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 $a_{\mathrm{H_2O}}$, 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.

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

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Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98105. *Received January 29, 1971*

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 $f_{\mathrm{SH^+}}/f_{\mathrm{tr^+}}$ for *p*-amino- relative to *p*-dimethylaminostyrene parallel those on $f_{\mathrm{BH^+}}/f_{\mathrm{B}}$ 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 $k_{\mathrm{hyd}}/a_{\mathrm{H_2O}}$ 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 I and II), were determined as described preiously,[1] from the ultraviolet spectra of reaction solutions allowed to reach equilibrium (9–12

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(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.

Table I. Values of k_{hyd} (sec^{-1}) and $[\mathrm{A}]_{\mathrm{es}}/[\mathrm{S}]_{\mathrm{es}}$ for *p*-Amino- and *p*-Dimethylaminostyrene at 80°[a,b]

			Para NH_2		Para NMe_2	
$[H_3O^+]$,[c] *M*	$-H_0'$ [d]	a_{H_2O}[e]	$[A']_{es}/[S']_{es}$	$10^5 k_{\mathrm{hyd}}'$	$[A''']_{es}/[S''']_{es}$	$10^6 k_{\mathrm{hyd}}'''$
2.24×10^{-6} [f]	−5.65	1	7.8[g]	(3.63 ± 0.08)[h]	12.0[g]	3.66[i]
0.001	−3.00	1	10.4[g]	54.5 ± 0.8	12.2[g]	71.2 ± 0.2
2.40×10^{-3} [j]	−2.62	1	10.7[g]	64.1[i]	12.4[g]	73.0[i]
0.010	−2.00	1	10.9	68.7 ± 0.5	12.7	76.2 ± 1.0
0.10	−1.00	0.997	10.9	72.5 ± 0.4	12.5	74.3 ± 0.7
0.94	0.26	0.964	10.3	72.3 ± 0.7	11.6	62.4 ± 1.1
1.63	0.66	0.928	9.8	73.5 ± 0.6	10.8	53.2 ± 0.3
2.78	1.23	0.846	8.7	76.5 ± 0.7	9.9	40.4 ± 0.4
3.55	1.58	0.777	8.3[k]	82.4 ± 0.3	9.3[k]	33.4 ± 0.2
4.33	1.95	0.690	7.8	95.7 ± 0.2	8.7	32.6 ± 0.3
5.26	2.45	0.567	7.4	147 ± 1	8.0	46.3 ± 0.1
5.92	2.84	0.470	7.0	254 ± 1	7.5	89.1 ± 0
6.71	3.31	0.357	6.5	606 ± 1	7.2	241 ± 5
7.26	3.70	0.283			7.0	581 ± 1

[a] Experimental $[A]_{es}/[S]_{es}$ values are averages of at least two determinations, deviation 0.2 at most and usually <0.1. [b] Values of $k_{\mathrm{hyd}} = k_{\mathrm{obsd}}/(1 + [S]_{es}/[A]_{es})$ are based on at least two determinations of k_{obsd}; average deviations are given. [c] Solutions of $HClO_4$ except where noted. [d] In dilute acid, log $[H_3O^+]$; the H_0' values are those of ref 22, at 25°. [e] Values of R. A. Robinson and O. J. Baker, *Trans. Roy. Soc. N. Z.*, **76**, 250 (1946), at 25°. [f] In 1:10 HOAc–OAc⁻ at 80°, $\mu = 0.1$ *M*. [g] Calculated, eq 1. [h] Value in 0.01 *M* HOAc–0.1 *M* OAc⁻. [i] Extrapolated value at zero buffer concentration. [j] In 2:1 $ClCH_2CO_2H$–$ClCH_2CO_2^-$ at 80°, $\mu = 0.1$ *M*. [k] Interpolated value.

Table II. Values of k_{hyd} (sec^{-1}) and $[\mathrm{A}]_{\mathrm{es}}/[\mathrm{S}]_{\mathrm{es}}$ for *p*-Dimethylamino-α-methylstyrene and *m*-Dimethylamino-α-methylstyrene at 80°[a,b]

	p-NMe_2-α-Me		*m*-NMe_2-α-Me	
$HClO_4$,[c] *M*	$[A]_{es}/[S]_{es}$	$10^6 k_{\mathrm{hyd}}$	$[A]_{es}/[S]_{es}$	$10^6 k_{\mathrm{hyd}}$
0.001	8.6[d]	902 ± 20	8.6[d]	0.206 ± 0.05
0.002	8.6[d]	970 ± 10		
0.005	8.6[d]	1003 ± 0	8.6[d]	0.235 ± 0.02
0.010	8.6	979 ± 20	8.6	0.320 ± 0.02
0.100	8.8	942 ± 0	8.6	2.09 ± 0.08
0.94	8.1	847 ± 18	8.3	57.9 ± 0.2
1.63	7.5	882 ± 10	7.7	176 ± 1
2.78	6.6	1650 ± 20	6.8	747 ± 2

[a] Values of k_{hyd} are averages of two determinations. [b] Values of $[A]_{es}/[S]_{es}$ are averages of two determinations, deviation from average ≤0.1. [c] H_0' and a_{H_2O}, at 25°, given in Table I. [d] Value assumed same as in 0.01 *M* $HClO_4$.

half-lives) mainly from the alcohol side.[4] The final spectra showed no detectable absorption by any other species, and in a few random determinations were the same whether obtained by hydration of the styrene or dehydration of the corresponding alcohol. All of the directly determined $[A]_{es}/[S]_{es}$ values were measured in solutions sufficiently acidic so that both alcohol and styrene were essentially completely in the anilinium ion form, *i.e.*, where $[A]_{es}/[S]_{es} = [AH^+]_e/[SH^+]_e$. Ratios of $[A]_{es}/[S]_{es}$ in the weakly acidic solutions, containing some free aniline, were calculated from $[AH^+]_e/[SH^+]_e$ as determined in 0.1 *M* $HClO_4$, and the acidity constants of aminostyrene and amino alcohol (eq 1).

