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Ionization of Anilines in Carboxylic Acid Solvents. Equilibrium Constants, Stoichiometry, Solvent and Substituent Effects, Electric Dipole Moments, and Proton Exchange[1]

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Abstract: On the basis of electric dipole moments, base ionization of substituted anilines and tertiary amines (B) in octanoic acid (HA) is best represented by the chemical equation $B \cdot HA + HA \rightleftarrows BH^+ \cdot A^- \cdot HA$ and appears not to be ultrafast. Equilibrium constants (K_i) for the ionization of a series of *N,N*-dialkylanilines were measured spectrophotometrically in acetic, propionic, and octanoic acid. Substituent effects on log K_i were approximately equal in these three solvents. Solvent effects on log K_i for several anilines conformed fairly well to a dipole-solvation model.

According to Eigen,[2] the kinetics of Brønsted acid-base reactions is usefully discussed in terms of the three-step scheme in eq 1-3.

$$HA + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \cdot HA \text{ (hydrogen-bond association)} \quad (1)$$

$$B \cdot HA \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} BH^+ \cdot A^- \text{ (ionization)} \quad (2)$$

$$BH^+ \cdot A^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} BH^+ + A^- \text{ (ion-pair dissociation)} \quad (3)$$

Eigen also suggested that many exoergic acid-base reactions are diffusion controlled, *i.e.*, $k_i > k_2$. This would imply that the rate constant for ionization (k_i) is greater than $\sim 10^{10}$ sec^{-1}. This is possible because the proton may tunnel through, rather than surmount, the potential barrier that separates the states $B \cdot HA$ and $BH^+ \cdot A^-$.[3] The actual proton tunneling frequency may be as high as 10^{12}–10^{14} sec^{-1}.[4] Proton transfer at such rates of speed has been called *ultrafast*.

In the present paper we investigate the speed of the ionization step in the ionization of anilines in carboxylic acid solvents by a combination of dipole moment and spectrophotometric measurements. Recent work by others[5-7] has demonstrated that electric dipole moments of hydrogen-bonded acid-base complexes are particularly informative about the nature of the ionization step. We hope to demonstrate that, when the degree of ionization is measured by an independent method, the electric dipole moments can also tell us whether proton transfer is ultrafast.

Carboxylic Acid Solvents. In terms of the general scheme in eq 1-3, the acid-base reactions of anilines in carboxylic acid solvents of low dielectric constant, such as acetic acid, are relatively simple because the concentrations of the "free" base B in (1) and of the dissociated ions BH^+ in (3) are stoichiometrically insignificant. The ionization step (eq 2) is therefore isolated. That the unprotonated aniline exists largely in the form of hydrogen-bonded complexes is indicated by the optical absorption in the region of the $n \rightarrow \pi^*$ transition, which closely resembles that in methanol and clearly differs from that in cyclohexane.[8,9] That the anilinium ion exists largely in the form of ion pairs is indicated by the small magnitude of the ion-pair dissociation constant.[9]

Concerning the *speed* of the ionization step, in acetic acid, an indirect estimate of the rate constant k_i is available from the analysis of proton exchange rates.[10-12] The minimum value for k_i is thus found to be in the range 1×10^8 to 3×10^9 sec^{-1} for a series of bases ranging from methylamine to *p*-fluoroaniline, for which the ionization constants K_i ($=k_i/k_{-i}$) in acetic acid range from 8×10^5 to 5. However, according to the most plausible reaction mechanism, k_i should be well above 10^9 sec^{-1} and might be as high as 10^{12}–10^{14} sec^{-1}, *i.e.*, of the characteristic magnitude for exoergic proton tunneling.[10]

Relaxation Time for Ionization and Electric Dipole Moment. To see why the dipole moment of an equilibrium mixture of acid-base complexes might indicate whether proton transfer is ultrafast, we must consider the time scales of various measurements. For the electronic absorption spectrum, the time scale is of the order of electronic transition times ($\sim 10^{-15}$ sec), which is short compared to the time scale for proton tunneling. Hence the ionized and un-ionized states in (2) would be observed as discrete molecular

species, that is, the absorption spectrum is a sum of discrete spectra assignable to the two states, as is in fact the case.[8,9,13]

