Protonation Constants of Very Weak Uncharged Bases in Acetonitrile

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Abstract: Acetonitrile is much more suitable for determination of the protonation constant $K^{f}_{BH^+}$ of very weak bases than is water (sulfolane, which is a considerably weaker base than AN, is still better than AN for this purpose). Protonation constants in AN of acetic, benzoic, substituted benzoic, oxalic, and glutaric acids, two esters, phenols, substituted phenols, some ethers, ketones, and amides have been determined from the effect of these solutes on the conductivity of methane- or trifluoromethanesulfonic acids in AN. Both acids are incompletely dissociated and, in addition, the latter is dimerized in AN. Values of $K^{f}_{BH^+}$ are listed in Table III. Assuming that the neutral contribution to the transfer activity coefficients of B and BH^+ is the same, values of the electrostatic contribution of the transfer activity coefficient, $\mathrm{p}^{AN}\gamma^{W}_{BH^+{}_{el}}$, of protonated acetic and benzoic acids, anisole, acetophenone, four amides, and dimethyl sulfoxide have been found to be of the order of 2, based on the assumption that ${}^{AN}\gamma^{W}_{Ph_4As^+} = {}^{AN}\gamma^{W}_{Ph_4B^-}$. This indicates that BH^+ is more strongly hydrogen bonded to water than to AN. On the basis of the ferrocene assumption, values of $\mathrm{p}^{AN}\gamma^{W}_{BH^+{}_{el}}$ close to zero are obtained, which is improbable. The relation between ${}^{AN}\Delta^{W} \log K = {}^{AN}\Delta^{W} \log (K^{f}_{BH_2^+}/K^{d}_{BH}) = \mathrm{p}^{AN}\gamma^{W}_{BH_2^+{}_{el}} - \mathrm{p}^{AN}\gamma^{W}_{B^-{}_{el}} - 2\mathrm{p}^{AN}\gamma^{W}_{H^+}$ of benzoic acids and phenols has been discussed. The quantity ${}^{AN}\Delta^{W} \log K$ denotes the difference in logarithm of the protonation constant in AN and in water. From the heteroconjugation constants with various hydrogen-bond donors in Table I, methanesulfonate is some eight times weaker a hydrogen-bond acceptor than chloride.

The most popular method for the determination of the protonation constant $K^{f}_{BH^+}$ (eq 3) of very weak bases B in water as the reference solvent consists of determining the ratio of the protonated to the unprotonated form of the base in water–acid mixtures by nmr,[1,2] Raman spectroscopy,[2] calorimetry[3,4] (heats of protonation of B), solvent extraction,[5] ultraviolet absorption,[6,7] and spectrophotometry with Hammett indicators.[8,9] Several authors[4,8,10] have emphasized the shortcomings involved in the use of concentrated acid solutions in water for evaluation of $K^{f}_{BH^+}$ and have ascribed them mainly to the invalidity of the Hammett–Deyrup activity coefficient postulate. As discussed in a recent paper by Yates, *et al.*,[11] different values of the acidity function (H_0, H_0''', H_A) are found with various series of bases, the differences increasing with concentration of acid and often depending on the kind of acids used ($HClO_4$, H_2SO_4, FSO_3H, etc.). Thus, if types of indicators other than nitroanilines are used for determination of $K^{f}_{BH^+}$, different values are found. In attempts to interpret these differences, Bunnett and Olson[12] proposed the ϕ parameter treatment and Yates and McClelland[13] the m value treatment. Moreover, in some instances $K^{f}_{BH^+}$ values obtained in concentrated acid solutions in water are unreliable or erroneous because of other reactions in addition to protonation (*e.g.*, hydrolysis of esters). These limitations in the determination of $K^{f}_{BH^+}$ in water–acid mixtures are essentially eliminated in aprotic–protophobic solvents in which dilute solutions of suitable acids are used to determine $K^{f}_{BH^+}$.

In recent years equilibrium studies of acid–base reactions and association in the gas phase, using ingenious techniques, have become increasingly popular and have yielded already important results.[14] The order of values of $K^{f}_{BH^+}$ in solvents can and does differ greatly from the order of proton affinities in the gas phase because of solvation effects in the former, including hydrogen bonding, ion–dipole interaction, and dielectric effects. The gas phase studies combined with those in solution provide valuable information regarding solvation of species involved in acid–base equilibria in the liquid phase, even though homo- and heteroconjugation in the gas phase may occur.

During the last 15 years we have made extensive studies of acid–base equilibria in aprotic protophobic solvents, with main emphasis on acetonitrile (AN). This has been the solvent used in the present study. Sulfolane, being a much weaker base than AN,[15,16] should be especially suitable for the determination of $K^{f}_{BH^+}$ of those bases too weak to yield reliable values in AN.

In general, we have calculated $K^{f}_{BH^+}$ from the effect of B on the conductance of methanesulfonic acid which is incompletely dissociated in AN. In solutions of this acid and B the following equilibria are involved, HX denoting a typical acid which is also a weak base B

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(carboxylic acids, phenols); see equilibria 1–4′. The

$$\mathrm{HA} + \mathrm{S} \rightleftharpoons \mathrm{H_s^+} + \mathrm{A^-} \qquad K^{\mathrm{d}}_{\mathrm{HA}} = a_{\mathrm{H^+}}a_{\mathrm{A^-}}/[\mathrm{HA}] \tag{1}$$

$$\mathrm{A^-} + \mathrm{HA} \rightleftharpoons \mathrm{HA_2^-} \qquad K^{\mathrm{f}}_{\mathrm{HA_2^-}} = [\mathrm{HA_2^-}]/[\mathrm{HA}][\mathrm{A^-}] \qquad f_{\mathrm{HA_2^-}} = f_{\mathrm{A^-}} \tag{2}$$

$$\mathrm{B} + \mathrm{H_s^+} \rightleftharpoons \mathrm{BH^+} \qquad K^{\mathrm{f}}_{\mathrm{BH^+}} = [\mathrm{BH^+}]/[\mathrm{B}][\mathrm{H_s^+}] \qquad f_{\mathrm{BH^+}} = f_{\mathrm{H^+}} \tag{3}$$

$$\mathrm{A^-} + \mathrm{HX(B)} \rightleftharpoons \mathrm{A^-}\ldots\mathrm{HX} \qquad K^{\mathrm{f}}_{\mathrm{A\cdot HX^-}} = [\mathrm{A^-}\ldots\mathrm{HX}]/[\mathrm{A^-}][\mathrm{HX}] \tag{4}$$

$$\mathrm{A^-} + \mathrm{2HX(2B)} \rightleftharpoons \mathrm{A^-}\ldots\mathrm{(2HX)} \qquad K^{\mathrm{f}}_{\mathrm{A\cdot 2HX^-}} = [\mathrm{A^-}\ldots 2(\mathrm{HX})]/[\mathrm{A^-}][\mathrm{HX}]^2 \tag{4′}$$

values of $K^{\mathrm{d}}_{\mathrm{HA}}$ and $K^{\mathrm{f}}_{\mathrm{HA_2^-}}$ are assumed not to be affected by addition of B. The ion pair $\mathrm{BH^+A^-}$ has been considered to be completely dissociated into ions at the low ionic strengths in the mixtures of acid and B. The equilibrium constants of reactions 4 and 4′ were calculated from the ionic solubility of potassium methanesulfonate (KA) in solutions of HX(B), taking into account complexation of $\mathrm{K^+}$ with HX(B).[17]

An example of the calculation of $K^{\mathrm{f}}_{\mathrm{BH^+}}$ is given in the experimental part. For those bases of which $K^{\mathrm{f}}_{\mathrm{BH^+}}$ was found to be of the order of 1 or less we have checked semiquantitatively the basicity of some of these bases from their effect on the conductance of the relatively strong acid, trifluoromethanesulfonic acid. In addition, we have calculated $K^{\mathrm{f}}_{\mathrm{BH^+}}$ of acetic acid from its effect on $[\mathrm{H_s^+}]$ in very dilute solutions of perchloric acid, which was added to AN in the form of an acetic acid solution, correction being made for the formation of $\mathrm{CH_3COOH_2^+}$.[18] In these experiments $[\mathrm{H_s^+}]$ was determined spectrophotometrically with Hammett indicators.

