$\dot{C}OH$ radical has ~50% reducing efficiency[13,14] compared to ~12% for DMF. Increasing the redox potential of the compound seems to increase the efficiency for reduction (electron transfer) by organic radicals. Electron transfer from radical anions (*e.g.*, $\cdot CO_2^-$ and $\cdot$thymine$^-$) to DMF is more efficient

$$\cdot CO_2^- + DMF \longrightarrow \cdot DMF^- + CO_2 \quad k = 9 \times 10^8\ M^{-1}\ sec^{-1}$$

$$\cdot thymine^- + DMF \longrightarrow \cdot DMF^- + thymine \quad k = 5 \times 10^9\ M^{-1}\ sec^{-1}$$

In the presence of stronger oxidizing agents such as NEM, quinones, and oxygen, the $\cdot DMF^-$ radical loses its electron to these solutes, *e.g.*

$$\cdot DMF^- + O_2 \longrightarrow DMF + \cdot O_2^- \quad k = 2.2 \times 10^9\ M^{-1}\ sec^{-1}$$

$$\cdot DMF^- + NEM \longrightarrow DMF + \cdot NEM^- \quad k = 2.2 \times 10^9\ M^{-1}\ sec^{-1}$$

These rates were determined by following the disappearance of $\cdot DMF^-$ or the appearance of $\cdot NEM^-$.

The reactions of free radicals with fumaric and maleic acids are much more complex than those with the diesters. Just as found with e_{aq}^- (Table I), the reactivity of organic radicals is dependent upon the state of protonation of the unsaturated dicarboxylic acids. While the dianions of these acids react with e_{aq}^- at an appreciable rate, the radicals $\cdot CO_2^-$ and $(CH_3)_2\dot{C}OH$ do not transfer an electron to them ($k < 10^6\ M^{-1}\ sec^{-1}$). The rate increases for the monoanion form and becomes relatively fast for the fully protonated acids (see Table III). The preferential addition reactions of free radicals to the dianion of these acids have recently been used[21] as a means of trapping free radicals. Based on the above results, one can now explain why these acids are efficient in trapping radicals.

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Thermodynamics of Acid–Base Equilibria. III. Ionization of Substituted Anilinium Ions

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Abstract: The standard enthalpies of ionization of 21 meta- and para-substituted anilinium ions have been determined calorimetrically in aqueous solution at 25°. Standard entropies of ionization have been calculated from the experimental enthalpies of ionization and the literature Gibbs free energies of ionization. Both the enthalpies and entropies of ionization show a good linear correlation with the Gibbs free energy of ionization. The experimental results have been analyzed in terms of Hepler's theory of substituent effects and have been compared to the predictions of electrostatic theory.

Because of the theoretical and practical interest in the ionization of organic acids in aqueous solution, numerous determinations of the thermodynamic functions of ionization for these acids have appeared in the literature. A recent review article by Larson and Hepler has summarized the available data.[2]

Reliable Gibbs free energies of ionization or pK_a's have now been obtained in aqueous solution for a majority of the known organic acids. However, the enthalpies and entropies of ionization are needed if the details of the ionization process are to be fully understood. Hepler and coworkers[2] have shown that the variation in the pK_a's of substituted phenols is almost entirely due to changes in the entropy of ionization. An analysis of the enthalpies and entropies of ionization of a wide variety of structurally different mono- and dicarboxylic acids by Christensen, Izatt, and Hansen[3] has shown that the Gibbs free energies of ionization correlate extremely well with the entropies of ionization whereas neither the Gibbs free energies nor the entropies demonstrate a distinct correlation with the enthalpies of ionization. This lack of a good correlation between the enthalpies of ionization and the other thermodynamic functions is probably due to the inherent difficulty in making accurate determinations of the very small enthalpies of ionization of carboxylic acids.

Recently Bolton, Fleming, and Hall[4] have reported a spectrophotometric determination of the thermodynamic functions of ionization for a number of meta- and para-substituted benzoic acids. Excellent correlations were obtained not only between $\Delta G°$ and $\Delta S°$, but also between $\Delta G°$ and $\Delta H°$. If it is assumed that the experimental uncertainty is on the order of ±50 cal/mol for $\Delta H°$, then correlation between $\Delta G°$ and $\Delta H°$ may be considered fortuitous at best.

