of hydration. In other words, if a symmetrical intermediate such as the α-methylbenzylic cation is formed, it cannot be reversibly formed in the forward hydration process.

Similar results have been obtained by Deno, who found that 2-phenylpropene in 17% D_2SO_4-C_2H_5OD was isotopically unchanged after 24% reaction.[5] Hydration of aliphatic olefins also proceeds without β hydrogen exchange.[3c,7,31] In the hydration of styrene-β,β-d_2, significant exchange was observed near the end of the conversion to the styrene–carbinol equilibrium mixture,[1b] *i.e.*, exchange late in the process was due to the overall reverse reaction of 1-phenylethanol dehydration, which attains an appreciable velocity when the styrene to carbinol ratio approaches equilibrium. With aliphatic olefins such as isobutylene no exchange has occurred even at essentially complete conversion to alcohol because k_{dehyd} is negligibly small relative to k_{hyd}.

The finding of no β hydrogen exchange in the forward hydration of styrene complements observations of Grunwald, *et al.*, on the dehydration of 1-phenylethanol.[11] They found that the rate of acid-catalyzed dehydration is about 1/100th the rate of racemization of the optically active alcohol. Furthermore, they concluded that the reaction coordinate for racemization lies on the reaction coordinate for dehydration. In other words, a symmetrical intermediate is reversibly formed prior to the rate-controlling step of dehydration. By the principle of microscopic reversibility that same symmetrical intermediate must be formed *after* the transition state of the rate-controlling step of hydration of styrene. Similar results and conclusions are given for the 2-phenyl-2-butanol system by Deno.[5]

The "symmetrical intermediate" that lies between the transition state of the rate-controlling step and the conjugate acid of 1-phenylethanol must be either directly nondissymmetric or capable of racemization prior to conversion to either styrene or 1-phenylethanol. By the same token it either has three equivalent β hydrogens or has the facility and time for equivalence of three hydrogens to occur. Grunwald, *et al.*, assigned it the structure of a symmetrically solvated α-methylbenzylic cation. Since the rate of ^{18}O exchange on 1-phenylethanol is slightly less than the rate of racemization ($k_{exch}/k_{rac} = 0.82$), the water molecules formed from protonated carbinol have not been completely displaced by solvent water and diffused away before return to $PhCH(CH_3)OH_2^+$.[11]

(30) The earlier reported value, $\rho^+ = -3.42$,[1a] did not include a point for p-nitrostyrene.

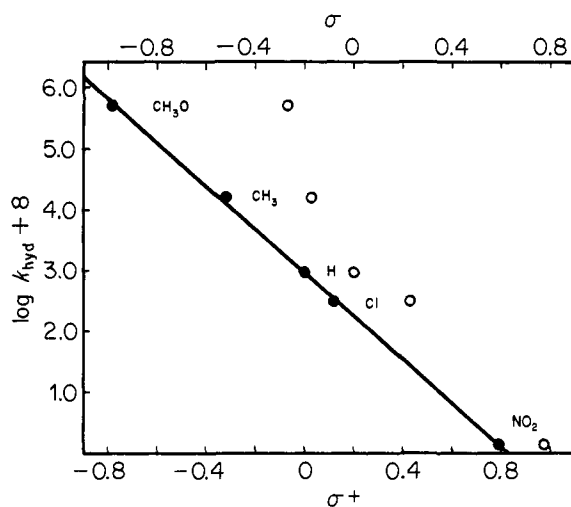(31) J. B. Levy, R. W. Taft, Jr., and L. P. Hammett, *J. Amer. Chem. Soc.*, 75, 1253 (1953).

Figure 3. Plot of log k_{hyd} against σ^+, closed circles, lower abscissas; against σ, open circles, upper abscissas.