Experimental Section

Chemicals. Acetonitrile has been purified as described previously.[19] Substituted benzoic acids,[20] phenols,[21] methanesulfonic acid,[22] potassium methanesulfonate,[17] potassium and cesium picrates,[17] and Hammett indicators[19] were products used previously. Tetrahydrofuran, ethyl acetate, trifluoroethanol, anisole, acetophenone, ethylene glycol, diethyl tartrate, and *trans*-1,2-cyclohexanediol were Baker or Aldrich Reagent grade, shaken overnight with type 4A molecular sieve (Baker) and distilled, the first three at 1 atm, the rest *in vacuo*. Acetone was puritified according to Jasinski,[23] while trifluoromethanesulfonic acid was generously supplied by the Minnesota Mining and Mfg. Co. and was distilled at atmospheric pressure. Oxalic and glutaric acids (Eastman Kodak White Label) were dried for 4 days in a vacuum desiccator over sulfuric acid and assay was by alkalimetric titration, 99.8 and 99.5%, respectively. Thioacetic acid and thioacetamide were Aldrich products, used without further purification. Amides were prepared by reaction of thionyl chloride with the acid and subsequent treatment with cold concentrated aqueous ammonia.[24] Hydrogen sulfide was a Matheson product dried over calcium sulfate. The hydrogen sulfide content of solutions in AN was determined iodometrically[25] after flooding 1 volume with 25 volumes of 1 *M* aqueous sodium hydroxide.

Techniques. Conductometric,[19] potentiometric $\mathrm{p}a_{\mathrm{H}}$ measurements with the glass electrode,[22] and spectrophotometric measurements[22] were performed as described elsewhere. The molar absorptivity, 0.54×10^4, at maximum absorption at 410 nm was found for 2-nitro-4,5-dichloroaniline which is identical with that of 2-nitro-4-chloroaniline.[19] The conductometric determination of ionic solubilities of potassium chloride,[20] methanesulfonate,[17] picrate,[17] and cesium picrate[17] in the presence of various solutes has been described.

Results

Conductometric Section. Ionic Mobilities. The following ionic mobilities in AN at infinite dilution were previously reported: $\mathrm{H^+} = 80$,[19] $\mathrm{K^+} = 76$,[26] $\mathrm{Cs^+} = 102$,[27] $\mathrm{Cl^-} = 89$,[28] $\mathrm{Pi^-} = 78$,[28] and $\mathrm{CH_3SO_3^-} = 90$.[22] The value of $\lambda_{0\mathrm{CF_3SO_3^-}}$ was taken the same as that of $\lambda_{0\mathrm{CH_3SO_3^-}}$. The mobilities of the methanesulfonate heteroconjugates with hydroxylic compounds (*i.e.*, methanol, glycols) were taken equal to $\lambda_{0\mathrm{CH_3SO_3^-}}$, as the effect of water on $\lambda_{0\mathrm{CH_3SO_3^-}}$ has been found to be very small.[17] For the other heteroconjugates of methanesulfonate and those of chloride $\lambda_{0\mathrm{HX\cdot Cl^-}} = \lambda_{0\mathrm{HX\cdot CH_3SO_3^-}}$, the latter taken equal to $\lambda_{0\mathrm{CH_3SO_3H\cdot CH_3SO_3^-}} = 65$.[22] The mobilities of the protonated weak bases $\mathrm{BH^+}$ were assumed the same as $\lambda_{0\mathrm{H^+}}$. Viscosity corrections were applied in all instances using the data in Figure 1.

Heteroconjugation Constants. When the weak base B is a weak Brønsted acid, HX, it is necessary to consider the formation of heteroconjugates $(\mathrm{HX})_n\mathrm{A^-}$ with methanesulfonate, $\mathrm{A^-}$, in the interpretation of conductance data of solutions of B in the presence of HA (eq 4 and 4′). Association constants of HX with methanesulfonate and with $\mathrm{K^+}$ were found conductometrically from the increase in ionic solubility of potassium methanesulfonate in the presence of HX. Experimental data are presented as plots of $[f_\pm^2[\mathrm{K^+}]^2 - K^{\mathrm{sp}}]/K^{\mathrm{sp}}$[21] in Figure 2. In order to facilitate the evaluation of $K^{\mathrm{f}}_{\mathrm{HX\cdot CH_3SO_3^-}}$, $K^{\mathrm{f}}_{\mathrm{HX\cdot K^+}}$ was found independently from the increase in ionic solubility of potassium and cesium picrates in the presence of HX.[23] Solubility data of these salts are plotted in Figure 3 in the same way as in Figure 2. Values of the calculated complexation constants of the above ions, including chloride ion for comparison,[20,29] are presented in Table I. Quite generally, heteroconjugation constants of HX with $\mathrm{Cl^-}$ are some ten times as large as those with $\mathrm{CH_3SO_3^-}$, indicating that chloride ion is a stronger hydrogen-bond acceptor than methanesulfonate.

Ionic Dissociation of Methane- and Trifluoromethanesulfonic Acids, HA. From conductivity data in freshly prepared solutions of methanesulfonic acid, a value of $\mathrm{p}K_{2\mathrm{HA}} = 6.1$ was calculated, in satisfactory agreement with 6.2 found previously.[17] The following equivalent conductivities at various concentrations were found in freshly prepared trifluoromethanesulfonic acid solutions: 4.23×10^{-4} *M*, 178; 8.40×10^{-4}, 161; 9.05×10^{-4}, 152; 1.65×10^{-3}, 142; 1.80×10^{-3}, 134; 4.45×10^{-3}, 71.0; 8.73×10^{-3}, 44.6; 2.06×10^{-2}, 22.1; 3.14×10^{-2}, 16.1; 4.69×10^{-2}, 12.5; $7.16 \times$

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Table I. Heteroconjugation Constants in AN of Additives, HX, to Anions and Association Constants of HX to K^+ or Cs^+