$$\frac{[A]_{es}}{[S]_{es}} = \frac{[AH^+]_e(K_{AH^+}{}^c + [H_3O^+])}{[SH^+]_e(K_{SH^+}{}^c + [H_3O^+])} \tag{1}$$

Values of $K_{HA}{}^c$. Values of the acid ionization constants of acetic acid and chloroacetic acid at 80° and ionic strength 0.1 *M* were obtained by extrapolation from known, accurate data. For acetic acid, the temperature dependence equation of Harned and Ehlers, which reproduces to high-precision thermodynamic K_{HOAc} values determined over the range 0–60°,[5] was used to calculate the thermodynamic constant at 80° (1.285×10^{-5}). Correction to ionic strength 0.1 *M* was made by use of the mean ionic activity coefficient of 0.1 *M* sodium chloride at 80° (slightly temperature dependent; data of ref 6), giving $K_{HOAc}{}^c = 2.24 \times 10^{-5}$. This procedure is justified since at temperatures up to 60° the mean ionic activity coefficient shows very little dependence on specific structure through ionic strength 0.1,[6] and that of acetic acid at $\mu = 0.1$ *M* is very nearly that of 0.1 *M* NaCl (compare data of ref 5 with that on pp 340 and 557 of ref 6). For chloroacetic acid, the thermodynamic acidity constant at 80° (6.87×10^{-4}) was calculated by use of the temperature equation of Ives and Pryor, precise for data determined over the range 15–35°.[7] Correction to ionic strength 0.1 *M* was made as above, giving $K_{HA}{}^c = 1.20 \times 10^{-3}$.

The extrapolated values of $K_{HOAc}{}^c$ and $K_{HA}{}^c$ (chloroacetic acid) were used rather than those based on pH meter readings, the precise meaning of which is unclear at 80°. However, values based directly on pH meter readings, $K_{HOAc}{}^c = 2.08 \times 10^{-5}$ and $K_{HA}{}^c = 1.00 \times 10^{-3}$, agree reasonably well with those calculated.

Values of $K_{SH^+}{}^c$ and $K_{AH^+}{}^c$. Ratios of $[S]/[SH^+]$, for aminostyrene, and $[A]/[AH^+]$, for corresponding amino alcohol, were determined in 4:1 acetic acid–sodium acetate buffer at 80° and ionic strength 0.1 by application of eq 2 to spectral data at the wavelength of maximum absorption by free amine. In this equation, ϵ is the absorptivity per stoichiometric mole of amine in the buffer solution at 80°, ϵ_S (>9000) is the molar absorptivity of free amine in water at 80°, and ϵ_{SH^+} (<900, flat) is that of anilinium ion, taken in 0.1 *M* $HClO_4$ at room temperature. All spectral readings were made before significant hydration–dehydration reaction had taken place. Free amine constituted 30–

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[4] Molarities were made low enough to avoid styrene polymerization,[1] which still took place if the solutions were allowed to stand much beyond 15 half-lives.

[5] H. S. Harned and R. W. Ehlers, *J. Amer. Chem. Soc.*, **55**, 652 (1933).

[6] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed, Reinhold, New York, N. Y., 1950, p 557.

[7] D. J. Ives and J. H. Pryor, *J. Chem. Soc.*, 2104 (1955).

Table III. Values of $K_{SH^+}{}^c$ and $K_{AH^+}{}^c$ for Aminostyrenes and Corresponding Amino Alcohols at 80° and μ = 0.1 M[a]

Compd	$10^6K_{SH^+}{}^c$	$10^6K_{AH^+}{}^c$
Para NH_2	20.7, 20.8	14.7
Para NMe_2	4.38, 4.43	4.23
p-NMe_2-α-Me		3.29

[a] $K_{SH^+}{}^c = [S][H_3O^+]/[SH^+]$ in 0.2000 M HOAc–0.0500 M NaOAc, 0.0500 M $NaClO_4$ at 80°. $[H_3O^+] = 8.96 \times 10^{-5}$ M, extrapolated value of $K_{HOAc}{}^c = 2.24 \times 10^{-5}$

70% of the equilibrium mixture. Calculation of the values of $K_{SH^+}{}^c = [S][H_3O^+]/[SH^+]$ and of $K_{AH^+}{}^c$ (Table III) are based on $[H_3O^+]$ as derived from the extrapolated value of $K_{HOAc}{}^c$ at 80° and ionic strength 0.1.

$$[S]/[SH^+] = (\epsilon - \epsilon_{SH^+})/(\epsilon_S - \epsilon) \qquad (2)$$

Rate Constants. First-order rate constants for reversible hydration, k_{obsd}, were obtained from visual slopes of log $(A - A_\infty)$ against time. Here A is the absorbancy of the reaction solution at any time, with the wavelength used corresponding to maximum or nearly maximum molar absorptivity of the particular styrene (240–260 mμ). The infinity values, A_∞, obtained after nine half-lives, were stable for several half-lives thereafter.[4] Initial A values were around 0.7 and final values <0.1. The first-order plots were linear to at least three half-lives, with practically no visible scatter, and k_{obsd} values in separate runs were generally duplicable to 2%.

Values of k_{hyd}, the first-order rate constant for hydration, and k_{dehyd}, the first-order rate constant for dehydration, were extracted from values of $k_{obsd} = k_{hyd} + k_{dehyd}$ and $[A]_{es}/[S]_{es} = k_{hyd}/k_{dehyd}$. Since $[A]_{es}/[S]_{es}$ is considerably greater than unity, errors in determining this quantity contribute little to errors in k_{hyd}, but much more to errors in k_{dehyd}. Values of k_{hyd} in $HClO_4$ are listed in Tables I, II, and IV. Values in buffer solutions for p-amino- and p-dimethylaminostyrene are listed in Table V.