The Mechanism. All the restrictions and requirements elaborated upon above are most simply fulfilled by a hydration mechanism of rate-controlling direct proton transfer to the β carbon of the styrene, eq 3. It is reasonable to assume that the necessary "symmetrical intermediate" is formed in this step and that it has the structure of a symmetrically solvated benzylic cation. Variations in which proton transfer occurs through intervening water molecules, *e.g.*

$$ArCH{=}CH_2 \; + \; H{-}OH \; + \; H{-}\overset{+}{O}H_2 \; \longrightarrow$$

$$\overset{+}{ArCHCH_3} \; + \; 2H_2O$$
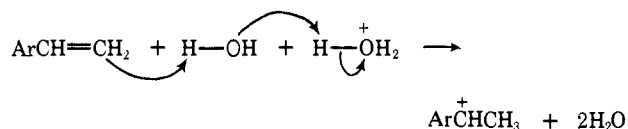
are not excluded, though not required.

A number of other *a priori* conceivable mechanisms can be excluded. Ruled out by the requirement that there be a symmetrical intermediate are mechanisms of synchronous protonation at β carbon and nucleophilic bonding of oxygen at α carbon, such as the cyclic process depicted in eq 5 or the termolecular process depicted in eq 6. Excluded on similar grounds is attack of hydronium ion on a styrene–water complex to give protonated alcohol, as in eq 7 (second step would have to be rate controlling to fulfill the composition requirements of the activated complex).

Consider next the possibility of a complex between styrene and a proton as an intermediate along the reaction coordinate as postulated by Taft in his early work on aliphatic olefin hydration. Rate-controlling formation of such a complex, as in the first step of eq 8, appears to be inconsistent with the ρ^+ correlation and the size of ρ^+. Rate-controlling rearrangement of the complex, as in the second step of eq 8, is ruled out by the requirement that the activated complex also contain a base. This requirement would be met by rate-controlling attack of water on the styrene–proton complex. However, such a step cannot directly be giving protonated carbinol, as in eq 9, since a symmetrical intermediate must lie between the transition state and protonated carbinol. On the other hand, it would be curious and illogical to have water attack on a styrene–proton complex to yield benzylic cation, as in eq 10, *i.e.*, can one have essentially the same water molecule,

Assigned mechanism

$$ArCH{=}CH_2 \ + \ H_3O^+ \ \xrightarrow{k_1}$$

$$\longrightarrow \ Ar\overset{+}{C}HCH_3 \quad (3)$$
$$HOH$$

Still possible

$$\longrightarrow \ Ar\overset{+}{C}HCH_3 \ + \ H_2O \quad (4)$$

Mechanisms ruled out

$$(5)$$

$$(6)$$

$$ArCH{=}CH_2 \ + \ H_2O \ \rightleftharpoons \ ArCH{=}CH_2{\cdot}H_2O \ \xrightarrow{H_3O^+}$$

$$ArCHCH_3 \ + \ H_2O \quad (7)$$
$$\underset{+OH_2}{|}$$

$$ArCH{=}CH_2 \ \underset{(\longleftarrow)}{\xrightarrow{H_3O^+}} \ \left[ArCH{=}CH_2 \atop | \atop H \right]^+ \ \longrightarrow \ Ar\overset{+}{C}HCH_3 \quad (8)$$

$$H_2O \ + \ \left[ArCH{=}CH_2 \atop | \atop H \right]^+ \ \longrightarrow \ ArCHCH_3 \quad (9)$$
$$\underset{+OH_2}{|}$$

$$H_2O \ + \ \left[ArCH{=}CH_2 \atop | \atop H \right]^+ \ \longrightarrow \ Ar\overset{+}{C}HCH_3 \ + \ H_2O \quad (10)$$

$$ArCH{=}CH_2 \ + \ H_3O^+ \ \longrightarrow \ \left[\text{complex} \right]^+ \quad (11)$$

$$\longrightarrow \ ArCHCH_3 \quad (12)$$
$$\underset{+OH_2}{|}$$

with at least the same oxygen in common, as both the reactant and product of a single step?