HX	$K^f_{HX\cdot Cl^-}$ [a]	$K^f_{2HX\cdot Cl^-}$ [a]	$K^f_{HX\cdot CH_3SO_3^-}$	$K^f_{2HX\cdot CH_3SO_3^-}$	$K^f_{HX\cdot Pi^-}$	$K^f_{HX\cdot K^+}$	$K^f_{HX\cdot Cs^+}$
Acetic acid	3.5×10^2	0	4.5×10^1 [b]	1.2×10^2 [b]		0	
Thioacetic acid			2.8 [b]	0 [b]		0	
Benzoic acid	1.6×10^2	1.2×10^2	4.7×10^1 [b]	5.8×10^1 [b]		0	
3-Nitrobenzoic acid	3.9×10^2	1.2×10^3	6.5×10^1 [b]	6.2×10^2 [b]		0	
Salicylic acid	5×10^2	1×10^2	1.2×10^2	8×10^2 [b]		0	
4-Bromophenol	2.4×10^2	1.8×10^3	3.4×10^1 [b]	1.4×10^2 [b]	~0	0	
4-Nitrobenzamide			3×10^1 [b]	0 [b]		0	
Hydrogen sulfide			~0 [b]	~0 [b]		~0 [b]	
Water	9	2.0×10^1	3.6 [a]	8 [a]	0.5 [a]	1.0 [a]	0.5 [a]
Methanol			2.0 [b]	4.0 [b]	0.6 [b]	0.5 [b]	(0.1) [b]
2,2,2-Trifluoroethanol			7 [b]	1.6×10^1 [b] 1.4×10^1 [c]	0.4 [b]	~0 [b]	
Ethylene glycol			1.3×10^1 [b]	2.2×10^1 [b] 6.2×10^1 [c]	1.8 [b]	2.0 [b,d]	
Diethyl tartrate			1.1×10^1 [b]	0	~0.2 [b]	2.4 [b]	

[a] References 21, 22, 30, and 35. [b] This work. [c] Values of $K^f_{3HX\cdot CH_3SO_3^-}$. [d] Average value of 2.2 from KCH_3SO_3 and 1.8 from KPi.

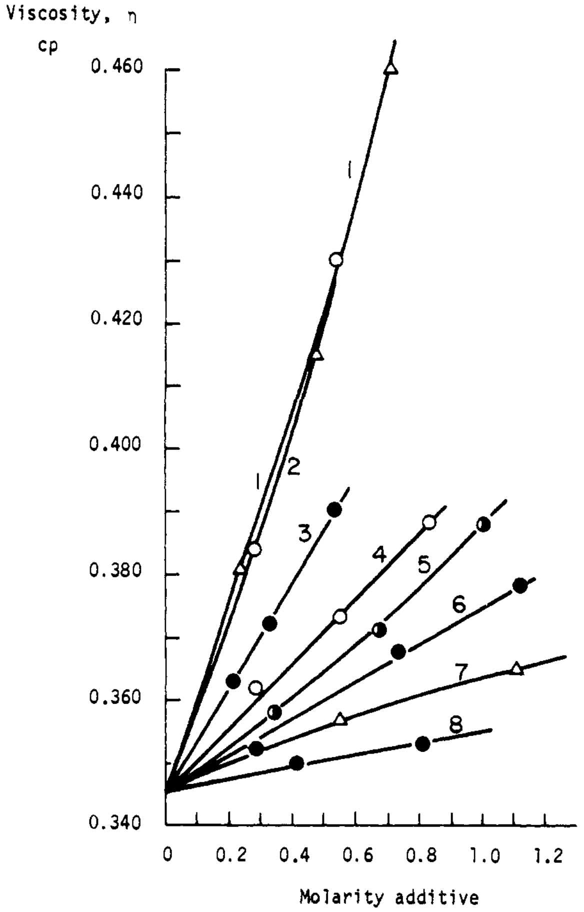

Figure 1. Plots of viscosity of solutions of additives in AN *vs.* molarity additive: (1) diethyl tartrate; (2) 3-nitrobenzoic acid; (3) benzoic acid; (4) ethyl benzoate; (5) acetophenone; (6) anisole; (7) 2,2,2-trifluoroethanol; (8) ethyl acetate. Viscosity of pure AN, 0.345 cP.

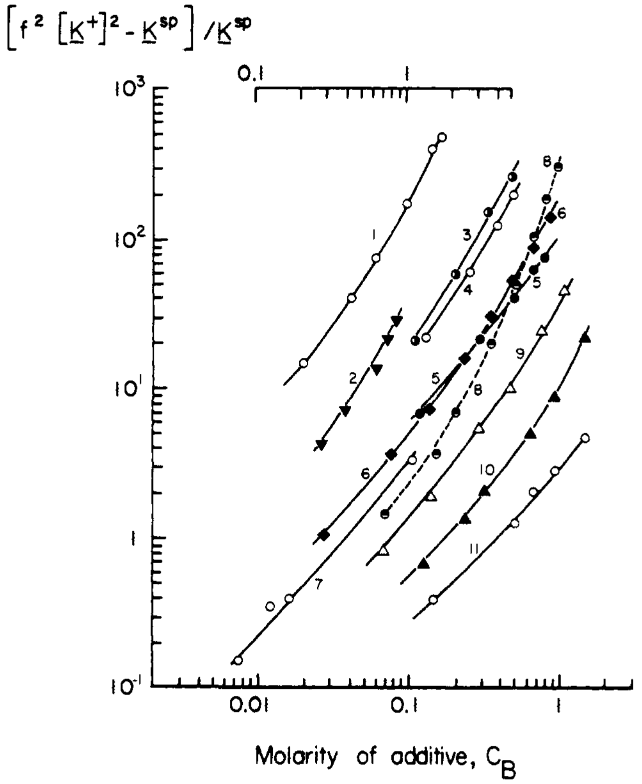

Figure 2. Plots of $[f^2[K^+]^2 - K^{sp}]/K^{sp}$ *vs.* C_B of potassium methanesulfonate in AN containing various additives B: (1) acetic acid; (2) diethyl tartrate; (3) salicylic acid; (4) 3-nitrobenzoic acid; (5) benzoic acid; (6) 4-bromophenol; (7) 4-nitrobenzamide; (8) ethylene glycol; (9) 2,2,2-trifluoroethanol; (10) methanol; (11) thioacetic acid. Top abscissa scale for 1 and 2, all others bottom abscissa.

10^{-2}, 9.47; and 0.260, 3.1. A plot of log Λ *vs.* log *c* has a slope of −0.74, a slope of −3/4 indicating simple dissociation of dimeric HA,[30,31] *viz.*, $(HA)_2 \rightleftarrows 2H^+ + 2A^-$. An average value of $K^d_{HA}/\sqrt{2\beta} = 4.7 \times 10^{-5}$ was obtained, $\beta = [(HA)_2]/[HA]^2$. It has been reported that fluorosulfuric acid is polymerized in sulfolane as solvent.[15] A more detailed study of equilibria in solutions of trifluoromethanesulfonic acid in AN is desirable but is beyond the scope of the present paper. The ionic dissociation of both sulfonic acids increases with time in AN, that of the stronger trifluoromethanesulfonic acid much more so than that of methanesulfonic acid. The specific conductivity of 0.0268 *M* trifluoromethanesulfonic acid increased from initially 7.0×10^{-4} to 7.2×10^{-4} after 15 min and to 8.0×10^{-4} ohm^{-1} cm^{-1} after 45 min, while that of 0.124 *M* methanesulfonic acid increased from 1.67×10^{-5} ini-

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Table II. Effect of Acetic Acid, HX, on Conductivity of Methane- or Trifluoromethanesulfonic Acid Solutions