In ionogenic processes such as the ionization of phenols and carboxylic acids, it has been established that entropy differences are mainly responsible for relative acidities of these acids. The study of a system involving organic cation acids would determine the relative

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(1) (a) School of Chemistry, Georgia Institute of Technology; (b) Department of Chemistry, Georgia State University.

(2) J. W. Larson and L. G. Hepler, "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969.

(3) J. J. Christensen, R. M. Izatt, and L. D. Hansen, *J. Amer. Chem. Soc.*, **89**, 213 (1967).

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importance of the enthalpy and entropy of ionization in an isoelectric reaction. Substituted anilinium ions provide a suitable system for such a study.

The pK_a's of several substituted anilinium ions have been determined by both Biggs[5] and Bolton[6,7] with an agreement at 25° of better than ±0.01 pK_a unit (±14 cal/mol in Gibbs free energy of ionization). However, an analysis of the temperature dependence of the pK_a data of both Biggs and Bolton provides enthalpies of ionization which differ by as much as 500–1000 cal/mol for many of the substituted anilinium ions. This leads to a variation in the entropies of ionization between the two investigators of as much as 3 cal deg^{-1} mol^{-1}.

Van de Poel and Slootmaekers[8] have calorimetrically determined the thermodynamic parameters of ionization for a number of substituted anilinium ions. Unfortunately, the range of substituents studied did not include highly electron-withdrawing substituents where direct resonance interaction between the substituent and the reaction center is possible in the uncharged species.

O'Hara[9] has determined the enthalpies of ionization of the *o*-, *m*-, and *p*-toluidinium ions calorimetrically in aqueous solution at 25°. The calorimetric values are somewhat different from the spectrophotometrically determined values of Bolton.[6a]

This study was undertaken to provide the necessary calorimetric data to establish the enthalpies of ionization for a large number of anilinium ions. When the enthalpies of ionization are precisely known the corresponding entropy values can then be calculated. It is the purpose of this investigation to analyze the thermodynamic results obtained in this study in terms of Hepler's theory of substituent effects[10,11] and to compare the experimental results with the predictions of electrostatic theory.

Experimental Section

The calorimeter used in this work has previously been described.[12] Minor changes have been made in the reaction vessel and the sample introduction system which have decreased the heat effect of sample introduction to 0.01 calorie.

All the anilines used were commercially available except *m*-cyanoaniline, which was obtained by the reduction of *m*-nitrobenzonitrile.[13] All the solid anilines, purified by vacuum sublimation, were determined to be at least 99.5% pure by differential scanning calorimetry.[14] The purified samples were stored in sealed glass ampoules until they were used. Because of the tendency of the liquid anilines to photolyze, samples were vacuum distilled daily in a distillation apparatus completely wrapped with aluminum foil. Without these precautions, reproducible results could not be obtained.

Calorimetric determinations were carried out in a reaction flask containing 1–10 mmol of the aniline and 0.241 mmol of sodium hydroxide in 980 ml of water. The sodium hydroxide was added to ensure that less than 0.1% of the sample would be protonated by the solvent. During an experiment a 5-ml sample of 5.63 *N* perchloric acid was introduced into the system. The total heat determined for this reaction is the sum of the heat of formation of 0.241 mmol of water, the heat of dilution of perchloric acid from 5.63 to 0.0287 *N*, and the heat of protonation of the aniline. From literature data for the heat of formation of water[15,16] and the heat of formation of aqueous perchloric acid solutions,[17] the first two terms are calculated to be 3.21 and 0.18 cal, respectively. These two terms constitute the heat which would be evolved in a blank reaction. The calculated heat of the blank reaction is, therefore, 3.39 cal.