Table IV. Values of k_{obsd} (sec^{-1}) for m-Aminostyrene and m-Dimethylaminostyrene at 80°[a]

$HClO_4$,[b] M	Meta NH_2 10^6k_{obsd}	Meta NMe_2 10^6k_{obsd}
0.94	0.243[c]	0.108[c]
1.63	0.535[c]	0.244[c]
2.78	2.32 ± 0.06	1.07 ± 0.04
4.33	16.7 ± 0.1	7.10 ± 0.10
5.26	52.6 ± 0.0	25.9 ± 0.3
5.92	126 ± 1	64.3 ± 0.2
6.71	375 ± 1	205 ± 2
7.26		491 ± 6

[a] $k_{obsd} = k_{hyd} + k_{dehyd}$; average of two determinations except where noted. [b] Values of H_0' and a_{H_2O}, at 25°, listed in Table I. [c] One determination.

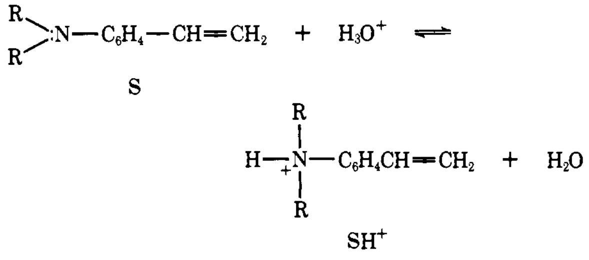
Discussion

In previous studies of the hydration of styrene and para substituted styrenes it has been established that the rate-controlling step is most probably direct proton transfer to the β carbon by hydronium ion, and by the acid component of a buffer, if present.[1] With aminostyrenes, carbon protonation may occur either on the free amine to give a singly protonated activated complex, tr$^+$ (eq 4) or on the anilinium ion to give a doubly protonated activated complex, tr^{2+} (eq 5). The complete Brønsted expression for the first-order rate constant of hydration is given by eq 6, in which K_{SH^+}, k_2, and k_3 are medium independent constants and the f terms are activity coefficients. The first term of eq 6 represents the "one-proton" hydration rate constant,

Table V. Values of k_{hyd} (sec^{-1}) and p-Amino- and p-Dimethylaminostyrene in Aqueous Buffers at 80°[a,b]

$[ClCH_2CO_2H]$, M	$[ClCH_2CO_2^-]$, M	$10^6k_{hyd}'$	$10^6k_{hyd}'''$
0.200[c]	0.100	148 ± 3	200 ± 2
0.150	0.075	127 ± 1	167 ± 1
0.100	0.050	106 ± 0	134 ± 1
0.050	0.025	85.7 ± 2.0	102 ± 0
0.020	0.010	72.2 ± 1.0	87.6 ± 0.8
0.100[d]	0.100		200 ± 0
[HOAc]	$[OAc^-]$	$10^6k_{hyd}'$	$10^6k_{hyd}'''$
0.0010[e]	0.0100		5.15[g]
0.0075	0.0750		14.8 ± 0.4
0.0100	0.1000	3.63 ± 0.08	
0.1000[f]	0.1000	31.7[g]	

[a] Ionic strength 0.1 M ($NaClO_4$). [b] k_{hyd} based on two determinations of k_{obsd}, except where noted. [c] $[H_3O^+] = 2.40 \times 10^{-3}$; $[S']/[SH^+] = 0.087$, $[S''']/[SH'''^+] = 0.018$. [d] $[H_3O^+] = 1.20 \times 10^{-3}$ M; $[S''']/[SH'''^+] = 0.037$. [e] $[H_3O^+] = 2.24 \times 10^{-6}$ M; $[S']/[SH'^+] = 92.9$; $[S''']/[SH'''^+] = 19.7$. [f] $[H_3O^+] = 2.24 \times 10^{-5}$ M; $[S']/[SH^+] = 9.29$. [g] Single determination.



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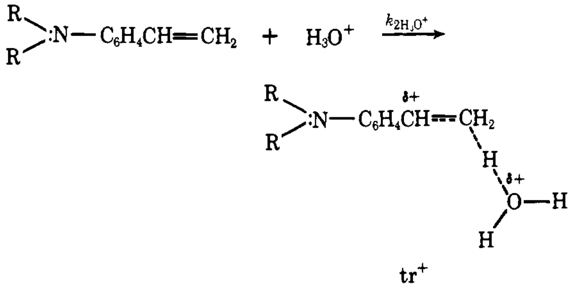

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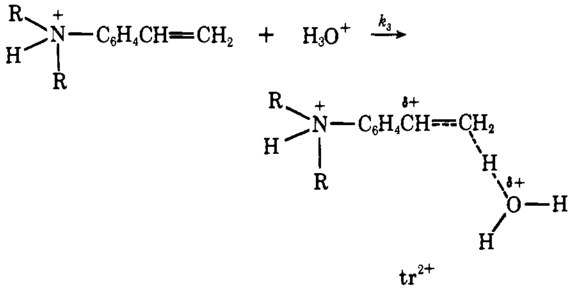

(5)

$$k_{hyd} = k_I + k_{II}\frac{[SH^+]}{[S] + [SH^+]}\left(k_{2H_3O^+}K_{SH^+}a_{H_2O}/f_{tr^+} + k_3a_{H_3O^+}f_{SH^+}/f_{tr^{2+}}\right) \qquad (6)$$