Consider lastly the possibility of a complex between styrene and hydronium ion as a possible intermediate along the reaction coordinate. Either its rate-control-

ling formation or decomposition would fulfill the compositional restrictions on the activated complex. Rate-controlling formation of a styrene-H_3O^+ complex, as in eq 11, appears to be inconsistent with the ρ^+ results. Furthermore, one would expect the changes in zero-point energies of the O–H bonds to be quite small, from ground state to transition state, and hence incompatible with the observed solvent isotope effects. Also, one would expect only relatively small difference in the free energy of specific hydrogen-bonding solvation of ground state (H_3O^+ + ArCH=CH_2) and transition state, and this is inconsistent with the steepness of the medium dependence of k_{hyd} (see discussion below). What about rate-controlling *decomposition* of the styrene-H_3O^+ complex? Direct rate-controlling rearrangement to protonated carbinol as in eq 12 violates the requirement that there be a symmetrical intermediate *after* the transition state of the rate-controlling step of hydration. However, rate-controlling conversion of the styrene-H_3O^+ complex to the required symmetrical intermediate, as in eq 4, could fulfill all the restrictions and requirements that have evolved from the data, although the overall process would appear to be somewhat redundant. The reaction coordinate for the multistep overall process would differ from that of direct proton transfer to β carbon only by an experimentally indetectable dip between styrene and rate-controlling transition state.

In summary, direct rate-controlling proton transfer to the β carbon of the styrene is logically and most simply in agreement with all the numerous observations. The complication of a reversibly formed styrene-H_3O^+ complex lying between the styrene and the symmetrical intermediate is allowed, but not required. Of the remaining mechanisms considered, most stand in direct violation of observation and the remainder have reasonable objections.

Degree of Proton Transfer. Having a bearing on the question of the degree of proton transfer in the activated complex of the assigned mechanism of hydration, eq 3, are four different kinds of data: (1) a tentative Brønsted α value for the hydration of p-methoxy-α-methylstyrene, (2) the magnitude of the reaction constant, ρ^+, (3) the magnitude of the solvent isotope effect, and (4) the acidity dependence of k_{hyd}. All these data are consistent with a degree of proton transfer that is more than "half-way" but not as far advanced as in the hydration of aliphatic alkenes.

The value of $\rho^+ = -3.58$ for hydration of the styrenes is consistent with an activated complex that is well on the way toward the benzylic cation. Its magnitude is perhaps a large fraction of that of the ρ^+ that would prevail for complete formation of benzylic cation. For example, in the equilibrium formation of cation in the protonation of substituted 1,1-diphenylpropenes, Deno has obtained a ρ^+ value of -4.0 per aryl ring.[13]

The size of the solvent isotope effects for styrene hydration, Table II, indicates an activated complex in which proton transfer lies neither at the far-advanced nor slightly advanced stage. That is, isotope effects on proton transfer rates are expected to be very small, or even inverse, when the activated complex lies at the extremes and should reach a maximum at "half-transfer."[22,32] The maximum possible solvent isotope

effect for proton transfer from hydronium ion to carbon is not expected to be very large (perhaps around 3.6 in dilute acid[21]) because of inverse secondary effects that accompany the conversion of two of the protons of hydronium ion to those of the developing water molecule of the activated complex.[7,21,22,24,25]

The solvent isotope effect in the hydration of isobutylene in 0.44 M HClO$_4$ vs. DClO$_4$ is only 1.45.[7] This is substantially smaller than the value obtained for p-methoxy-α-methylstyrene under comparable conditions, as well as the values obtained for the other styrenes in more concentrated acid. The small isotope effect for isobutylene hydration indicates an activated complex in which proton transfer is either relatively far or slightly advanced, the former being a priori more likely. Gold has given evidence on this point. Based on his theoretical treatment of the rates of slow proton transfers in H$_2$O–D$_2$O mixtures, and the variation in the kinetic solvent isotope effect and product isotope effects [(CH$_3$)$_3$COH vs. DCH$_2$C(CH$_3$)$_2$OH] in such mixtures, Gold extracted a value for the Brønsted α of 0.85 ± 0.10. Values of α near the upper limit of unity are associated with an advanced degree of proton transfer in the activated complex of proton transfer reactions (see, e.g., ref 18, Chapter VIII).[7]