On the other hand, for the dielectric constant of polar liquids, the time scale is of the order of molecular rotation times, which for solutes and solvents of the sort we are considering is of the order of 10^{-11} sec.[14] In the case of acid-base ionization, one would compare the mean dielectric relaxation time τ_D of the complexes with the relaxation time $(k_i + k_{-i})^{-1}$ for chemical exchange. Recent reviews have emphasized the effect of chemical exchange on dielectric relaxation at high frequencies.[14-16] However, there is also a noticeable effect on the dielectric constant at audiofrequencies and hence on the apparent dipole moment.[17] Thus, for the equilibrium mixture of ionized and un-ionized acid-base complexes, if $(k_i + k_{-i}) \gg 1/\tau_D$, the observed dipole moment will be an average that is typical of a *single molecular species*. That is, if the relative populations and dipole vectors of $B \cdot HA$ and $BH^+ \cdot A^-$ in (2) are x and μ_u and $(1 - x)$ and $\mu_\pm$, respectively, then the observed dipole vector is given by eq 4.[18]

$$\mu_{obsd} = x\mu_u + (1 - x)\mu_\pm; \quad (k_i + k_{-i}) \gg 1/\tau_D \quad (4)$$

By contrast, if $(k_i + k_{-i}) \ll 1/\tau_D$, the observed dipole moment for the equilibrium mixture will be an average that is typical of *two discrete molecular species*. Under these conditions, dielectric relaxation is "fast" and leads to the establishment of separate Boltzmann distributions of dipole orientations in the electric field. The formal polarization per formula weight of the equilibrium mixture ($B \cdot HA + BH^+ \cdot A^-$) is therefore a sum of independent contributions, as in (5). Here P_u and $P_\pm$ denote the molar polarizations due to the un-ionized and ionized molecules, respectively.

$$P_{formal} = xP_u + (1 - x)P_\pm \quad (5)$$

Following Jadzyn and Malecki[7] we shall assume that the molecular polarizabilities α_u and $\alpha_\pm$ are equal to obtain eq 6.

$$\mu_{obsd} = [x\mu_u^2 + (1 - x)\mu_\pm^2]^{1/2}; \quad (k_i + k_{-i}) \ll 1/\tau_D \quad (6)$$

Except when $\mu_u = \mu_\pm$, the root-mean-square (rms) average (eq 6) will be greater than the mean-vector average (eq 4). Thus, if x, μ_u, and $\mu_\pm$ are known, a distinction between the two cases is theoretically possible.

Experimental Considerations and Findings. In practice, to distinguish between the two cases, one would like to have $0.2 < x < 0.8$ and a large difference between μ_u and $\mu_\pm$. It is necessary to predict μ_u and $\mu_\pm$ from dipole moments of model compounds, which necessarily entails some loss of accuracy. However, previous work suggests that this may not be serious. The difference between μ_u and $\mu_\pm$ is relatively large and the interaction moment $\delta\mu = \mu_{complex} - \mu_{HA} - \mu_B$ for un-ionized complexes is independent of acid-base strength and approximately 0.5 D.[5,6,7,19]

In the present work we chose octanoic acid for the solvent because of the low dielectric constant ($D = 2.457$ at 26.2°), which effectively represses any ion-pair dissociation and the attendant electrolytic conductance, thus allowing electric dipole moments to be measured with high accuracy.[20] Values of μ_{obsd} will be reported for *N,N*-diethylaniline ($K_i = 0.51$) and *N,N,*4-trimethylaniline ($K_i = 0.22$). The dipole moment of 4-bromo-*N,N*-diethylaniline ($K_i \sim 0.02$) served as a model for predicting μ_u, and that of *N,N*-dimethylbenzylamine ($K_i \approx 63$) served for predicting $\mu_\pm$. The last ionization constant is predicted by a linear free energy relationship. In order to establish that relationship and to study the effect of the dielectric constant on K_i, we also measured K_i for a series of anilines in acetic acid ($D = 6.15$ at 26.2°) and propionic acid ($D = 3.32$ at 26.2°).

We found that μ_{obsd} for *N,N*-diethylaniline and *N,N,*4-trimethylaniline, while not in perfect agreement with the predictions of either model, are definitely closer to prediction by eq 6 than by eq 4. The conclusion that $(k_i + k_{-i}) < 1/\tau_D$ (*i.e.*, $< 10^{11}$ sec^{-1}) seems justified.

Solvation of $BH^+ \cdot A^-$. In view of the usual importance of proton tunneling in the ionization of oxygen and nitrogen acids and bases, the present result is perhaps surprising. However, the actual data obtained for μ_u and $\mu_\pm$ may offer an explanation. While μ_u is consistent with a 1-to-1 comlex of the type $B \cdot HA$, $\mu_\pm$ is not consistent with known dipole moments of ion pairs of the type $BH^+ \cdot A^-$. For example, μ for $Et_3NH^+ \cdot O_2CCCl_3^-$ in dioxane is 9.6 D,[5] while $\mu_\pm$ for $Me_2BzNH^+ \cdot O_2C.C_7H_{15}^-$ in octanoic acid is 5.25 D. The relatively small dipole moment in octanoic acid could be consistent with an ion pair of the type $BH^+ \cdot A^- \cdot HA$ and a geometrical structure such as that shown in Figure 1, in which the anion is homoconjugated to a solvent molecule.[21] The ionization therefore is not simply the transfer of a proton but also requires the reorientation of at least one solvent molecule.