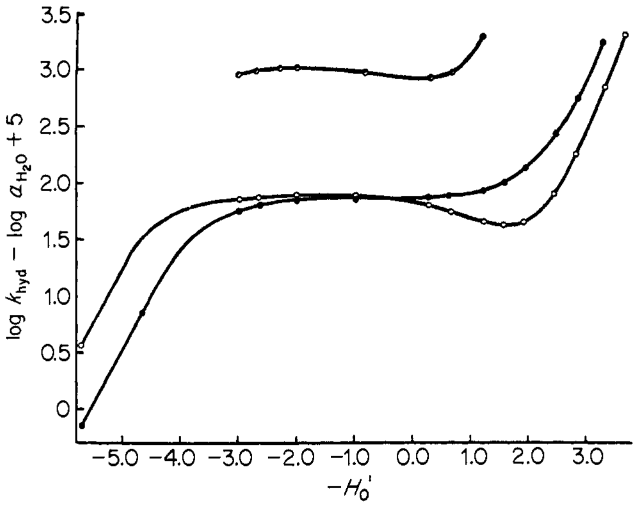

Figure 1. ●, *p*-aminostyrene; ○, *p*-dimethylaminostyrene; ◐, *p*-dimethylamino-α-methylstyrene. Values of k_{hyd} in buffers are extrapolated to zero buffer concentration.

k_I, and the second term represents the "two-proton" hydration rate constant, k_{II}.

In accordance with the rate eq 6, three distinct regions of acidity behavior have been observed for the hydration of the *p*-aminostyrenes. This is illustrated in Figure 1, which is a plot of log k_{hyd} − log a_{H_2O} against acidity, *i.e.*, against log $[H_3O^+]$ in dilute acid and $-H_0'$ in nondilute perchloric acid. Since the rate constant for carbon protonation of free *p*-aminostyrene is much larger than that for carbon protonation of the corresponding anilinium ion, *i.e.*, $k_{2H_3O^+} \gg k_3$, the "one-proton" process represented by the first term of eq 6 predominates over a wide range of the acidity of the medium. In the most weakly acidic solution, 1:10 acetic acid–acetate ion buffer, the ground state is largely free aminostyrene, S. As the acidity is then increased, k_{hyd} increases steeply along with $[SH^+]/([S] + [SH^+])$, then levels off as $[SH^+]/([S] + [SH^+])$ approaches unity, *i.e.*, $k_I > k_{II}$. That is, the predominantly formed activated complex is still tr^+, containing the same number of protons as SH^+, hence k_{hyd} is independent of the acidity of the medium *per se*. Finally, in the solutions of still higher acidity, the relative concentration of free aminostyrene becomes so minute that carbon protonation of the anilinium ion, eq 5, can compete; *i.e.*, the acid-dependent second term of eq 6 becomes significant. As the acidity is increased even further, this steeply increasing term finally overwhelms the acid-independent first term and tr_2^{2+}, containing one more proton than the anilinium ion ground state, becomes the predominantly formed activated complex.

The mechanistic assignment of eq 3 and 4 requires that the hydration of the aminostyrenes show general acid catalysis when the ground state is the amine, since the activated complex contains the additional elements of a proton donor. On the other hand, general base catalysis should be shown when the ground state is the ammonium ion, since the activated complex of the rate-controlling step differs in composition from the ground state only by the elements of the conjugate base of the proton donor. Both phenomena have been observed.

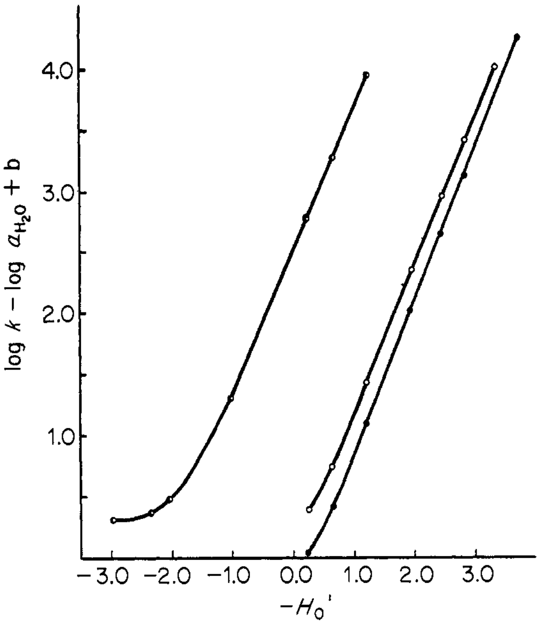

Figure 2. ◐, log k_{hyd} − log a_{H_2O} for m-$Me_2NC_6H_4C(CH_3){=}CH_2$; ○, log k_{obsd} − log a_{H_2O} for m-$H_2NC_6H_4CH{=}CH_2$; ●, log k_{obsd} − log a_{H_2O} for m-$Me_2NC_6H_4CH{=}CH_2$.

General acid catalysis in the hydration of *p*-aminostyrene, henceforth labeled S′, and *p*-dimethylaminostyrene, labeled S‴, has been found in acetic acid buffers, in which the ground state is largely free amine.[8] The data are shown in Table V. That this is general acid and not general base catalysis is shown by the comparison of the data for *p*-aminostyrene in 1:10 and 1:1 buffer. After correction for the amount of $S'H^+$ present and subtraction of the hydronium ion contribution, the contribution of the buffer to k_{hyd}' $([S'] + [SH'^+])/[S']$ is 3.51×10^{-4} sec^{-1} in the 1:1 buffer and 3.67×10^{-5} in the 1:10 buffer, a factor of 9.4. Since [HOAc] is ten times as great in the former buffer, but $[OAc^-]$ is the same, catalysis is by molecular acetic acid and not by acetate ion.

Hydration also is catalyzed by chloroacetic acid–chloroacetate ion buffers (Table V and Figure 3), in which the ground state is largely anilinium ion. That this is now experimental general *base* catalysis is shown by the fact that k_{hyd}'''[8] has the same value in 0.100 *M* $ClCH_2CO_2H$–0.100 *M* $ClCH_2CO_2^-$ as in 0.200 *M* $ClCH_2CO_2H$–0.100 *M* $ClCH_2CO_2^-$.