C_{HX}	Specific conductivity, $ohm^{-1} cm^{-1} \times 10^5$	$\Sigma[H^+]$, $M \times 10^4$	f^2	V	y	$K^f_{H_2X^+}$
			$C_{CH_3SO_3H}$ = 0.149 M			
0	2.5_5	1.7	0.92	1.0	1.00	
0.148	4.2_6	2.8_7	0.92	10	2.8	$1.2_7 \times 10^1$
0.210	4.9_3	3.3_0	0.92	16	3.6_5	$1.2_7 \times 10^1$
0.375	6.0_3	4.0_5	0.92	35	5.3_5	$1.1_6 \times 10^1$
0.540	7.2_0	4.8_2	0.91	60	7.4_5	$1.2_0 \times 10^1$
0.860	9.3_5	6.2_8	0.91	119	12.0	$1.2_8 \times 10^1$
						Av 1.2×10^1
			$C_{CF_3SO_3H}$ = 0.0530 M			
0	$38._6$	$25._4$	0.7_1	1.00	1.00	
0.214	$48._6$	$31._0$	0.68	1.00	1.4_9	$2._3$
0.416	$50._6$	$34._0$	0.67	1.00	1.8_0	$1._9$
0.83	5.3_2	$35._5$	0.66	1.00	1.9_6	$1._2$
						Av $1._8$

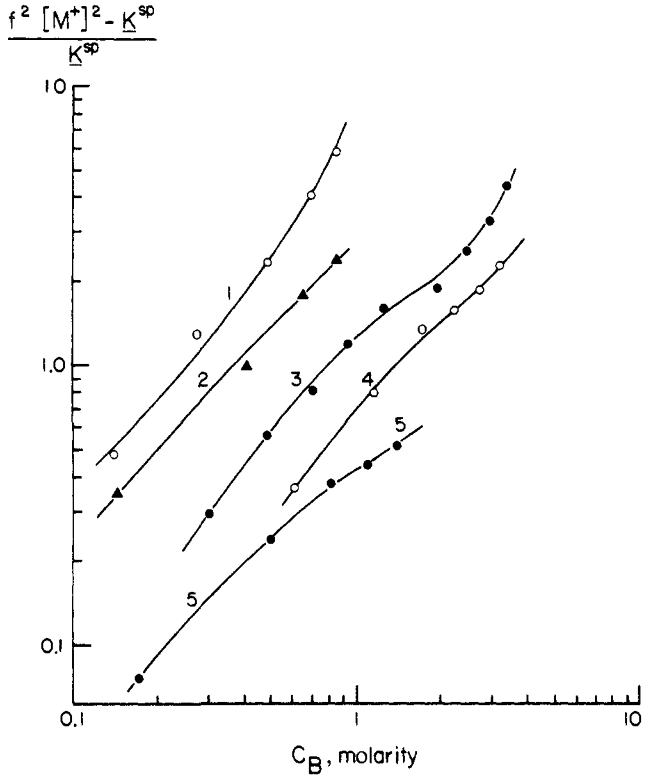

Figure 3. Plots of $[f^2[M^+]^2 - K^{sp}]/K^{sp}$ *vs.* C_B of potassium or cesium picrates in AN containing additives B: (1) ethylene glycol; (2) diethyl tartrate; (3) methanol and (5) trifluoroethanol with potassium picrate; (4) methanol with cesium picrate.

tially to 1.73×10^{-5} after 33 min, 1.90×10^{-5} after 4.7 hr, and 2.48×10^{-5} ohm^{-1} cm^{-1} after 33 hr. In view of this "aging" effect, all experiments involving measurements of the effect of B on the dissociation of the sulfonic acids were run within 15 min of preparation of the solutions. The slower rate of aging plus the extensive homoconjugation in methanesulfonic acid solutions, which represses BHA formation, constitute distinct advantages in the use of this acid over perchloric and trifluoromethanesulfonic acids for the study of the protonation of B. The mechanism of aging of acids in AN appears to be very involved and is the subject of further study.[32,33]

Determination of $K^f_{BH^+}$ from Dissociation of Sulfonic Acids in the Presence of HX(B). In solutions of HA in the presence of HX, the following electroneutrality condition holds.

$$[H_s^+] + [H_2X^+] = [A^-] + [HA_2^-] + [HX \cdot A^-] + [(HX)_2A^-] \quad (5)$$

$$([H_s^+] + [H_2X^+])/[H_s^+]_0 = \Sigma[H^+]/[H_s^+]_0 = \sqrt{\frac{y[V + K^f_{HA_2^-}[HA]]}{1 + K^f_{HA_2^-}[HA]}} \quad (6)$$

Substituting eq 5 into eq 1–4, eq 6 results, where the subscript zero denotes the absence of HX, $V \equiv 1 + K^f_{HX \cdot A^-}[HA] + \ldots$,[34] and $y \equiv 1 + K^f_{H_2X^+}[HX] + \ldots$.[34] As an example, Table II presents conductance data of methane- and trifluoromethanesulfonic acids with acetic acid as the base. Conductance data obtained at various concentrations of all other bases are available on microfilm.[35] Values of $K^f_{H_2X^+}$ in Table II calculated from conductance data of acetic acid in methanesulfonic acid do not vary with the concentration of acetic acid. Smaller values which decrease with increasing acetic acid concentration are found when trifluoromethanesulfonic acid is used. In systems involving the latter, ion pair formation of $CH_3COOH_2^+CF_3SO_3^-$ may be extensive. Equilibria in trifluoromethanesulfonic acid solutions appear to be quite involved. An example of calculation of $K^f_{BH^+}$ of acetic acid in methanesulfonic acid solution follows. Specific conductivities in 0.149 M CH_3SO_3H in the absence and in the presence of 0.540 M acetic acid are 2.55×10^{-5} and 7.20×10^{-5} ohm^{-1} cm^{-1}, corrected for viscosity, 0.346 and 0.353 cP, respectively, yielding $\Sigma[H^+]/[H_s^+]_0 = 2.7_7$. Using the values of $K^f_{HA_2^-} = 7 \times 10^3$,[17] $K^f_{HOAc \cdot CH_3SO_3^-} = 4.5 \times 10^1$, and $K^f_{2HOAc \cdot CH_3SO_3^-} = 1.2 \times 10^2$ (Table I), $V = 6 \times 10^1$ from eq 6 and $y = 7.4_5$. This yields $K_{CH_3COOH_2^+} = 1.2 \times 10^1$. The analytical and equilibrium concentrations of acetic acid and of methanesulfonic acid can be taken equal. A summary of the protonation constants, $K^f_{H_2X^+}$, of a number of other weak bases B in AN is presented in Table III. In most

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Table III. Protonation of Weak Bases in Acetonitrile