Experimental Section

Materials. Baker Analyzed acetic acid was selectively crystallized three times in 5-lb lots according to Ceska.[8] Certified propionic acid was refluxed with potassium permanganate overnight. The acid was fractionally distilled at atmospheric pressure; the middle fraction, boiling at 140-141°, was collected. Highest purity octanoic acid was partially frozen twice, followed by reduced pressure distillation three times. The middle fraction was collected at a reduced pressure at which the head temperature was 100°. All operations were performed, and the solvents were stored in the dark, under nitrogen. The amount of water present in each acid was well below 10^{-2} *M*, as determined by titration with Karl Fischer reagent.

For spectrophotometry, 99.9 mol % pure certified methanol was used without further purification. Fischer Certified 1-octanol, 2-octanol, and 4-octanol were twice distilled under reduced pressure. Center fractions were collected and stored in the dark under nitrogen.

Fischer thiophene-free benzene was fractionally distilled and the middle fraction collected and stored in the dark over 4-Å molecular sieves.

The tertiary anilines were purchased in the highest purity commercially available. *N,N*-Diethyl-, *N,N*-di-*n*-butyl-, *N,N*-dimethyl-3-methyl-, and *N,N*-diethyl-4-methylanilines were obtained from Fisher Scientific Co.; *N,N*-dimethyl-4-methylaniline was obtained from Aldrich Chemical Co.; *N,N*-di-*n*-propyl-, *N,N*-dimethyl-4-bromo-, *N,N*-diethyl-4-bromo-, and *N,N*-diethylanilines were obtained from Eastman Organic. Highest purity *N,N*-dimethylbenzylamine was obtained from Fisher Scientific Co.

The liquid anilines were distilled under vacuum and the middle fractions were collected. The solid anilines were recrystallized from ethanol-water and stored in a desiccator.

Solution Preparation. Solutes were weighed out on a microbalance with an accuracy of better than 0.25%. Liquid anilines were weighed out immediately after distillation. In each case, care was taken to minimize possible air oxidation of the anilines and access of moisture to the solutions. Dilutions were routinely done in a drybox filled with nitrogen gas. Dielectric constant measurements were made in a nitrogen thermostat. Spectrophotometric and density measurements were made in tightly glass-stoppered containers. In all cases, the measurements were completed within 4 hr after solution preparation.

Spectrophotometry. Optical density was measured with an Hitachi Perkin-Elmer Model 323 recording spectrophotometer, with typical accuracy of 0.25%. Solutions were placed in 10 or 5 mm Beckman precision quartz cells and were maintained at 26.2 ± 0.1° by means of a water-jacketed thermostatted cell holder. Ultraviolet spectra were recorded between 360 nm and the instruments's cut-off point due to solvent absorption. For the carboxylic

acids this point was ~250 nm, and for the alcohols spectra were taken to 210 nm.

Dielectric Constants. The basic instrument was a General Radio type 1615 transformer ratio arm bridge. The measuring system was similar to that described by Grunwald and Effio,[22] except that General Radio Model 1238 detector and Model 1316 oscillator were used. The stainless-steel guarded three-terminal cells described previously[22] were modified, by insertion of two posts, to ensure that the electrodes are rigidly in the same relative position about the cylindrical cell axis. The air capacitance of these cells was 18 pF. Cells containing the solvent and three solutions were suspended side-by-side in a nitrogen atmosphere maintained precisely at 26.2° inside a 26.2° water-jacketed Pyrex vessel similar in shape to that described previously.[22] Temperature equilibration required 1–2 hr.

Measurements were made on solutions in benzene and octanoic acid. In each experiment, capacitance and conductance were measured at six frequencies ranging from 2 to 50 kHz.

Equations for bridge balance have been given by Pribadi and Kay.[23] Treatment of the data and calculation of the dielectric constant at zero frequency followed previous practice.[22] Conductances were in the range $0.04–1 \times 10^{-9}$ ohm^{-1} cm^{-1} and did not increase appreciably when base was added.

For octanoic acid solutions, the capacitance was about 44 pF and could be measured with a precision of ±0.002 pF, which corresponds to $\pm 1 \times 10^{-4}$ in D. Values of D_0 for the pure solvent, determined with four cells that were equilibrated side-by-side in the dry-nitrogen thermostat, showed a standard deviation of 5×10^{-4}. This latter value should be a conservative estimate of the accuracy of the measured dielectric increments $\Delta D = D_{soln} - D_0$.