There is an interesting, but predictable, difference in the acidity behavior of k_{hyd} for *m*- as compared to *p*-aminostyrenes, in that the "two-proton" hydration, eq 5, becomes predominant at much lower acidity for the former (compare Figures 1 and 2). This is to be expected, since k_2 is undoubtedly much smaller for *m*-aminostyrenes, in which the amino substituent is no longer in conjugation, whereas k_3 and K_{SH^+} (eq 6) should not be changed nearly so much.[10]

(8) As in the symbols, H_0' and H_0''',[9] a single prime designates primary amine and a triple prime designates tertiary amine.

(9) E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, **86**, 2671 (1964).

(10) Based on $\rho^+ = -3.58$,[1a] and σ^+ values of ref 11, k_2 should be $>10^3$ larger for *p*- as compared to *m*-dimethylaminostyrene.

(11) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 204.

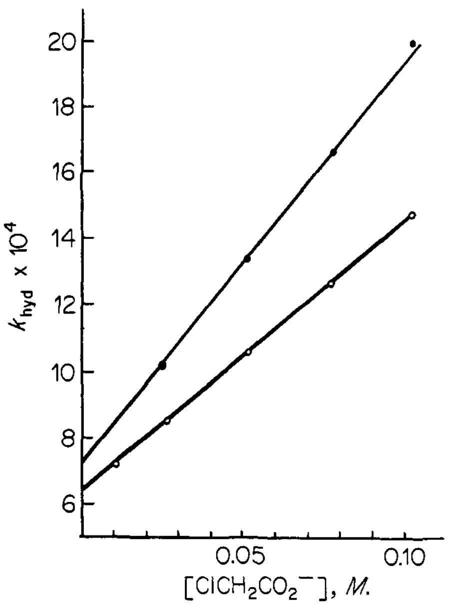

Figure 3. ○, *p*-aminostyrene; slope, 8.39×10^{-3} M^{-1} sec^{-1}; intercept, 6.41×10^{-4} sec^{-1}; ●, *p*-dimethylaminostyrene; slope, 1.25×10^{-2} M^{-1} sec^{-1}; intercept, 7.31×10^{-4} sec^{-1}.

It is also to be noted that the incursion of the two-proton process occurs at a somewhat lower acidity for *p*-dimethylamino-α-methylstyrene than for *p*-dimethylaminostyrene. This is not surprising since better dispersal of positive charge into the α-methyl substituent (*vs.* α-H) should reduce the relative role of the para substituents, *i.e.*, reduce k_2/k_3. This same factor also is reflected in the smaller magnitude of the ρ^+ value for hydration of α-methylstyrenes ($\rho^+ = 3.2$)[12] as compared to styrenes ($\rho^+ = -3.6$).[1a]

Degree of Proton Transfer in tr$^+$. Table VI lists values of catalytic constants, $k_{2HA_i}{}^{c}$, obtained for the catalyzing acids H_3O^+, $ClCH_2CO_2H$, and HOAc in the hydrations of *p*-amino- and *p*-dimethylaminostyrene. These are second-order concentration rate constants at 80° and ionic strength 0.1 *M* for the rate-controlling step of carbon protonation of free aminostyrene (eq 4).

Table VI. Values of Catalytic Constants, $k_{2HA_i}{}^{c}$. (M^{-1} sec^{-1}), for *p*-Amino- and *p*-Dimethylaminostyrene at 80°^{a}

Catalyst	$k_{2HA_i}{}^{c\prime}$	$k_{2HA_i}{}^{c\prime\prime\prime}$	$K_{HA_i}{}^{c}$
H_3O^+	3.49^b 3.35^c	16.9^b 16.9^c 17.2^d	55.5
$ClCH_2CO_2H$	5.26×10^{-2}	34.6×10^{-2}	1.20×10^{-3}
HOAc	2.89×10^{-3} 2.73×10^{-3}	1.56×10^{-2}	2.24×10^{-5}

^{a} All values at 80° and ionic strength 0.1 *M*. ^{b} From $k_{hyd} = k_{2H_3O^+}{}^{c} K_{SH^+}{}^{c}$ in 0.1 *M* $HClO_4$. ^{c} From extrapolation of results in $ClCH_2COOH$–$ClCH_2CO_2^-$ buffers. ^{d} From extrapolation of results in HOAc–OAc$^-$ buffer.

In 0.1 *M* $HClO_4$ the rate equation 6 reduces to $k_{hyd} = k_{2H_3O^+}{}^{c}K_{SH^+}{}^{c}$ since $[SH^+]/([S] + [SH^+])$ is essentially unity and there is a negligible "two-proton" contribution (eq 5) to the rate. Hence, values of $k_{2H_3O^+}{}^{c\prime}$ and $k_{2H_3O^+}{}^{c\prime\prime\prime}$ for primary and tertiary aminostyrenes, respectively,[8] were calculated directly from the measured k_{hyd} values in 0.1 *M* $HClO_4$ listed in Table I and the $K_{SH^+}{}^{c}$ values in Table III. Values of $k_{2H_3O^+}{}^{c}$ also were obtained by extrapolation of the k_{hyd} values in buffers to zero buffer concentration and agree well with those obtained from k_{hyd} in 0.1 *M* $HClO_4$ (Table VI).

In the buffer solutions, eq 7 and 8 are the appropriate equivalent expressions for k_{hyd} in terms of measurable quantities. In the chloroacetic acid buffers, $[SH^+]/([S] + [SH^+])$ is near unity and there is experimental base catalysis by the chloroacetate ion (discussed above). Hence, eq 7 was plotted (Figure 3). Values of $K_{SH^+}{}^{c}k_{2HA}{}^{c}/K_{HA}{}^{c}$ were obtained from the slopes of Figure 3, and $k_{2H_3O^+}{}^{c}K_{SH^+}{}^{c}$ from the intercept after correction for the small fraction of S present. From these values and the known $K_{SH^+}{}^{c}$ and $K_{HA}{}^{c}$ values catalytic constants for chloroacetic acid and hydronium ion were obtained.