Base, B	$(\log K^{f}_{\mathrm{BH}^+})_{\mathrm{W}}$	$(\log K^{f}_{\mathrm{BH}^+})_{\mathrm{AN}}$[o]	${}^{\mathrm{AN}}\Delta^{\mathrm{W}} \log K^{f}_{\mathrm{BH}^+}$	$\mathrm{p}^{\mathrm{AN}}\gamma^{\mathrm{W}}_{\mathrm{B}}$	$\mathrm{p}^{\mathrm{AN}}\gamma^{\mathrm{W}}_{\mathrm{BH}^+}$[u]	$\mathrm{p}^{\mathrm{AN}}\gamma^{\mathrm{W}}_{\mathrm{BH}^+_{\mathrm{el}}}$[v]
Acetic acid	−6.1[a]	+1.1, +0.3[y]	7.2	−0.4	−1.3	-1.7_1
Thioacetic acid		+0.1				
Ethyl acetate	(−6.5)	≤−0.7	≤5.8	(+1.6)		
Oxalic acid		$+0.2_5$				
Glutaric acid		+0.7				
Benzoic acid	−7.3[b]	$+0.0_4$[y,s]	7.3	+1.5	+0.7	−1.6
4-Methylbenzoic acid	-6.9_2[b]	$+0.3_7$	7.3	+1.8	+0.8	−1.6
3-Nitrobenzoic acid	−8.0[b]	+0.3	8.3	$+1.6_4$	+1.8	−0.6
3,5-Dinitrobenzoic acid	−8.7[b]	+0.3	9.0	+1.8	+2.7	−0.1
2-Nitrobenzoic acid	−7.0[c]	+0.3	7.3	$+1.3_5$	+0.6	
2-Hydroxybenzoic acid	−6.8[c]	$+0.0_6$	6.9	+1.7	+0.5	
2,6-Dihydroxybenzoic acid		+0.1				
Phenol	−6.7[d]	+0.4	7.1			
4-Bromophenol		+0.4				
4-Nitrophenol	−9.1[e]	$+0.5_4$	9.6			
3-Hydroxyphenol		$+0.2_5$				
2-Nitrophenol		+0.1				
2-Hydroxyphenol		+0.3				
Diethyl ether	(−5.1),[w] (−3.6)[m]	+0.4[p]	(5.5), (4.0)			(−2.6), (−4.1)
Tetrahydrofuran	−2.1[d]	+1.1	3.2			−4.8
Anisole	−6.5[d]	-0.5_4, −0.3[y]	6.0			−2.1
Acetone	−7.2[f,g]	−0.1	7.1	+1.0[t]	0.0	−1.0
Acetophenone	−6.1[h]	-0.1_4	6.0			−2.1
Acetamide	+0.3,[a] +0.4[i]	+6.0[p]	5.7			−2.4
Thioacetamide		+4.7				
N,*N*-Dimethylformamide	0.0[j,k]	+6.1[q]	6.1			−2.0
Benzamide	-2.1_6[l]	$+3.7_6$	6.9	+0.4	−1.8	−2.2
3-Bromobenzamide	-2.7_5[l]	$+3.0_4$	5.8	+1.4	−0.9	−2.3
4-Nitrobenzamide	-3.2_3[l]	$+2.8_2$	6.0_5	+0.4	−1.7	−2.1
Dimethyl sulfoxide	0.0[m]	+5.8[q]	5.8			−2.3
Hydrogen sulfide		0.5		$+0.9_5$		
Water	(−6.7[w,x])	+2.2,[p] +3.9[r]	(4.5)			
Methanol	−2.3[n]	+2.4,[p] +3.2[r]	4.7	-0.2_5[t]	−3.7	
2,2,2-Trifluoroethanol		[s], +0.1[r]				
Ethylene glycol		+1.5, +2.7[r]				
2,3-Butanediol		+1.7, +2.2[r]				
trans-1,2-Cyclohexanediol		+1.6, +2.7[r]				
Diethyl tartrate		$+0.6_5$				

[a] A. Goldfarb, A. Mele, and N. Gutstein, *J. Amer. Chem. Soc.*, **77**, 6194 (1955). [b] Reference 44; value for 3,5-dinitrobenzoic acid extrapolated from Hammett plot of log $K^{f}_{\mathrm{BH}^+}$ *vs.* σ. [c] R. Stewart and M. Granger, *Can. J. Chem.*, **39**, 2508 (1961). [d] E. Arnett and C. Wu, *J. Amer. Chem. Soc.*, **82**, 5660 (1960); **82**, 4999 (1960). [e] Reference 45. [f] Reference 3. [g] H. Campbell and J. Edward, *Can. J. Chem.*, **38**, 2109 (1960). [h] C. Davies and T. Giesman, *J. Amer. Chem. Soc.*, **76**, 3507 (1954). [i] J. Koskikalio and S. Syrjaepalo, *Suom. Kemistilehti B*, **37**, 420 (1965). [j] R. Huisgea and H. Brade, *Ber.*, **90**, 1432 (1957). [k] R. Schaal, *J. Chim. Phys.*, **52**, 719 (1955). [l] Reference 7. [m] Reference 43, p 325. [n] Average value of −2.2 (ref 3) and −2.5 (N. Deno and J. Turner, *J. Org. Chem.*, **31**, 1969 (1966)). [o] This work. [p] Reference 35; I. M. Kolthoff and M. K. Chantooni, Jr., *J. Amer. Chem. Soc.*, **92**, 2236 (1970). [q] Reference 40. [r] Value of log $K^{f}_{\mathrm{B_2H}^+}$. [s] $K^{f}_{\mathrm{BH}^+} \sim 0$. [t] Calculated from free energies of solution of B in water and AN from data in ref 42 (see text). [u] $\mathrm{p}^{\mathrm{AN}}\gamma^{\mathrm{W}}_{\mathrm{H}^+} = -8.1$, ref 41. [v] $\mathrm{p}^{\mathrm{AN}}\gamma^{\mathrm{W}}_{\mathrm{H_a}} = -0.8$, unpublished results. [w] N. Deno and R. Taft, *J. Amer. Chem. Soc.*, **76**, 244 (1954). [x] Reference 5. [y] Value obtained with CF_3SO_3H, all others with CH_3SO_3H.

cases the acid used was methanesulfonic acid; a few very weak bases were also studied in trifluoromethanesulfonic acid solutions in which they were found to behave as such.

Spectrophotometric Determination of $K^{f}_{\mathrm{BH}^+}$ of Acetic Acid Using Hammett Indicators in Perchloric Acid Solutions. To interpret the results in Table IV of $[\mathrm{IH}^+]/[\mathrm{I}]$ of 2-nitro-4-chloro- (I) and 2-nitro-4,5-dichloroaniline in perchloric acid solutions containing various amounts of acetic acid, it was necessary to show that acetic acid does not form complexes with I. This has been done by determining conductometrically the ionic solubility of potassium chloride in the presence of I and in the presence of both I and acetic acid. The data are presented in Table V. The electroneutrality condition is

$$[\mathrm{K}^+] = [\mathrm{Cl}^-] + [\mathrm{HOAc}\cdot\mathrm{Cl}^-] + [\mathrm{I}\cdot\mathrm{Cl}^-] \quad (7)$$

while eq 8 and 9 represent the material balances in this

$$C_{\mathrm{HOAc}} = [\mathrm{HOAc}] + [\mathrm{HOAc}\cdot\mathrm{Cl}^-] + [\mathrm{I}\cdot\mathrm{HOAc}] \simeq [\mathrm{HOAc}] \quad (8)$$

$$C_{\mathrm{I}} = [\mathrm{I}] + [\mathrm{I}\cdot\mathrm{Cl}^-] + [\mathrm{I}\cdot\mathrm{HOAc}] \simeq [\mathrm{I}] \quad (9)$$

system. The approximations in eq 8 and 9 are valid since $C_{\mathrm{HOAc}} \gg [\mathrm{HOAc}\cdot\mathrm{Cl}^-]$, $[\mathrm{I}\cdot\mathrm{HOAc}]$ and $C_{\mathrm{I}} \gg [\mathrm{I}\cdot\mathrm{Cl}^-]$, $[\mathrm{I}\cdot\mathrm{HOAc}]$.