For benzene solutions, the capacitance was about 41 pF and could be measured with a precision of 0.003 pF, which corresponds to $\pm 2 \times 10^{-4}$ in D. Values of D_0 for the pure solvent, determined with four cells that were equilibrated side-by-side, showed a standard deviation of 2×10^{-4}.

The magnitudes of the dielectric increments ranged from 0.005 to 0.060.

Special care was taken in cleaning the cells. Electrodes and Teflon stoppers were rinsed with acetone and methanol and allowed to soak in methanol for 30 min. Each component was rinsed finally with methanol and dried by continuous pumping for 2 hr in a vacuum desiccator.

Density Measurements. Densities were measured for 0.02–0.08 *m* solutions and solvents in benzene and octanoic acid with a precision of better than 0.01%, using calibrated twin-necked pycnometers with graduated necks. Temperature was maintained precisely at 26.2°. Temperature equilibration required 2–3 hr.

Within the experimental error, density was in all cases a linear function of molal concentration. The results, expressed in terms of the apparent molal volume of the solute (φV_2/ml mol^{-1}) are as follows: *N,N*-diethyl-4-bromoaniline, 159 ± 2 (benzene), 177 ± 2 (octanoic acid); *N,N*-diethylaniline, 150 ± 3 (benzene), 158 ± 2 (octanoic acid); *N,N*-dimethylbenzylamine, 161 ± 4 (benzene); 127 ± 3 (octanoic acid); *N,N*,4-trimethylaniline, 158 ± 4 (octanoic acid).

Results

Ionization Constants. The concentration of un-ionized aniline in the equilibrium mixture was measured by means of the absorption band due to the $^1A \rightarrow {}^1L_b$ transition.[24] For the *N,N*-dialkyl anilines examined in this work, the band maximum (λ_{max}) for this band occurs in the region 280–315 nm. The absorbance due to ionized species is negligible in this region, as shown by the absence of this band in the presence of excess perchloric acid.

To deduce the concentration of un-ionized aniline from the optical density, the molar extinction coefficient (ϵ) must of course be known. In previous work, ϵ_{max} at the band maximum (λ_{max}) in the carboxylic acid solvent was assumed to be equal to ϵ_{max} for the corresponding band of the un-ionized aniline in an alcohol solvent. Isaacs, in early work, used ϵ_{max} as measured in ethanol.[25] Puar and Grunwald[11] used ϵ_{max} as measured in methanol. This assumption can now be tested.

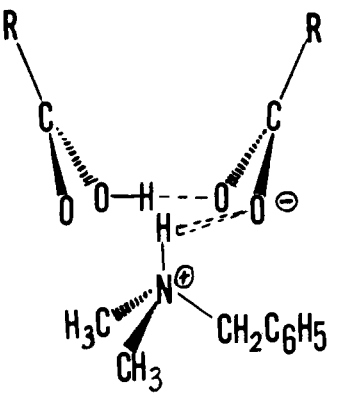

Figure 1. A possible structure for the solvent-homoconjugated *N,N*-dimethylbenzylammonium octanoate ion pair. In the structure shown, the O—H···O atoms are assumed to be collinear, the C—O—H bond angle is 105°, and the angle between the O—C=O planes is 30°.

Some of the tertiary anilines are so weakly ionized in octanoic acid that an estimate of K_i (always less than 0.15) can be made by linear free energy correlation with sufficient accuracy to establish ϵ_{max} in this solvent to 2% or better. Results obtained in this way are shown in Table I. It is seen that ϵ_{max} in methanol agrees with ϵ_{max} in octanoic acid, with a mean deviation of 2.0%. In propionic acid, a single comparison gives a deviation of 9.6%. Accordingly, in estimating errors for K_i, we shall assume 10% errors for ϵ_{max} in acetic and propionic acid and 3% errors for ϵ_{max} in octanoic acid.

Table I. Optical Properties for the First Uv Absorption Band of Un-ionized Aniline Bases

Aniline	Solvent (K_i)[a]	λ_{max}, nm	ϵ_{max}, %[b]
N,N-Me_2	MeOH	298	1942
	1-OctOH	299	2134
	2-OctOH	298	2158
	4-OctOH	298	2229
	$C_7H_{15}CO_2H$ (0.058)	299	1897 (−2.3%)
N,N-Me_2-4-Br	MeOH	310	1961
	$C_7H_{15}CO_2H$ (0.005)	312	1963 (+0.1%)
	$C_2H_5CO_2H$ (0.043)	310	1772 (−9.6%)
N,N-*n*-Pr_2	MeOH	305	2275
	$C_7H_{15}CO_2H$ (0.141)	305	2376 (+4.4%)
N,N-3-Me_3	MeOH	298	2025
	$C_7H_{15}CO_2H$ (0.138)	299	1999 (−1.3%)
N,N-Et_2-4-Br	MeOH	315	2108
	$C_7H_{15}CO_2H$ (0.035)	315	2141 (+1.6%)

[a] K_i is estimated from linear free energy relationship. [b] (%) = % discrepancy relative to ϵ_{max} in MeOH.