The heat of the blank reaction was determined in an experiment such as the one described above, but with no aniline in the solution. The average value obtained from several such determinations is 3.41 ± 0.06 cal, which agrees well with the calculated value, and thus establishes both the precision and the accuracy of the calorimetry system. Therefore, in each experiment, the heat of protonation can be directly determined.

$$\Delta H(\text{protonation}) = \frac{3.39 - Q(\text{reaction})}{(\text{millimoles of aniline})} \qquad (1)$$

$$Q(\text{reaction}) = \text{total heat evolved}$$

This method was used for all the anilines studied except *m*-cyanoaniline, *m*-nitroaniline, *p*-cyanoaniline, and *p*-nitroaniline. These anilines are too weakly basic to be completely protonated by the above method. Therefore, it was necessary to determine what fraction of the sample was protonated in each experiment. After each calorimetric determination, the solution was titrated to a phenolphthalein endpoint with standard sodium hydroxide to determine accurately the concentration of perchloric acid in the solution. If the initial aniline concentration and the pK_a of the anilinium ion are also known, the fraction protonated (α) can be calculated.

$$\alpha = (A - X)/(A) \qquad (2)$$

$$X = -{}^1/_2(H - A + K_a) + {}^1/_2[(H - A + K_a)^2 - 4(-AK_a)]^{1/2}$$

where H is the dilute perchloric acid concentration, A is the initial aniline concentration, and K_a is the dissociation constant of the anilinium ion. At this low ionic strength, the ratio of the activity coefficients of H_3O^+ and AH^+ is approximately unity.

The weak basicity of these anilines eliminates the possibility of protonation of the aniline by water, so no sodium hydroxide was added to the aqueous solutions of the aniline for these determinations. Therefore, the heat of the blank reaction in these experiments is 0.18 cal, the heat of dilution of perchloric acid. Once α is known, the heat of protonation can be calculated directly.

$$\Delta H(\text{protonation}) = \frac{0.18 - Q(\text{reaction})}{\alpha(\text{millimoles of aniline})} \qquad (3)$$

$$Q(\text{reaction}) = \text{total heat evolved}$$

At least five calorimetric determinations were made for each aniline studied. All calculations were carried out on the RCA Spectra 70 computer at Georgia State University.

Results

The enthalpies of ionization of 21 substituted anilinium ions in aqueous solution were determined calorimetrically at an ionic strength of $I = 0.0287$. The results of five determinations along with the average value and standard deviation for each anilinium ion are shown in Table I. In order to convert the experimental values to the standard state infinite dilution values, it is necessary to know the heats of dilution of the anilinium perchlorates. Using the heat of dilution of ammonium perchlorate (−37 cal/mol) as an estimate for the heat of dilution of the anilinium perchlorates, and the heat of

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Table I. Enthalpies of Ionization of Substituted Anilinium Ions

Substituent	$\Delta H°$ of ionization, kcal/mol						
	Run 1	Run 2	Run 3	Run 4	Run 5	Average	Lit. values
H	7.43	7.39	7.46	7.44	7.43	7.43 ± 0.02	7.38 (6a) 6.52 (5) 7.26 (8) 7.24 (18)
p-OCH$_3$	8.53	8.50	8.52	8.50	8.51	8.51 ± 0.01	8.34 (7) 7.57 (5) 8.21 (8)
p-OCH$_2$CH$_3$	8.56	8.62	8.57	8.48	8.44	8.53 ± 0.07	8.15 (8)
p-CH$_3$	7.95	7.94	7.75	7.83	7.71	7.86 ± 0.11	8.06 (6a) 6.97 (5) 7.59 (8) 7.60 (9)
p-CH$_2$CH$_3$	7.75	7.73	7.79	7.70	7.72	7.74 ± 0.03	
p-F	7.71	7.80	7.79	7.77	7.72	7.76 ± 0.04	7.45 (8)
p-Cl	6.75	6.79	6.66	6.57	6.60	6.67 ± 0.09	6.63 (7) 6.47 (5) 6.42 (8)
p-Br	6.55	6.46	6.55	6.46	6.50	6.50 ± 0.05	6.70 (7) 6.13 (5)
p-I	6.47	6.49	6.52	6.54	6.45	6.50 ± 0.04	6.55 (7) 6.05 (5)
p-CN	4.53	4.66	4.54	4.66	4.50	4.58 ± 0.08	
p-NO$_2$	4.12	4.13	4.11	4.13	4.11	4.12 ± 0.01	3.42 (7) 3.11 (5)
m-OCH$_3$	7.12	7.09	7.10	7.12	7.13	7.11 ± 0.02	7.01 (6b) 6.47 (5) 6.89 (8)
m-OCH$_2$CH$_3$	7.03	7.09	7.06	7.04	7.02	7.05 ± 0.03	6.66 (8)
m-CH$_3$	7.57	7.60	7.57	7.56	7.57	7.58 ± 0.02	7.47 (6a) 6.51 (5) 7.37 (8) 7.37 (9)
m-CH$_2$CH$_3$	7.29	7.26	7.35	7.28	7.36	7.31 ± 0.04	
m-F	6.57	6.58	6.61	6.56	6.50	6.56 ± 0.04	6.23 (8)
m-Cl	6.43	6.41	6.49	6.45	6.45	6.45 ± 0.03	6.27 (6b) 5.63 (5) 6.31 (8)
m-Br	6.58	6.62	6.58	6.60	6.58	6.59 ± 0.02	6.25 (6b) 5.55 (5)
m-I	6.76	6.80	6.75	6.74	6.84	6.78 ± 0.04	6.33 (6b) 5.88 (5)
m-CN	5.71	5.80	5.75	5.65	5.79	5.74 ± 0.06	
m-NO$_2$	5.37	5.40	5.44	5.37	5.30	5.37 ± 0.05	4.98 (6b) 4.79 (5)