In the acetic acid buffers, the ground state is largely S, *i.e.*, experimental general acid catalysis prevails. Hence eq 8 was applied to the k_{hyd} data for *p*-dimethylaminostyrene in the two concentrations of 1:10 HOAc–OAc$^-$ used. This gave values of $k_{2HOAc}{}^{c\prime\prime\prime}$ from the "slope," and $k_{2H_3O^+}{}^{c\prime\prime\prime}$ from the "intercept," after correction for 4.8% SH$^+$ in equilibrium with S‴. For *p*-aminostyrene, this approach could not be used since $k_{hyd}{}'$ was determined at only one buffer concentration at the same buffer ratio. Instead, the contribution of H_3O^+ catalysis to $k_{hyd}{}'$ was calculated by application of the $k_{2H_3O^+}{}^{c\prime}$ value obtained in 0.1 *M* $HClO_4$, and $k_{2HOAc}{}^{c\prime}$ calculated from the residual rate,

$$k_{hyd} = \frac{[SH^+]}{[S] + [SH^+]}(k_{2H_3O^+}{}^{c}K_{SH^+}{}^{c} + k_{2HA}{}^{c}K_{SH^+}{}^{c}[A^-]/K_{HA}{}^{c}) \quad (7)$$

$$k_{hyd} = \frac{[S]}{[S] + [SH^+]}(k_{2H_3O^+}{}^{c}[H_3O^+] + k_{2HA}{}^{c}[HA]) \quad (8)$$

with the small extent of SH$^+$ present also being taken into account. The values thus obtained in 1:10 and 1:1 HOAc–OAc$^-$ buffers agree reasonably well (Table VI).

Not unexpectedly, the Brønsted plots of log $k_{HA_i}{}^{c}$ *vs.* log $K_{HA_i}{}^{c}$ for the three catalyzing acids are not linear.[13] Presumably, the badly behaved point is that for H_3O^+, which generally, and this instance also, falls considerably below the line defined by other catalyzing acids.[14] The Brønsted α values defined by $ClCH_2COOH$ and HOAc alone are 0.74 for *p*-aminostyrene and 0.78 for *p*-dimethylaminostyrene. These values are consistent with the conclusion reached in the hydration of other styrenes[1a] that proton transfer is more than "half-way" advanced in the activated complex of the rate-controlling step, but not as far advanced as in the activated complex of isobutylene hydration.

In the hydration of *p*-methoxy-α-methylstyrene,[1a] catalytic constants were evaluated only for formic acid and the hydronium ion. The Brønsted "slope" for these two catalyzing acids, at 50°, was 0.49. In the same ball park are the Brønsted "slopes" between acetic

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

(13) Since the acid ionization constants are formally defined as $K_{HA_i}{}^{c} = [H_3O^+][A_i]/[HA_i]$, the usual value $K_{H_3O^+}{}^{c} = [H_2O] = 55.5$ was assigned. This value is of doubtful quantitative significance since the conjugate base of H_3O^+ is also the medium.[14] It is probably a coincidence that an assigned value of unity to $K_{H_3O^+}{}^{c}$ places the point for H_3O^+ nearly on line.

(14) R. P. Bell, "Acid-Base Catalysis," Oxford University Press, London, England, 1941, Chapter V.

Table VII. Values of k_{I} (sec^{-1}), k_{II} (sec^{-1}), and Relative f_{SH^+}/f_{tr^+} for *p*-Amino- and *p*-Dimethylaminostyrene at 80°[a]

HClO$_4$, *M*	$H_0' - H_0'''$[b,c]	$10^6 k_I'$	$10^6 k_{II}'$	f_{SH^+}'/f_{tr^+}'	$10^6 k_I'''$	$10^6 k_{II}'''$	f_{SH^+}'''/f_{tr^+}'''	$f_{PhNH_3^+}/f_{PhNHMe_2^+}$[b,d]
0.01		70.0	~0	1.00	76.2	~0	1.00	
0.10		72.5	~0	1.04	74.3	~0	0.98	
0.94	0.21	72.0	0.3	1.07	62.2	0.2	0.85	1.07
1.63	0.31	72.5	1.0	1.16	52.8	0.4	0.75	1.15
2.78	0.53	72.8	3.7	1.23	38.8	1.6	0.60	1.42
3.55	0.68	73.8	8.5	1.36	29.7	3.7	0.50	1.65
4.33	0.85	75.0	20.7	1.55	23.6	9.0	0.45	2.10
5.26	1.03	(79.2)	67.8	(2.00)[e]	(16.8)	29.5	(0.39)[e]	2.64
5.92	1.11	(83)	171		(14.8)	74.3		
6.71	1.17	(85)	521		(14.6)	226.4		
7.26	1.23				(10)	571		

[a] $f_{SH^+}/f_{tr^+} = (k_I/a_{H_2O})/(k_I/a_{H_2O})_{0.01\,M}$. [b] Values in H_2SO_4 at 25° interpolated to common H_0' in HClO$_4$. [c] Values of ref 12 and 22. [d] Values of ref 21. [e] Values in parentheses sensitive to interative procedure in separating k_I and k_{II}.

acid and the hydronium ion for *p*-aminostyrene, 0.48, and *p*-dimethylaminostyrene, 0.47.