The larger solvent isotope effect for the styrenes thus implies then that proton transfer in the activated complex is less advanced than for isobutylene. This is in agreement with the Bell–Leffler–Hammond principle, i.e., the more the product of the proton-transfer step is stabilized relative to the initial state (by p-XC$_6$H$_4$ vs. CH$_3$), the more the activated complex should resemble the initial state. By the same token it would appear more likely that proton transfer in the activated complex of styrene hydration lies between "half-way" and the far-advanced stage, rather than before "half-way."

For the hydration of p-methoxy-α-methylstyrene a Brønsted α value can be calculated from the observed values of the catalytic constants $k_{H_3O^+}$ and k_{HCO_2H} (Table III) and the acidity constants: $K_{HCO_2H} = 1.748 \times 10^{-4}$ [33] and, for want of a better value, $K_{H_3O^+} = 55.5$.[18] The α value thus obtained, 0.49,[34] is of course highly tentative since it is based on only two points, one of which is notoriously misbehaved in other systems, i.e., the point for hydronium ion.[18] For other systems, the point for hydronium ion in Brønsted plots of log k_{HA_i} against log K_{HA_i} lies significantly below the line defined by a large number of other catalyzing acids (i.e., $k_{H_3O^+}$ "too small" and/or $K_{H_3O^+}$ "too large"). More particularly, the α value for carbon protonation of p-aminostyrene is 0.74 as determined by acetic acid and chloroacetic acid, and the point for hydronium also lies significantly below the "line."[20] Thus, the true α value is probably greater than 0.49, and hence consistent with proton transfer in the activated complex lying more than "half-way."

As regards the influence of mineral acid molarity on the solvent isotope effect, there is a pronounced tendency, especially in the middle range of acid molarities, for $k_{H_3O^+}/k_{D_3O^+}$ to increase with acid molarity (Table

II). One is tempted to attribute this to a shift in the degree of proton transfer in the activated complex toward "midstage" with increasing potential energy of the lyonium ion. On the other hand, the results could be due to medium effects producing variations in the terms other than k_1^H/k_1^D in the ratio $k_{H_3O^+}/k_{D_3O^+}$ = $(k_1^H/k_1^D)(a_{H_3O^+}/a_{D_3O^+})(f_S^H f_{\pm}^D/f_S^D f_{\pm}^H)$. However, ratios of the latter type have been found constant in H$_2$SO$_4$–D$_2$SO$_4$ solutions. Thus, Högfeldt and Bigeleisen have reported that the acidity function D_0 of deuteriosulfuric acid, as determined by Hammett indicator bases, runs parallel to H_0 of sulfuric acid over the range 1–12 M acid.[35] It remains to be determined whether such a parallelism pertains to HClO$_4$–DClO$_4$ solutions. Stoichiometric L$_2$O and LClO$_4$ molarities are practically the same for HClO$_4$ and DClO$_4$ over a wide range.[36]

Substituent effects on $k_{H_3O^+}/k_{D_3O^+}$ are obscured by the above noted effect of mineral acid molarity, since the differing reactivity of the styrenes precluded determination of these ratios over a common mineral acid range for all. However, at a nearly common acid molarity, $k_{H_3O^+}/k_{D_3O^+}$ values for the para CH$_3$ (2.31 in 4.96 M acid), the para H (2.27 in 4.91 M acid), and the para Cl compounds (2.29 in 4.86 M acid) are virtually the same.