Substituting eq 8 and 9, $K^{\mathrm{sp}}_{\mathrm{KCl}} \equiv a_{\mathrm{K}^+}a_{\mathrm{Cl}^-}$, $K^{f}_{\mathrm{HOAc}\cdot\mathrm{Cl}^-} \equiv [\mathrm{HOAc}\cdot\mathrm{Cl}^-]/[\mathrm{HOAc}][\mathrm{Cl}^-]$, and $K^{f}_{\mathrm{I}\cdot\mathrm{Cl}} \equiv [\mathrm{I}\cdot\mathrm{Cl}^-]/[\mathrm{I}][\mathrm{Cl}^-]$, into eq 7, eq 10 results. Values of $K^{\mathrm{sp}}_{\mathrm{KCl}} = 1.1 \times 10^{-8}$[20] and $K^{f}_{\mathrm{HOAc}\cdot\mathrm{Cl}^-} = 3.6 \times 10^{2}$[29] have been

Table IV. Determination of $K^f_{CH_3COOH_2^+}$ in Perchloric Acid with Hammett Indicators, I

[HOAc], M	[IH$^+$]/[I]	[IH$^+$], $M \times 10^4$	[H$_s^+$], $M \times 10^4$	[CH$_3$COOH$_2^+$], $M \times 10^4$	$K^f_{CH_3COOH_2^+} \times 10^{-1}$
I = 2-Nitro-4-chloroaniline; $C_I = 1.35 \times 10^{-4}\ M$; $C_{HClO_4} = 3.13 \times 10^{-4}\ M$					
0.0122	3.1	1.02	1.0		
0.0238	$2._8$	1.00	1.0	$0._5$	1.2
0.0470	$2._5$	0.96	0.9_6	0.7	0.9
0.0700	$2._2$	0.93	0.9_3	0.9	0.9
0.0814	$1._9$	0.88	0.8_8	1.1_5	1.2
0.128	$1._5$	0.81	0.8_1	1.4	1.2
0.246	1.0	0.69	0.6_9	1.8	1.2
0.366	0.7_8	0.59	0.5_9	2.1	1.2
0.475	0.6_5	0.53	0.5_3	$2._2$	1.2
$C_I = 1.35 \times 10^{-4}\ M$; $C_{HClO_4} = 6.26 \times 10^{-4}\ M$					
0	(13.0)^a				
0.0244	$10._0$	1.23	$3._7$		
0.0694	$7._1$	1.16	3.5	1.5	(0.6)
0.108	$5._1$	1.12	2.6	2.6	0.9
0.198	$3._1$	1.02	1.5	3.7	1.1
0.256	$2._4$	0.95	1.2	4.1	1.3
0.412	$1._7$	0.84	0.8_3	4.6	1.3
0.474	$1._3$	0.75	0.6_3	$4._9$	1.6
					Av 1.2×10^1
I = 2-Nitro-4,5-dichloroaniline; $C_I = 1.22 \times 10^{-4}\ M$; $C_{HClO_4} = 3.00 \times 10^{-3}\ M$					
0	(4.0)^a				
0.108	3.0	0.93	23	7	
0.216	1.3	0.68	10	20	0.9
0.327	0.7_4	0.52	5.7	24	1.3
0.438	0.5	0.40	3.8	26	1.6
0.598	0.3_3	0.32	2.5	28	1.9

^{a} Extrapolated to zero concentration of acetic acid.

Table V. Solubility of Potassium Chloride in AN in the Presence of *o*-Nitro-*p*-chloroaniline (I) and Acetic Acid

C_I	C_{HOAc}	Specific conductivity $\times 10^4$	Λ_{KCl} or $\Lambda_{K(HOAc\cdot Cl^-)}$	[K$^+$], $M \times 10^4$	f^2	$\frac{f^2[K^+]^2 - K^{sp}}{K^{sp}}$ Obsd	Calcd^a	$\frac{f^2[K^+]^2 - K^{sp}}{K^{sp}[I]} = K^f_{I\cdot Cl^-}$
0	0	0.17_8	171	1.0_4	0.91			
0.0365	0	0.22_5	140	1.6_1	0.91	1.39		3.8×10^1
0.0957	0	0.29_1	137	2.1_3	0.91	3.20		3.3×10^1
0.160	0	0.37_4	135	2.7_6	0.90	6.00		3.7×10^1
0.214	0	0.43_1	134	3.2_1	0.90	8.18		3.8×10^1
0.273	0	0.48_7	133	3.6_6	0.89	11.2		4.1×10^1
0.273	0.068	0.85_5	131	6.5_2	0.84	35.4	34.5	
0.273	0.137	1.19	129	9.22	0.81	69.1	59.4	
0.273	0.238	1.51	127	11.9	0.78	112	96	
0.351	0.244	1.59	127	12.5	0.77	110	$100._5$	
								Av 3.7×10^1

^{a} Calculated assuming negligible formation of I·HOAc, HOAc·Cl$^-$, and I·Cl$^-$ (see text).

previously reported. From the data in the absence of acetic acid in Table V $K^f_{I\cdot Cl^-} = 3.7 \times 10^1$, which

$$f^2[K^+]^2 = K^{sp}_{KCl}[1 + K^f_{HOAc\cdot Cl^-}C_{HOAc} + K^f_{I\cdot Cl^-}C_I] \quad (10)$$

$$f_{K^+} = f_{Cl^-} = f_{HOAc\cdot Cl^-} = f_{I\cdot Cl^-}$$

indicates that 2-nitro-4-chloroaniline is about four times weaker a hydrogen-bond donor toward chloride than is benzoic acid (Table I). Weaker heteroconjugates were previously found[34] between 2-nitroaniline and benzoate ($K^f_{2\text{-NA}\cdot Bz^-} = 5.0$, $K^f_{2(2\text{-NA})\cdot Bz^-} = 6.8$). Agreement between calculated and experimental values in Table V of $[f^2[K^+]^2 - K^{sp}_{KCl}]/K^{sp}_{KCl}$ in the presence of both I and HOAc is excellent. It is reasonable to assume that 2-nitro-4,5-dichloroaniline is not complexed by acetic acid.

Spectrophotometrically determined values of [IH$^+$]/[I] of 2-nitro-4-chloroaniline in perchloric acid solutions containing various concentrations of acetic acid have been reported previously.[17] Additional data with this indicator and with 2-nitro-4,5-dichloroaniline are in Table IV. The acetic acid introduced with the perchloric acid in acetic acid has been taken into account in the calculation of the value of $K^f_{CH_3COOH_2^+}$ of 1.2×10^1, which is in good agreement with that of 1.3×10^1 in methanesulfonic acid solutions.

Solubilities of Weak Bases, B, in AN and Water. These data were needed in order to obtain values of the transfer activity coefficient,[36] $p^{AN}\gamma^{W}_{BH^+}$, reported in Table III (see Discussion). In AN and in water the

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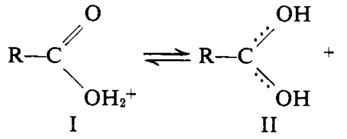
(36) There is general agreement between workers in the field to use the term "transfer activity coefficient" instead of medium effect, medium activity coefficient, transfer coefficient, degenerate activity coefficient, and other notations. The use of "distribution coefficient" originally proposed by N. Bjerrum and E. Larson, *Z. Phys. Chem.*, 127, 368 (1927), which was used by I. M. Kolthoff, *Pure Appl. Chem.*, 25, 305 (1971), is misleading because it refers to the transfer activity coefficient between two solvents which are mutually saturated with each other.