Medium Effects on f_{SH^+}/f_{tr^+}. Relative values of f_{SH^+}'/f_{tr^+}', for *p*-aminostyrene, and f_{SH^+}'''/f_{tr^+}''', for *p*-dimethylaminostyrene, are listed in Table VII.[8] These were obtained from relative values of $k_I = k_2K_{SH^+}a_{H_2O}f_{SH^+}/f_{tr^+}$, which contributes predominantly to the observed k_{hyd} values in the region 0.01 to about 4.33 *M* HClO$_4$. Small corrections for k_{II} in the sum $k_{hyd} = k_I + k_{II}$ were made as follows. Firstly, k_{II} in the highest acid molarity was calculated from k_{hyd} by subtracting a small contribution of k_I, the latter value being obtained by extrapolation of log k_{hyd} *vs.* $-H_0'$ through points corresponding to highly predominant one-proton hydration. Values of k_{II} in the lower acid molarities then were calculated by setting $-$d log k_{II}/dH_0 = 1.03. The value 1.03 pertains to the *m*-aminostyrenes, which hydrate by the "two-proton" mechanism, eq 5.[15] The lower limit value of $-$d log k_{II}/dH_0 is 0.98, based on k_{hyd} for *p*-dimethylaminostyrene between 6.71 and 7.26 *M* HClO$_4$, where k_{hyd} is nearly freed of k_I. The values of k_I', k_I''', k_{II}', and k_{II}''' thus obtained are listed in Table VII. Up through 4.33 *M* HClO$_4$, the k_{II} corrections are small and values of k_I are not very sensitive to a change in $-$d log k_{II}/dH_0 or the value of k_{II} estimated for the highest acid molarity.

The behaviors of f_{SH^+}'/f_{tr^+}' and f_{SH^+}'''/f_{tr^+}''' in 0.01–5.26 *M* HClO$_4$ clearly diverge, although the effect in these still highly aqueous solutions is not overly large.[16] For any one of the four solutes, the medium effect on the free energy is of course dependent in a complicated way upon both changing solute–solvent and solvent–solvent interactions.[12,17,18] One may dissect the free energy of solution into two arbitrary thermodynamic changes: first the creation for the solute of the necessary cavity in the solvent structure (nonspecific "solution," endothermic), followed by solvent reorientation, *e.g.*, hydrogen bonding, to specific solute sites. Nonspecific solvation has been shown to be an important factor, even in the free energy of solution of polar and ionic species.[17b] Hence, its possible role in the behavior of either f_{SH^+}'/f_{tr^+}' or f_{SH^+}'''/f_{tr^+}''' cannot be dismissed, since the activated complexes have an increased molar volume by virtue of containing the elements of a water molecule more than the ground-state anilinium ions. However, since the change in volume, and shape, from SH$^+$ to tr$^+$ is essentially the same for the primary and tertiary amine systems, the effect of nonspecific solvation on the *relative* behavior of f_{SH^+}'/f_{tr^+}' and f_{SH^+}'''/f_{tr^+}''' will be assumed to be relatively unimportant. It will be further assumed that specific solvation effects on f_{tr^+}' and f_{tr^+}''' also approximately cancel. Not only are the two activated complexes similarly constituted, but the degree of proton transfer in these states is probably very nearly the same; witness the near equality of the Brønsted α values (previous section of Discussion). This leaves as the major culprit specific solvation of SH$'^+$ *vs.* SH$'''^+$. At this point one may apply the specific solvation arguments first used by Taft to account for the differing acidity dependence of equilibrium N protonation of primary and tertiary amines.[19] This approach also consistently accounts for the relative behavior of similar activity coefficient ratios in which there is a net cancellation of molar volumes (some of these instances are cited in the adjoining article[1a]) and has been applied to relative f_{SH^+}/f_{tr^+} behavior in an A-1 reaction.[2]

As regards the SH$^+$ ground states, the main sites for specific solvation are three acidic N–H protons in SH$^+$, and one such in SH$'''^+$, of about the same positive character as any one of the three in SH$'^+$. Therefore, SH$'^+$ is more prone than SH$'''^+$ to specific hydrogen bonding stabilization by water. Hence, as HClO$_4$ molarity is increased, *i.e.*, the availability of water for specific solvation decreased (reflected in decreasing a_{H_2O}), SH$'^+$ has relatively more to lose in the way of such stabilization, *i.e.*, specific solvation would act to increase $f_{SH^+}'/f_{SH}'''^+$.[20] This same factor may be acting on f_{tr^+}'/f_{tr^+}''' in the same direction since the amino groups of the activated complexes share some of the positive charge. However, the effect on the activated complexes should definitely be weaker than on the anilinium ion ground states. The net effect of specific hydrogen bonding solvation of δ^+ hydrogens would

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(15) For *m*-aminostyrene, $-$d log k_{obsd}/dH_0' = 1.06 and for *m*-dimethylaminostyrene, $-$d log k_{obsd}/dH_0' = 1.07. One obtains $-$d log k_{hyd}/dH_0' = 1.03 for both by assuming k_{hyd}/k_{obsd} changes the same as for the corresponding *p*-aminostyrenes.

(16) In terms of free energy, the fivefold change in $f_{SH^+}'f_{tr^+}'''/f_{SH^+}'''f_{tr^+}'$ between 0.01 and 5.26 *M* HClO$_4$ amounts to 1150 cal/mol.

(17) (a) E. M. Arnett and G, W. Mach, *J. Amer. Chem. Soc.*, **88**, 1177 (1966); (b) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *ibid.*, **87**, 1541 (1965).

(18) With an activated complex there is the further possibility of its internal structure, *e.g.*, degree of proton transfer, being changed by the change in medium.

(19) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **82**, 2865 (1960).