dilution of perchloric acid (−54 cal/mol) at an ionic strength of $I = 0.0287$, the correction term is approximately −17 cal/mol.[17] Since this value is within the standard deviation of the best data in Table I, a correction of this magnitude would be superfluous. Therefore, the average values shown in Table I are the standard enthalpies of ionization of the corresponding anilinium ions with an estimated uncertainty of ±50 cal/mol.

For comparison, the enthalpies of ionization determined by other workers are included in Table I. Both Biggs,[5] in a preliminary survey, and Bolton[6,7] calculated enthalpies of ionization for several anilinium ions from pK_a temperature dependence studies. The calorimetric data from this study agree favorably with the work of Bolton for all compounds studied by both Biggs and Bolton, indicating that the pK_a data of Bolton should be preferred. Differences between the enthalpies of ionization from this study and from Bolton's work tend to become larger than the sum of the experimental uncertainties whenever the pK_a of the anilinium ion is less than 3.6. However, the only serious discrepancy in the data is for the *p*-nitroanilinium ion, for which the calorimetric value is 700 cal/mol greater than the value reported by Bolton.

Hepler[18] reported a calorimetrically determined value for the enthalpy of ionization of aqueous anilinium ion which is 200 cal/mol lower than the value obtained in this study. Unlike the value obtained in this study, Hepler's value was derived from the difference between the heat of solution of aniline into aqueous HCl and into pure water. Furthermore, both the ionic strength and sample concentration were much higher in Hepler's study. Therefore, the value obtained in this study is preferred.

In the work of Van de Poel[8] on substituted anilinium ions no apparent effort was made to prevent the anilines from being slightly protonated by the solvent before the actual protonation occurred in the calorimeter. If the pK_a of an anilinium ion is greater than 4.5, a significant amount of the aniline will be protonated in aqueous solution at pH 7.0. For example, *p*-methoxyaniline (pK_a = 5.357) would be about 2% protonated at pH 7.0, thus causing an error of about 170 cal/mol in the

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(18) W. F. O'Hara, H. C. Ko, M. N. Ackermann, and L. G. Hepler, *J. Phys. Chem.*, 71, 3107 (1967).

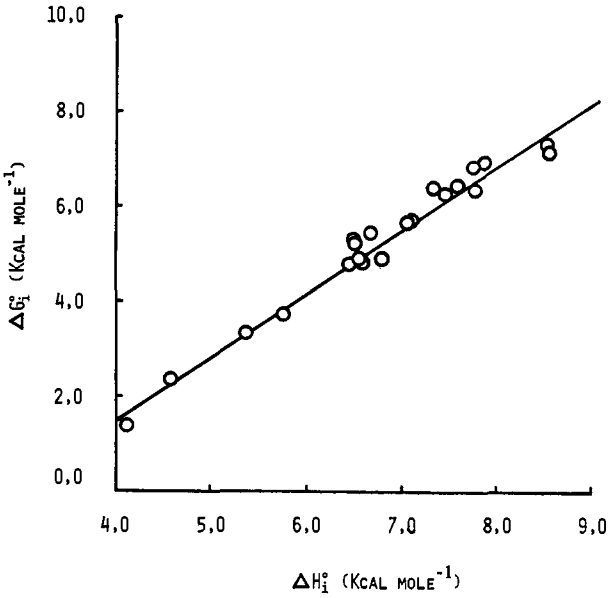

Figure 1. A plot of ΔG° *vs.* ΔH° for the 21 anilinium ions included in this study.