The Acidity Dependence of k_{hyd}. Based on the mechanistic assignment of eq 3, the formal relationship between observed first-order rate constants and H_0', the acidity function based on primary aniline indicators,[12] is given by eq 13. In this equation, k_1 is the medium-independent second-order rate constant and f_S, $f_{\pm}$, f_B, and f_{BH^+} represent, respectively, activity coefficients of styrene, activated complex, aniline indicator, and indicator conjugate acid. Equation 14 is the corresponding relationship between log k_{hyd} and $H_{R'}$, which has been defined as the acidity function for equilibrium protonation of 1,1-diarylolefins.[13] Since the values of $H_{R'}$ are obtained from values of H_R (eq 15), the function for the complex ionization of triarylcarbinols,[13,37] the activity coefficients of triarylcarbonium ion and triarylcarbinol, f_{R^+} and f_{ROH}, are retained in eq 14.[37b]

$$\log k_{hyd} - \log a_{H_2O} =$$
$$\log k_1 - H_0' + \log (f_S f_{BH'^+}/f_{\pm} f_{B'}) \quad (13)$$

$$\log k_{hyd} - \log a_{H_2O} = \log k_1 -$$
$$H_{R'} + \log (f_S f_{R^+}/f_{\pm} f_{ROH}) \quad (14)$$

$$H_{R'} = H_R - \log a_{H_2O} \quad (15)$$

The slopes of the fairly linear plots of log k_{hyd} – log a_{H_2O} against $-H_0'$, Figure 1, are all considerably greater than unity. Those against $-H_{R'} = H_R - \log a_{H_2O}$, Figure 2, are all less than unity (slopes are listed in Table II). In other words, the behavior of $f_S/f_{\pm}$ with changing perchloric acid medium lies between the behavior $f_{B'}/f_{BH'^+}$ and f_{ROH}/f_{R^+}, and somewhat closer to the behavior of the latter. This is consistent with an activated complex in which specific solvation by water molecules is relatively weak,[17] and hence

(32) F. H. Westheimer, Chem. Rev., 61, 265 (1961); J. Bigeleisen, Pure Appl. Chem., 8, 217 (1964).

(33) H. S. Harned and Ernbree, J. Amer. Chem. Soc., 56, 1042 (1934).

(34) The value of α = 0.34 quoted by Gold and Kessick[7] is incorrect due to an error in the reported values of $k_{H_3O^+}$ and k_{HCO_2H} in ref 1a.[19]

(35) (a) E. Högfeldt and J. Bigeleisen, J. Amer. Chem. Soc., 82, 15 (1960); (b) P. A. H. Wyatt, J. Chem. Soc. B, 1570 (1970).

(36) Private communication, Professor Howard Burkett.

(37) (a) E. M. Arnett and G. W. Mach, J. Amer. Chem. Soc., 86, 2671 (1964); (b) E. M. Arnett and G. W. Mach, ibid., 88, 1177 (1966).

consistent with the conclusion based on other evidence that the activated complex lies closer to the carbonium ion side in the transformation depicted by eq 3.

Little can be made of the apparent substituent effect on the acidity behavior of log k_{hyd} − log a_{H_2O}, which shows a tendency to become steeper as styrene reactivity decreases, since the $HClO_4$ range used was of necessity varied with styrene reactivity. It is to be noted that for the two compounds examined over the same range of $HClO_4$ molarity, styrene itself and p-chlorostyrene, the H_R' (and H_0') slopes are virtually identical.

Hydration of p- and m-Aminostyrenes. Medium Dependence of f_{SH^+}/f_{tr^+}

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Abstract: The hydration of p- and m-aminostyrenes in a wide range of aqueous acidic media has been studied. For p-aminostyrenes, rate-controlling proton transfer to the β carbon of the amine prevails up to about 5 M $HClO_4$ and then is overwhelmed in stronger acid by carbon protonation of the anilinium ion. For m-aminostyrenes, carbon protonation of amine is competitive with carbon protonation of anilinium ion only in relatively dilute acid. Brønsted α values for hydration of p-amino- and p-dimethylaminostyrene in dilute aqueous buffer solutions, and other results, are consistent with proton transfer in the activated complex lying between "half-way" and far advanced. Medium effects on f_{SH^+}/f_{tr^+} for p-amino- relative to p-dimethylaminostyrene parallel those on f_{BH^+}/f_B for primary relative to tertiary aniline indicators.