solubilities of the following substituted benzoic acids were found: 4-methyl, 0.163, 0.00278; unsubstituted, 0.85, 0.028;[37] 3-nitro, 0.78,[29] 0.0204;[37] 3,5-dinitro, 0.23,[29] 0.00634;[38] 2-nitro, 0.98,[29] 0.044;[39] and 2-hydroxy, 0.057, 0.016.[37] Corrected for ionic solubility, the molecular solubilities in water are 0.00246, 0.028, 0.0177, 0.00380, 0.044, and 0.012 M respectively for these acids in the order given. Ionic dissociation of these acids in AN is negligible as compared to the solubility. Furthermore, the solubilities in AN and in water of the following substituted benzamides have been determined: unsubstituted, 0.198, 0.470; 3-bromo, 0.00685, 0.172; and 4-nitro, 0.046 and 0.180 M, respectively. The solubility of hydrogen sulfide in AN was found to be 26.3 g of H_2S $l.^{-1}$ at 735-mm total pressure, or 0.915 M at 1 atm of H_2S over the solution. The corresponding value in water is 0.10 M.[38]

Since acetic acid, acetone, and methanol are miscible in all proportions in water and AN, values of $\mathrm{p}^{\mathrm{AN}}\gamma^{\mathrm{W}}{}_{\mathrm{B}}$ were calculated indirectly. The value of $\mathrm{p}^{\mathrm{AN}}\gamma^{\mathrm{W}}{}_{\mathrm{HOAc}}$ in Table III was found from $\mathrm{p}K^{\mathrm{d}}{}_{\mathrm{HOAc}} = 22.3$ in AN[40] and 4.8 in water, $\mathrm{p}^{\mathrm{AN}}\gamma^{\mathrm{W}}{}_{\mathrm{H^+}} = -8.1$,[41] and $\mathrm{p}^{\mathrm{AN}}\gamma^{\mathrm{W}}{}_{\mathrm{OAc^-}} = -9.8$,[41] previously reported. Values of $\mathrm{p}^{\mathrm{AN}}\gamma^{\mathrm{W}}{}_{\mathrm{B}}$ for acetone and methanol were calculated by Parker, *et al.*,[42] from Henry's law constants and solubility data.

Discussion

From a comparison of values of $(\log K^{\mathrm{f}}{}_{\mathrm{BH^+}})_{\mathrm{AN}}$ in Table III, which are considered to be reliable within ±0.2 unit, with those in water, indication may be obtained of which values in water appear to be unacceptable. For example, ethyl acetate has a constant which is at least 60 times smaller than that of acetic acid while in water as a reference solvent the reported value is only 4 times smaller. It is suspected that in the concentrated acid solution in water the ester is saponified.[43] Stewart and Yates[44] have presented strong evidence of carboxyl oxygen protonation of carboxylic acids (structure II) in water from the similarity of protonation in the benzoic acid and acetophenone series and from consideration of resonance stabilization of II. The



resonance stabilized protonated form cannot occur in the esters, thus accounting at least in part for the much smaller value of $K^{\mathrm{f}}{}_{\mathrm{BH^+}}$ in AN of ethyl acetate than of acetic acid (Table V). As expected, benzoic acid in AN behaves as a weaker base than acetic acid by about 1 unit, as in water. Within experimental error, and as expected from the constants of ethyl acetate and acetic and benzoic acids, no indication of protonation of ethyl benzoate in AN has been found; even a 0.5 M solution in 0.2 M methanesulfonic acid did not change the conductance (corrected for viscosity) of the acid. It is of interest to note that in AN $K^{\mathrm{f}}{}_{\mathrm{BH^+}}$ of benzoic acids is entirely independent of substitution, while in water a Hammett plot of $\log K^{\mathrm{f}}{}_{\mathrm{BH^+}}$ *vs.* σ (meta substituents) is claimed to yield a ρ value of -1.09.[44] It is also striking that $K^{\mathrm{f}}{}_{\mathrm{BH^+}}$ in AN of phenols is virtually unaffected by substitution with 2- and 4-nitro, 2-hydroxy, and 4-bromo groups. Of these substituted phenols, only a value for 4-nitrophenol of $K^{\mathrm{f}}{}_{\mathrm{BH^+}}$ of $10^{-9.1}$ has been reported in water,[45] which is more than 200 times smaller than that of unsubstituted phenol. On the other hand, the ratio of $K^{\mathrm{f}}{}_{\mathrm{BH^+}}$ values of the three benzamides (Table III) is the same in water as in AN. A very large effect of introduction of nitro and chlorine into aniline on $K^{\mathrm{f}}{}_{\mathrm{BH^+}}$ is observed both in water and AN. This effect is clear from values of $\log K^{\mathrm{f}}{}_{\mathrm{BH^+}} = 10.6$ of unsubstituted, 7.6 for 3-nitro-, 4.9 for 2-nitro-, 4.2 for 2-nitro-4-chloro-, and 3.1 for 2-nitro-4,5-dichloroaniline as determined in this laboratory.[17,34,40] These values of $\log K^{\mathrm{f}}{}_{\mathrm{BH^+}}$ in AN for the substituted anilines differ by 5.2 units from those in water. Hence these substituents apparently have the same effect on $\log K^{\mathrm{f}}{}_{\mathrm{BH^+}}$ of the anilines in water and AN.

The value of ${}^{\mathrm{AN}}\Delta^{\mathrm{W}} \log K^{\mathrm{f}}{}_{\mathrm{BH^+}}$ in AN and water for diethyl ether varies between +4.0 and 5.5, dependent on which value in the literature for $K^{\mathrm{f}}{}_{\mathrm{BH^+}}$ in water is used. The value of ${}^{\mathrm{AN}}\Delta^{\mathrm{W}} \log K^{\mathrm{f}}{}_{\mathrm{BH^+}}$ of tetrahydrofuran is abnormally small; it is suspected that the value reported in water should be much more negative. On the other hand, ${}^{\mathrm{AN}}\Delta^{\mathrm{W}} \log K^{\mathrm{f}}{}_{\mathrm{BH^+}}$ for anisole is of the same order of magnitude as that of the benzamides.

As expected, the phenols are much weaker bases than the aliphatic alcohols and water; water and the lower alcohols having about the same basic strength in AN.[34] Substitution by fluorine of three hydrogen atoms in ethanol greatly reduces the basic strength, 2,2,2-trifluoroethanol having a constant some 100 times smaller than that of methanol. The similarity of the values of the protonation constant of ethylene glycol and 2,3-butanediol with that of 1,2-cyclohexanediol, which is some four times less than that of methanol or water, suggests that *intra*molecular hydrogen bonding in BH^+, which would tend to stabilize BH^+, is absent. The much smaller protonation constant of diethyl tartrate, as compared to those of the above three diols, is likely due to an unfavorable inductive effect of the ester group. No evidence of diprotonation is found in any of the glycols. The glycols, with the exception of diethyl tartrate, form a hydrogen-bonded $BH^+\cdot B$ entity, as do the simple alcohols.[34] As expected, $K^{\mathrm{f}}{}_{\mathrm{BH^+}}$ of hydrogen sulfide is some 50 times smaller than that of water, no indication of $H_3S^+(H_2S)_x$ formation having been obtained. A similar effect of substitution of oxygen by sulfur is found on $K^{\mathrm{f}}{}_{\mathrm{BH^+}}$ in thioacetic acid and in thioacetamide.

It was found previously[19] that the acid strength $(K^{\mathrm{d}}{}_{\mathrm{HA}})$ of substituted benzoic acids parallels the hydrogen-bond donating strength toward chloride. From values of $K^{\mathrm{f}}{}_{\mathrm{HX\cdot Cl^-}}$ and $K^{\mathrm{f}}{}_{\mathrm{HX\cdot CH_3SO_3^-}}$ it appears that the hydrogen bond between chloride in AN with all acids listed in Table I is stronger than that with methanesulfonate, the values of $K^{\mathrm{f}}{}_{\mathrm{HX\cdot Cl^-}}$ being some four to

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(41) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Phys. Chem.*, **76**, 2024 (1972).