(20) The argument used here essentially duplicates the qualitative aspects of Taft's treatment of $f_{BH^+}'f_B'''/f_B'f_{BH^+}'''$ ratios.[19]

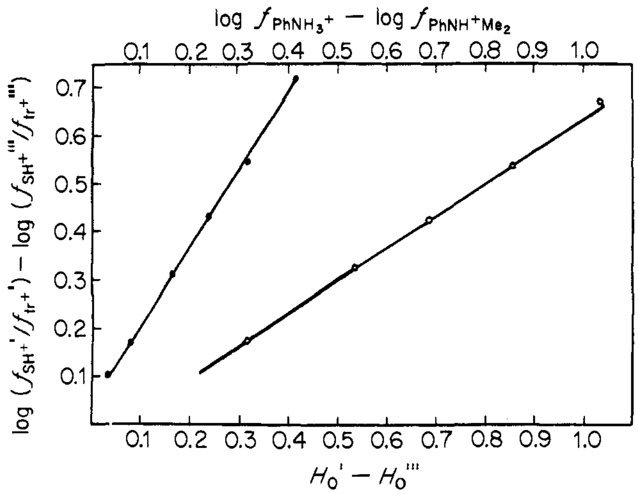

Figure 4. Plot of log $(f_{SH^+}'/f_{tr^+}') - \log(f_{SH^+}'''/f_{tr^+}''')$ against $H_0' - H_0'''$ (○) and against $\log f_{PhNH_3^+} - \log f_{PhNMe_2^+}$ (●).

thus be to cause $f_{SH^+}'f_{tr^+}/'''f_{tr^+}'f_{SH^+}'''$ to increase as $HClO_4$ molarity is increased.

In agreement with the above rationalization, there is an approximately linear relationship between log $(f_{SH^+}'/f_{tr^+}') - \log(f_{SH^+}'''/f_{tr^+}''')$ and $H_0' - H_0'''$, as seen in Figure 4. The slope of the line is 0.65. The difference between acidity functions for aniline *vs.* dimethylaniline indicators, $H_0' - H_0''' = \log(f_{BH^+}'/f_B') - \log(f_{BH^+}'''/f_B''')$, is generally believed to be due mainly to medium effects on f_{BH^+}' relative to f_{BH^+}''' and to a lesser extent to medium effects on the relative activity coefficients of the free amines (see the discussion of this in ref 12 and 17a). Figure 4 also shows a correlation, slope 1.4, between log $(f_{SH^+}'/f_{tr^+}') - \log(f_{SH^+}'''/f_{tr^+}''')$ and the $\log f_{PhNH_3^+} - \log f_{PhNH^+Me_2}$ data of Boyd.[21] The $H_0' - H_0'''$ values[12] and the data of Boyd, both for sulfuric acid solutions at 25°, have been interpolated to common H_0' values in aqueous perchloric acid,[22] the medium in which the styrene hydrations were carried out.[23] No temperature correction (the kinetic data are at 80°) was attempted. Over the range of H_0' values used, the temperature dependence of H_0' *vs.* acid molarity in sulfuric acid is fairly small,[24] and presumably that of $H_0' - H_0'''$ even smaller.

The "Two-Proton" Process. In Figure 2 is plotted the acidity dependence of the hydration of the *m*-aminostyrenes, which occurs predominantly by the "two-proton" process, eq 5, except in relatively dilute perchloric acid (ground state is SH^+ throughout). For *m*-dimethylamino-α-methylstyrene the slope of $\log k_{hyd} - \log a_{H_2O}$ *vs.* $-H_0'$ is 1.20 in the linear portion of the graph. For *m*-amino- and *m*-dimethylaminostyrene the slopes of $\log k_{obsd} - \log a_{H_2O}$ *vs.* $-H_0'$ are 1.24 and 1.26, respectively. The latter plots are for k_{obsd} rather than k_{hyd} since the equilibrium percentage of styrene was not determined for these two compounds. However, k_{hyd} would have nearly the same acidity dependence as k_{obsd} since the percentage of styrene is small at equilibrium and furthermore not drastically acidity dependent. For example, if one assumes that $[SH^+]_e/[AH^+]_e$ has the same values as for the corresponding *p*-aminostyrenes,[25] $-d(\log k_{hyd} - \log a_{H_2O})/dH_0'$ would be 1.22 and 1.24 for *m*-amino- and *m*-dimethylaminostyrene, respectively. For *p*-dimethylaminostyrene the limiting slope, Figure 1, is 1.24 between 6.71 and 7.26 *M* $HClO_4$, where the "two-proton" hydration has nearly swamped out the "one-proton" contribution.

These slopes are substantially smaller than for neutral para substituted styrenes at 25°, reported in the adjoining article.[1a] Perhaps this is due to relatively less loss of solvent orientation in proceeding from a monocationic ground state to a dicationic activated complex as compared to neutral ground state going to monocationic activated complex. It is to be noted that the acidity dependence of the "two-proton" process is practically the same for amino- and dimethylaminostyrenes, in contrast to what was observed for the "one-proton" process. However, in the process $SH^+ \rightarrow tr^{2+}$, the ammonium ion substituent remains formally unchanged and hence, differential solvation of the substituent is of lesser importance.

It is of interest to note that both $-NH_3^+$ and $-NHMe_2^+$ substituents are slightly less deactivating in the para than in the meta position (compare the rate constants in highest molarity $HClO_4$, Tables I and III). This is contrary to the reported σ^+ order for para and meta $-NMe_3^+$ (chloride), $\sigma_{para}^+ = 0.408$ and $\sigma_{meta}^+ = 0.359$,[11] but in agreement with the σ order. Also, para NH_3^+ is slightly less deactivating than para $NHMe_2^+$ (compare k_{hyd} values at 6.71 *M* $HClO_4$, Table I, or k_{II} values, Table VI), and meta NH_3^+ is slightly less deactivating than meta $NHMe_2^+$ (compare k_{obsd} values in Table IV). Apparently, the presumed greater dispersal of positive charge within the $-NHMe_2^+$ substituent, which should make it less deactivating, is offset by other factors, including perhaps solvation effects.

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(21) R. H, Boyd, *J. Amer. Chem. Soc.*, **85**, 1555 (1963).

(22) K. Yates and H. Wai, *ibid.*, **86**, 5408 (1964).

(23) Over the range of comparison, H_0' values in $HClO_4$ are nearly the same as those in H_2SO_4 of the same molarity.

(24) C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, **91**, 6654 (1969).

(25) Note that $[AH^+]_e/[SH^+]_e$ values for *p*- and *m*-dimethylamino-α-methylstyrene are practically the same in all $HClO_4$ molarities used (Table II).