In the adjoining paper and in previous papers evidence has been presented that the most probable rate-controlling step in the acid-catalyzed hydration of styrenes is direct proton transfer to the β carbon of the styrene.[1] A study of the hydration of p- and m-aminostyrenes was undertaken with the expectation that, for the para isomers at least, the predominant rate-controlling process over a wide range of acid medium would be carbon protonation of free aminostyrene rather than of the anilinium ion. In that event, beginning in dilute acid, both the ground state, anilinium ion, and the activated complex would contain a single proton with the latter state having the additional composition of a molecule of water. Changes in the experimental rate constant then would be independent in the acidity *per se* and k_{hyd}/a_{H_2O} would directly measure medium effects on the free energy of the activated complex relative to a protonated ground state in an A-SE2 process. Previously, a similar study was carried out on an A-1 process, the hydrolysis of the dimethyl acetal of 2-pyridine- and 2-quinolinealdehydes, in which both activated complex and ground state in acid solution contained a single proton but also had the same net composition. The relative free energies of these states were found to vary significantly with mineral acid medium (*i.e.*, molarity $HClO_4$). Moreover, the dependence of the medium effect on structure, in particular sterically blocking solvent access to an acidic proton, indicated an important role for specific solvation by water.[2]

Experimental Section[3]

Compounds. The aminostyrenes and corresponding 1-arylethanols, all known compounds, were prepared by standard methods. Final purification, sublimation, and recrystallization of solids and fractional distillation of liquids was carried out until spectral properties were constant: p-aminostyrene, bp 73° (2 mm); p-dimethylaminostyrene, bp 94° (2 mm); m-dimethylaminostyrene, bp 72° (2 mm); p-dimethylamino-α-methylstyrene, mp 77–78°; m-dimethylamino-α-methylstyrene, bp 88° (2 mm); 1-p-aminophenylethanol, mp 62–63°; 1-p-dimethylaminophenylethanol, mp 62–63°; 1-m-dimethylaminophenylethanol, bp 102° (2 mm); 2-p-dimethylaminophenyl-2-propanol, mp 40–41°; 2-m-dimethylaminophenyl-2-propanol, mp 72–73°.

Rate and Equilibrium Constants. First-order rate constants on solutions *ca.* 5 × 10⁻⁵ M in styrene were determined by the ultraviolet spectrophotometric method previously described.[1] Styrene to 1-phenylethanol ratios at equilibrium were determined as previously described in solutions of the 1-phenylethanol that had been allowed to dehydrate for 9–12 half-lives.[1] Values of [S]/[SH⁺], initial free aniline to anilinium ion concentration, also were determined by the ultraviolet spectrophotometric method in acetic acid buffer at wavelengths corresponding to maximum absorption by styrene.

Results

Alcohol–Styrene Ratios. Hydration of the aminostyrenes or dehydration of the corresponding amino alcohol gave equilibrium mixtures containing approximately 10% styrene. Values of the ratio of stoichiometric alcohol to stoichiometric styrene concentration, $[A]_{es}/[S]_{es}$ (Tables 1 and 11), were determined as described previously[1] from the ultraviolet spectra of reaction solutions allowed to reach equilibrium (9–12

(1) (a) W. M. Schubert and J. R. Keeffe, *J. Amer. Chem. Soc.*, **94**, 559 (1972); W. M. Schubert, B. Lamm, and J. R. Keeffe, *ibid.*, **86**, 4727 (1964); W. M. Schubert and B. Lamm, *ibid.*, **88**, 120 (1966); W. M. Schubert and G. W. Barfknecht, *ibid.*, **92**, 207 (1970).

(2) W. M. Schubert, H. Burkett, and A. L. Schy, *ibid.*, **86**, 2520 (1964).

(3) Experimental procedures and properties of the compounds used are described in detail in the Ph.D. Thesis of J. L. Jensen, University of Washington, 1967.