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(45) V. Gold and D. Satchell, *J. Chem. Soc.*, 3609 (1955).

Table VI. Calculated Values of $p^{AN}\gamma^{W}_{H_2X^{+}_{el}} - p^{AN}\gamma^{W}_{X^{-}_{el}}$

Acid	$\log K^{f}_{H_2X^+}$ (Table III) AN	W	pK^{d}_{HX} AN	W	$^{AN}\Delta^{W} \log K$	$p^{AN}\gamma^{W}_{H_2X^{+}_{el}} -$ $p^{AN}\gamma^{W}_{X^{-}_{el}}$
Acetic acid	+1.1	−6.1	22.3	4.8	24.7	8.5
Benzoic acid	+0.1	−7.3	20.7	4.2	23.9	7.7
3-Nitrobenzoic acid	+0.3	−8.0	19.3	3.5	24.1	7.9
3,5-Dinitrobenzoic acid	+0.3	−8.7[a]	16.9	2.8	23.1	(6.9)[a]
Phenol	+0.4	−6.7	27.2	10.0	24.3	(8.1)[b]
4-Nitrophenol	+0.5	−9.1	20.7	7.2	23.1	(6.9)[b]

[a] From Hammett plot of $\log K^{f}_{H_2X^+}$ in water *vs.* σ. [b] It is questionable whether for phenolates (Ph) $p\gamma_{Ph^{-}_{n}} = p\gamma_{PhH} - p\gamma_{H_a}$.

eight times as large as $K^{f}_{HX\cdot CH_3SO_3^-}$. As expected, trifluoroethanol acts as a stronger hydrogen-bond donor toward methanesulfonate than do water or methanol, $K^{f}_{HX\cdot CH_3SO_3^-}$ of the fluorinated alcohol being some two to three times that of the nonfluorinated compounds. The value of $K^{f}_{HX\cdot CH_3SO_3^-}$ of thioacetic acid is 16 times smaller than that of acetic acid. This suggests that thioacetic acid is present predominantly in the thiol form in AN as in acetone[46] from nmr studies.

Transfer Activity Coefficient of Protonated Weak Bases between AN and Water. The difference in log $K^{f}_{BH^+}$ between AN and water in terms of transfer activity coefficients is expressed by eq 11. Assuming in eq

$$^{AN}\Delta^{W} \log K^{f}_{BH^+} = p^{AN}\gamma^{W}_{BH^+} - p^{AN}\gamma^{W}_{H^+} - p^{AN}\gamma^{W}_{B} \quad (11)$$

11 that the neutral contribution to the transfer activity coefficient of the protonated base is equal to that of the unprotonated base, *i.e.*, $\gamma_{BH^+} = \gamma_{B}$, as was done similarly for benzoic acids, HX, and their anions, X^-,[29] and taking $p^{AN}\gamma^{W}_{BH^+} = p^{AN}\gamma^{W}_{BH^{+}_{n}} + p^{AN}\gamma^{W}_{BH^{+}_{el}}$,[29] eq 12 results. The assumption that

$$^{AN}\Delta^{W} \log K^{f}_{BH^+} = p^{AN}\gamma^{W}_{BH^{+}_{el}} - p^{AN}\gamma^{W}_{H^+} \quad (12)$$

$\gamma_{BH^{+}_{n}} = p\gamma_{B}$ is of doubtful validity when BH^+ and B are two different tautomeric forms. When B is a Brønsted acid, HX, the hydrogen-bond accepting transfer coefficient, $p\gamma_{H_a}$, should be considered, $p\gamma_{HX} = p\gamma_{(n)} + p\gamma_{H_a}$,[29] and we get

$$^{AN}\Delta^{W} \log K^{f}_{H_2X^+} = p^{AN}\gamma^{W}_{H_2X^{+}_{el}} - p^{AN}\gamma^{W}_{H_a} - p^{AN}\gamma^{W}_{H^+} \quad (12')$$

On the basis of the $\gamma_{AsPh_4^+} = \gamma_{BPh_4^-}$ assumption, values of $p^{AN}\gamma^{W}_{BH^+}$ in Table III were calculated from eq 11 taking $p^{AN}\gamma^{W}_{H^+} = -8.1$,[41] while values of $p^{AN}\gamma^{W}_{BH^{+}_{el}}$ were calculated from eq 12′ using $p^{AN}\gamma^{W}_{H_a} = -0.8$ (unpublished results). With the exception of tetrahydrofuran, benzoic acids, and acetone, the values of $p^{AN}\gamma^{W}_{BH^{+}_{el}}$ are equal to -2.2 ± 0.3 (Table III). It is reasonable to conclude that this negative value of $p^{AN}\gamma^{W}_{BH^{-}_{el}}$ indicates considerably stronger hydrogen bonding of BH^+ to water than to AN. The value of $p^{AN}\gamma^{W}_{BH^{+}_{el}}$ of −1.65 for benzoic and 4-methylbenzoic acids also indicates much stronger hydrogen bonding of H_2X^+ to water than to AN. These values of $p^{AN}\gamma^{W}_{BH^{+}_{el}}$ become 2.3 units more positive when the calculation of $^{AN}\gamma^{W}_{i}$ is based on the ferrocene assumption, rather than the tetraphenylborate assumption[41] ($p^{AN}\gamma^{W}_{H^+}$ becomes −5.8 instead of −8.1). On the basis of the ferrocene assumption $p^{AN}\gamma^{W}_{BH^{-}_{el}}$ is of the order of 0 to +0.5, which is highly improbable, considering that the Born effect, combined with the stronger hydrogen bonding of BH^+ with water than with AN, undoubtedly has a larger effect on $p^{AN}\gamma^{W}_{BH^{+}_{el}}$ than ion–dipole interaction.

Considering the diprotonation of the carboxylate ions, X^-, to H_2X^+, it is of interest to consider a relation between $p^{AN}\gamma^{W}_{H_2X^{+}_{el}}$ and $p^{AN}\gamma^{W}_{X^{-}_{el}}$. Using the notation

$$^{AN}\Delta^{W} \log K = {}^{AN}\Delta^{W} \log K^{f}_{H_2X^-} - {}^{AN}\Delta^{W} \log K^{d}_{HA} \quad (13)$$

we obtain

$$^{AN}\Delta^{W} \log K = p^{AN}\gamma^{W}_{H_2X^+} - p^{AN}\gamma^{W}_{X^-} - 2p^{AN}\gamma^{W}_{H^+} \simeq p^{AN}\gamma^{W}_{H_2X^{+}_{el}} - p^{AN}\gamma^{W}_{X^{-}_{el}} - 2p^{AN}\gamma^{W}_{H^+} \quad (14)$$

Data of $p^{AN}\gamma^{W}_{H_2X^+} - p^{AN}\gamma^{W}_{X^{-}_{el}}$ for acetic acid, benzoic acid and its 3-nitro substitute, phenol, and 4-nitrophenol are listed in the last column of Table VI; they are found to be of the order of +7. Considering that $p^{AN}\gamma^{W}_{H_2X^{+}_{el}}$ is of the order of −1.7 for the carboxylic acids, the values of $p^{AN}\gamma^{W}_{X^{-}_{el}}$ are of the order of −9. Since the charge on X^- is localized, this value is reasonable.

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Supplementary Material Available. Conductance data obtained at various concentrations of all other bases will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-8539.

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