Results obtained for K_i, and their estimated errors, are summarized in Table II. The errors are due largely to the stated errors of prediction of ϵ_{max}.

Electric Dipole Moments. Within the experimental error, dielectric constant varied linearly with solute concentration over the entire range (0.005–0.06 *M*). Dipole moments of the solutes were calculated from the molar dielectric increments, $S = dD/dc_2$, according to Onsager's theory. Details have been given elsewhere.[26]

Results are listed in Table III. The calculation of the dipole moments utilized data listed in that table, as well as apparent molal volumes φV_2 listed in the preceding section. In calculating dipole moments in octanoic acid, it was assumed that the un-ionized base is a solvate with the formula B · HA and that the ionized species is a solvate with the formula $BH^+ \cdot A^- \cdot HA$. Thus the molar volume V_2 and refraction R_2 of the solute were taken to be, $V_2 = \varphi V_2 + xV_1 + 2(1 - x)V_2$, and $R_2 = R(\text{pure solute}) + xR_1 +$

Table II. Base Ionization Constants of Tertiary Anilines in Acetic Acid, Propionic Acid, and Octanoic Acid at 26.2° (The ϵ_{max} and λ_{max} Measured in Methanol Are Given)

Aniline	MeOH ϵ_{max}	MeOH λ_{max}	K_i^{HAc}	K_i^{HPro}	K_i^{HOct}
N,N-Me_2	1942	298	12.4 ± 1.3	0.84 ± 0.18	0.058[a]
N,N-Me_2 4-Br	1961	310	1.10 ± 0.21	0.043[a]	0.005[a]
N,N,3-Me_3	2025	298	30.3 ± 3.1	1.44 ± 0.24	0.138[a]
N,N,4-Me_3	1665	304	57.3 ± 5.8	1.89 ± 0.29	0.22 ± 0.04
N,N-Et_2	2231	304	127 ± 13	10.3 ± 1.1	0.51 ± 0.05
N,N-Et_2 4-Me	2108	315	303 ± 30	18.4 ± 1.9	1.42 ± 0.07
N,N-*n*-Pr_2	2275	305	31.0 ± 3.2	1.23 ± 0.22	0.141[a]
N,N-*n*-Bu_2	2481	305	37.3 ± 3.8	1.72 ± 0.27	0.20 ± 0.04

[a] K_i is estimated from linear free energy relationship.

Table III. Dielectric Data and Electric Dipole Moments

Aniline	R_D[a]	Benzene[b] S	Benzene[b] μ_2	Octanoic acid[c] S	Octanoic acid[c] μ_2
N,N-Et_2-4-Br	58.27	1.632 ± 0.029	3.76	1.630 ± 0.037	3.87
N,N,4-Me_3	44.74		1.30[d]	0.845 ± 0.047	3.01
N,N-Et_2	49.40		1.76[e]	1.451 ± 0.062	3.79
N,N-Dimethylbenzylamine	45.96	0.039 ± 0.036	0.72	3.04 ± 0.15	5.25

[a] Molar refraction of pure liquid substrate. [b] Solvent properties at 26.2°: n_D 1.4975 (R. R. Dreisback and R. A. Martin, *Ind. Eng. Chem.*, **41**, 2875 (1949), ρ 0.8718, D_0 2.2696. [c] Solvent properties at 26.2°: n_D 1.4256 (J. A. Riddick and W. B. Bunger, "Techniques of Chemistry II. Organic Solvents: Physical Properties and Methods of Purification," 3rd ed, Wiley-Interscience, New York, N.Y., 1970), ρ 0.9050, D_0 2.4566. [d] A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963. [e] K. K. Srivastava and J. K. Vij, *Bull. Chem. Soc. Japan*, **43**, 2307 (1970).