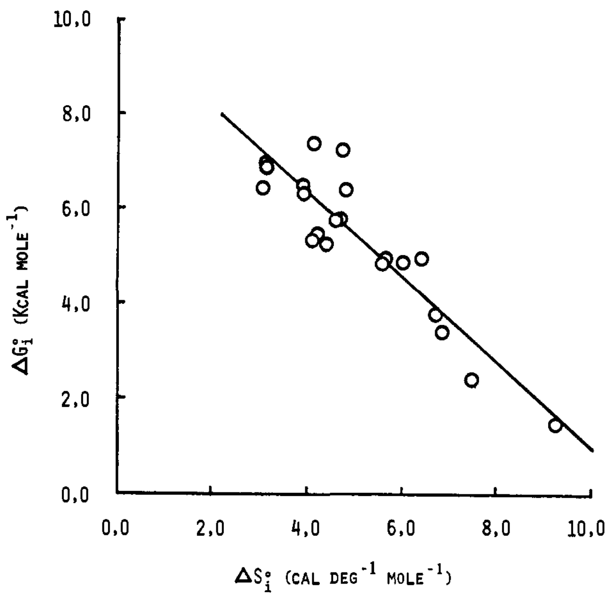

Figure 2. A plot of ΔG° *vs.* ΔS° for the 21 anilinium ions included in this study.

enthalpy of ionization. In all likelihood, the pH of the solution was less than 7.0 due to the presence of dissolved carbon dioxide, so the error would be greater than 170 cal/mol. Since Van de Poel's values are consistently 200–400 cal/mol lower than the values obtained in this study, the discrepancy is probably due to a failure to ensure that initially the aniline was completely unprotonated.

Using the calorimetrically determined standard enthalpies of ionization (ΔH°) from this study and the literature values for the standard Gibbs free energies of ionization (ΔG°) determined by Bolton[6,7] and other workers,[8,19,20] the standard entropies of ionization (ΔS°) have been calculated. These results have been tabulated in Table II for the 21 anilinium ions included in this study.

A plot of ΔG° *vs.* ΔH° is shown in Figure 1. This plot, which includes values for the unsubstituted anilinium ion and 20 meta- and para-substituted anilinium ions, is linear with a slope of 1.344 and a correlation coefficient of 0.9859. No other acid system is known to give such a high correlation of ΔG° with ΔH° over such a wide range of values.

A plot of ΔG° *vs.* ΔS° is shown in Figure 2. This plot indicates that ΔG° is also linearly related to ΔS°, with a slope of −900° and a correlation coefficient of 0.9144. Similar relationships between ΔG° and ΔS° have been found for phenols,[2] carboxylic acids,[3] and thiols.[21] In those acids the correlation is better and the slope varies from −200° to −350°, which is close to the value of −218° predicted from the Bjerrum electrostatic theory.[22] On the basis of these differences it appears that anilinium ions provide a system which is unique not only in that ΔG° is linearly related to both ΔH° and ΔS°, but also in that the system clearly does not seem to fit simple electrostatic theory.

Table II. Thermodynamics of Ionization of Substituted Anilinium Ions in Water at 298°K[a]

	Substituent	ΔG°	ΔH°	ΔS°	Ref[b]
1.	H	6.27	7.43	3.89	6a
2.	p-OCH$_3$	7.31	8.51	4.02	7
3.	p-OCH$_2$CH$_3$	7.16	8.53	4.60	8
4.	p-CH$_3$	6.94	7.86	3.09	6a
5.	p-CH$_2$CH$_3$	6.82	7.74	3.09	19
6.	p-F	6.34	7.76	4.76	8
7.	p-Cl	5.44	6.67	4.13	7
8.	p-Br	5.30	6.50	4.02	7
9.	p-I	5.21	6.50	4.33	7
10.	p-CN	2.37	4.58	7.41	20
11.	p-NO$_2$	1.39	4.12	9.16	7
12.	m-OCH$_3$	5.73	7.11	4.63	6b
13.	m-OCH$_2$CH$_3$	5.68	7.05	4.60	8
14.	m-CH$_3$	6.43	7.58	3.86	6a
15.	m-CH$_2$CH$_3$	6.41	7.31	3.02	19
16.	m-F	4.89	6.56	5.60	8
17.	m-Cl	4.80	6.45	5.53	6b
18.	m-Br	4.81	6.59	5.97	6b
19.	m-I	4.89	6.78	6.34	6b
20.	m-CN	3.75	5.74	6.67	20
21.	m-NO$_2$	3.35	5.37	6.78	6b