$2(1 - x)R_1$, respectively, where $x = 1/(1 + K_i)$. While this approach is consistent with our final conclusions, it should be stressed that the assumption of specific solvation numbers has little effect on the value obtained for the dipole moment.[27]

Discussion

Linear Free Energy Correlations. Grunwald and Ceska[28] have pointed out that substituent effects in reactions of aniline in which the transition state resembles an ion pair are better correlated with log K_i in acetic acid than with log K_B for the base dissociation of the aniline in water. The reason for this seems to be that base dissociation involves both ionization and ion-pair dissociation (eq 2 and 3) and that substituent effects on ion-pair dissociation are not well correlated with those on ionization.[9]

The data in Table II enable us to compare substituent effects on ionization constants measured in three solvents whose molecules have comparable acid strength but whose hydrogen-bonded solvent structure and dielectric constant are quite different. On plotting log K_i in propionic acid or log K_i in octanoic acid *vs.* log K_i in acetic acid, we obtain fairly good straight lines of practically unit slope. Least-squares analysis leads to the following results: log K_i^{HPro} = 1.07 log K_i^{HAc} − 1.41, r = 0.93, σ = 0.15; log K_i^{HOct} = 0.97 log K_i^{HAc} − 2.30, r = 0.96, σ = 0.09. Here, r denotes the correlation coefficient and σ the standard error of fit. If we constrain the slopes to be unity, the correlation does *not* deteriorate significantly.

This quantitative similarity of substituent effects suggests that solvent participation and solvation-shell structures are closely similar in the ionization of tertiary anilines in the three solvents. The facts are also consistent with an electrostatic model of dipole solvation (see below).[7,29]

We have also plotted log K_i for base ionization in the carboxylic acid solvents *vs.* pK_A for acid dissociation of the corresponding *N,N*-dialkylanilinium ion in water. While there is a strong linear correlation, the slope of the plot is clearly different from unity. The most extensive set of data is available for K_i in acetic acid. Least-squares analysis leads to the following result: log K_i^{HAc} = 0.56 pK_A^{HOH} − 1.65, r = 0.83, σ = 0.21. The slope, 0.56, now obtained for tertiary anilines may be compared with the slope, 1.14, previously obtained in a similar correlation for primary anilines.[30] For the ionization of substituted phenol–triethylamine complexes in aprotic solvents, the slope of the linear relationship between log K_i and pK_A^{HOH} of the phenols is 0.43.[7] Although, in the present work, the substitution takes place mostly on the nitrogen atom rather than in the aromatic ring, and although solvation effects in acetic acid are different from those in aprotic solvents, the similarity of the present slope to that for the phenol–triethylamine complexes and the striking difference from that for primary anilines suggests that the order of alkyl substitution on the nitrogen atom has a marked effect.

Effect of Dielectric Constant. A familiar electrostatic model treats the ionization process as an increase in the electric moment of a nonpolarizable dipole at the center of a spherical cavity in a dielectric continuum.[7,31] According to this model, the standard free energy change of ionization, $\Delta G_i°$, consists of an intrinsic term ($\Delta G_0°$) plus a dipole solvation term, as in (7). Here, N_0 denotes Avogadro's number, and $r_\pm$ and r_u denote the radii of the respective cavities. Following Jadzyn and Malecki,[7] we shall assume that $r_\pm = r_u$ and introduce a molar volume parameter V such that $V = 4\pi N_0 r_\pm^3/3$. Substituting in (7), recalling that $\Delta G_i° = -2.303RT \log K_i$, expressing dipole moments in Debye units, and introducing explicit values for the constants, we then obtain eq 8, in which $\Delta\mu^2 = \mu_\pm^2 - \mu_u^2$.

$$\Delta G_i° = \Delta G_0° - \frac{N_0(D-1)}{(2D+1)}\left(\frac{\mu_\pm^2}{r_\pm^3} - \frac{\mu_u^2}{r_u^3}\right) \quad (7)$$

$$\log K_i = \log K_0 + \frac{7940}{T}\frac{\Delta\mu^2}{V}\frac{(D-1)}{(2D+1)} \quad (8)$$

According to the data for *N,N*-dimethylbenzylamine listed in Table III, an order-of-magnitude estimate for $\Delta\mu^2$ is $27D^2$. For V, a plausible guess is that V is comparable to the molar volume of the solvated ion pair, which varies with the size of the solvent carboxylic acid molecules.

Table IV. Test of Dipole Solvation Model, Equation 8

Aniline	V(in HAc)[a]	$\Delta\mu^{2}$ [b]	log K_0[b]	r
N,N,4-Me_3	258	92	-2.02 ± 0.42	0.975
N,N-Et_2	274	101	-1.62 ± 0.01	0.999
N,N-Et_2-4-Me	291	103	-1.19 ± 0.15	0.997
N,N-n-Bu_2	340	121	-2.18 ± 0.37	0.982

[a] Molar volume in ml mol^{-1}; V(in HPro) = V(in HAc) + 36 ml; V(in HOct) = V(in HAc) + 224 ml. [b] Parameters in eq 8.

Table V. Dipole Moment Analysis for Partly Ionized Bases in Octanoic Acid[a]

Aniline	μ_u	$\mu_\pm$	μ_2 (eq 4)	μ_2 (eq 6)	μ_{obsd}
N,N-Et_2	1.88	5.27	3.03 ± 0.08	3.42 ± 0.12	3.79
N,N,4-Me_3	1.43	5.41	2.15 ± 0.11	2.64 ± 0.15	3.01

[a] Electric dipole moments (μ_u, $\mu_\pm$, μ_2, μ_{obsd}) are stated in Debyes.

The application of eq 8 to our data for K_i in acetic, propionic, and octanoic acid is illustrated in Table IV. In applying eq 8, we assume again that the acid strength of these carboxylic acids is practically the same. In all cases, the variation of log K_i with $(D - 1)/[(2D + 1)V]$ is linear with a high correlation coefficient. However, the values obtained for $\Delta\mu^2$ from the slopes are substantially greater than expected.

Analysis of Dipole Moments. In this section, we shall analyze the dipole moments that are presented in Table III.

N,N-**Diethyl-4-bromoaniline** was chosen as the model substance for which the effect of ionization on the dipole moment is negligible.[32] The electric dipole moment in benzene, 3.76 D, is slightly smaller than that in octanoic acid, 3.87 D. It may be argued that the difference is still within the limits of error of the Onsager theory when applied to solvents of very different chemical type. However, we wish to show that if the difference is taken to be real, it could be due to the alignment of an octanoic acid molecule at the hydrogen-bonding site of the aniline nitrogen, provided there is little or no hindrance to rotation about the N···H–O hydrogen-bond axis. An increase of 0.11 D in the apparent dipole moment would be produced by an additional moment of 0.30 D directed tetrahedrally along the N···HO bond axis. By comparison, the component of the molecular dipole moment along the OH bond direction in formic acid monomer is 0.32 D.[33]

N,N-**Dimethylbenzylamine** was chosen as the model substance for which ionization in octanoic is practically complete.[34] The dipole moment in benzene, 0.72 D, may be compared with a moment of 0.86 D for triethylamine.[35] The smallness of the difference suggests relative ease of rotation about the N-benzyl bond. The dipole moment in octanoic acid, 5.25 D, is surprisingly small when compared to dipole moments of related triethylammonium salts in nonpolar aprotic solvents. For instance, μ = 9.6 D for $Et_3NH^+O_2CCl_3^-$ in dioxane[5] and 11.7 D for $Et_3NH^+ \cdot$ picrate$^-$ in benzene.[36] From the first of these values, by correcting for the difference between C–Cl and H–C bond moments,[37] we predict a minimum moment of 7.7 D for ionized $Et_3NH^+Ac^-$, and of 7.5 D for N,N-dimethylbenzylammonium octanoate.

Homoconjugation can reduce this dipole moment substantially. Thus, Figure 1 shows a plausible structure in which the dipole moment of RCOOH tends to oppose the moment due to the ionic charges. Unfortunately, precise calculation of the resultant moment for the homoconjugated ion pair involves numerous assumptions concerning detailed geometry and bonding. Of the specific structures we have tried, using bond moments for C=O, C—O, and O—H listed by Smyth,[37] none had a calculated dipole moment greater than 6.7 D, and moments of less than 6.0 D became possible as the two O–C–O planes became more nearly parallel. Furthermore, if the bonding in the homoconjugated anion were such as to delocalize the negative charge over both carboxyl groups (analogous to the charge delocalization in HF_2^-), the effect would be to bring the electrical center of the anion still closer to that of the cation, with a resulting further reduction in dipole moment.

N,N-**Diethylaniline and** N,N,**4-trimethylaniline** were the substrates chosen to test for ultrafast proton transfer. The ionization constants for these bases in octanoic acid are 0.51 ± 0.05 and 0.22 ± 0.04, respectively, and are within the range in which differences between eq 4 and 6 are measurable. Our dipole-moment analysis for these substrates is shown in Table V. The dipole moments μ_u are obtained by adding 0.30 D vectorially at a tetrahedral angle to the dipole vectors measured in benzene, to allow for the hydrogen bonding to an octanoic acid molecule (see above). The dipole moments $\mu_\pm$ are obtained by making small changes (phenyl or p-tolyl for benzyl) in the dipole vector observed for N,N-dimethylbenzylammonium octanoate in octanoic acid. In applying eq 4, we estimated an upper limit to μ_{obsd} by calculating the algebraic mean, $x\mu_u + (1 - x)\mu_\pm$, rather than the vector mean. The error limits in the estimates are based solely on the error limits in K_i; there is likely to be further error in the estimation of μ_u and $\mu_\pm$.

It is clear from Table V that neither method of prediction leads to a result in perfect agreement with experiment. However, the rms average predicted by use of eq 6 is much closer to the observed result, suggesting that this method of averaging is physically sound. If this be granted, then the dipole moments show that the rate constant for proton exchange is smaller than that for molecular rotation of the hydrogen-bonded complexes.

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Nuclear Magnetic Resonance Studies of the Di-, Tri-, and Tetramethylammonium Ions Oriented in Middle Nematic Soap Phases

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Abstract: Preparative methods are described for the production of middle nematic soap phases from dimethyl-, trimethyl-, and tetramethylammonium decyl sulfates. The nuclear magnetic resonance (nmr) spectra of the oriented ions have been investigated. In the case of dimethylammonium ion, both the N-14 and N-15 containing ions give useful structural information and a set of reasonable geometric parameters have been obtained from minimum assumptions. The spectra depend on the pH of the water used to prepare the phases and since degrees of orientation do not vary widely in the phases prepared, this permits the analysis to proceed in stages. The neutral phase yields an A_3A_3' spectrum, the acidified phase an $A_3A_3'B_2$ spectrum, while the N-15 labeled ion in an acidified phase provides an $A_3A_3'B_2M$ spectrum. Distances of closest approach of methyl protons indicate some hindered rotation on purely steric grounds. The orientation of the trimethylammonium ion in acidified middle phases gives an extremely complex $A_3A_3'A_3''B$ spin system which, because of overlapping transitions, has not been analyzed. No structural information is possible from the analyzed $A_3A_3'A_3''$ spectrum in neutral phases. There is some evidence from the increase in line width of the apparently single transition that the tetramethylammonium ion is oriented in the middle nematic phase prepared.

Lyotropic nematic middle phases[2] have been used since 1967[3] as orienting media for small molecules. Recent work from this laboratory[4,5] has shown that these phases can be generalized in practice to include complex ion detergents. Simple monatomic species such as alkali metal ions are ordered by the superstructure of the nematic phase and exhibit first-order quadrupole splittings in their nuclear magnetic resonance spectra (nmr).[6] Both cationic and anionic[4,5] detergents of complex ions can be prepared as components of middle phases, which then manifest the ordering of the complex ion by typical nmr spectra, which contain information on intra-ionic dipole–dipole coupling.[7-9] These spectra provide an experimental determination of the internuclear distance ratios in the same manner as the spectra from oriented molecules in thermotropic nematic phases.[7-9] We have recently shown that both small cations and anions are ordered in the electrical double layer of a cationic detergent phase.[10-12]

The study of these methylammonium ions with emphasis on the dimethylammonium ion correlates well with several other studies of ions. The structural characteristics of dimethyltin, methylammonium, acetate, methylmercury, and trimethyllead ions have also been investigated.[11,13-15]

Experimental Section

(a) **Preparation of Compounds.** Di- and trimethylammonium decyl sulfates were prepared by two methods from the hydrochlorides and sodium decyl sulfate.

Method I. Dowex 50 exchange resin (25 ml) was washed with 20 ml of 1 *N* HCl to convert it into the acid form and then washed with distilled water until the effluent was neutral to pH paper. Aqueous solutions of the hydrochlorides (1 gm/50 ml) were passed slowly through the exchange column until the effluent had the same pH as the original solutions. The column was then further washed with distilled water (100 ml) and subsequently with a solution of 5 g of sodium decyl sulfate in 30 ml of water. The fraction which was slowly emitted from the column at this point was com-

Table I. Typical Compositions of Middle Nematic Phases Prepared from Dimethylammonium Decyl Sulfate (DMADS) and Trimethylammonium Decyl Sulfate (TMADS)[a]

Component	Weight, mg	Wt %
	Phase I	
DMADS (N-15)	358	39.4
Decanol	42	4.6
Sodium sulfate	61	6.7
H_2O (pH ~1.5)	447	49.3
	Phase II	
TMADS	568	48.0
Decanol	68	5.7
Sodium sulfate	62	5.2
D_2O	485	41.1
	Phase III	
NaDS	424	40.4
Decanol	57	5.4
TeMA sulfate	51	4.9
D_2O	518	49.3

[a] Phase I was the phase used to orient the N-15 substituted dimethylammonium ion. Water was acidified with sulfuric acid in phase I to slow down proton exchange of the NH_2^+ protons. The abbreviation NaDS corresponds to sodium decyl sulfate and TeMA to tetramethylammonium. Many phases were prepared during this study and no particular difficulty was encountered.[4,5]