[a] ΔG° and ΔH° values in kilocalories per mole; ΔS° values in calories per mole per degree. [b] Source of literature ΔG° value.

Discussion

Comparison of Anilinium Ions with Primary Ammonium Ions. Protonated primary amines provide a system for which the ionization process is expected to be quite similar to that for anilinium ions. However, in an analysis of the thermodynamics of ionization of a large number of protonated primary amines, Christensen and coworkers have reported that the correlation between ΔG° and ΔS° is rather poor for primary ammonium ions,[23] with a least-squares slope of −41.7°. This value is vastly different from both the slope predicted by electrostatic theory and from the slope ob-

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tained in this study for anilinium ions. Included in this analysis are a number of compounds which are known to exist as zwitterions in aqueous solution. If these compounds are deleted from Christensen's data, the resulting plot of $\Delta G°$ *vs.* $\Delta S°$ for 25 primary ammonium ions has a least-squares slope of $-439°$. Although the correlation coefficient of 0.7341 is still rather poor, this slope is much closer to the value predicted from simple electrostatic theory. Furthermore, a plot of $\Delta G°$ *vs.* $\Delta H°$ for the same primary ammonium ions has a slope of 1.217 and a correlation coefficient of 0.8716. This slope is very close to the value of 1.344 found for anilinium ions, which indicates that the two ionization processes are indeed similar. The lack of a good correlation between $\Delta G°$ and $\Delta S°$ in primary ammonium ions indicates that the phenomena responsible for changes in $\Delta S°$ are not simply electrostatic, but are rather a combination of specific solvation and electrostatic effects.[23]

Hepler's Theory of Substituent Effects. For symmetrical proton transfer reactions such as

$$HA_1 + A_2 \longrightarrow A_1 + HA_2 \qquad (4)$$

where HA_1 and HA_2 are two structurally similar acids differing only by a dipolar substituent, and A_1 and A_2 are the respective conjugate bases, Hepler[10] has proposed that the overall effect of a dipolar substituent may be divided into internal and external contributions. Based on the assumptions that (a) the external contributions to the enthalpy and entropy changes are related by a constant β, and (b) the internal contribution to the entropy is zero, the following results are obtained.

$$\Delta G° = \Delta H_{\text{int}} + (\beta - T)\Delta S° \qquad (5)$$

$$\Delta H° = \Delta H_{\text{int}} + \beta\Delta S° \qquad (6)$$

In order to calculate ΔH_{int} from the measured thermodynamic data, it is necessary to determine a value for β, which Hepler has assigned a value of 280°. Since the assumed value of β is very close to T (298°), it follows that $\Delta G° \approx \Delta H_{\text{int}}$. Values of ΔH_{int} calculated in this fashion have been found to correlate well with Hammett σ or Taft σ^* parameters. Based on the assumption that two different reaction series which show proportional $\Delta G°$ values should also show proportional ΔH_{int} values, Bolton and Hall have proposed a general method for the calculation of β values.[7] From eq 6, it can be shown that

$$\Delta H_A° = \theta\Delta H_B° - \theta\beta_B\Delta S_B° + \beta_A\Delta S_A° \qquad (7)$$

where $\Delta H°$ and $\Delta S°$ are the standard substituent induced enthalpy and entropy changes for reaction series A and B, θ is the ratio of the internal enthalpy changes for series A and B, and β_A and β_B are the respective Hepler proportionality constants mentioned above. Using the anilinium ion data reported in this study for reaction series A and the thermodynamic data on meta- and para- substituted phenols reported in the recent literature[2] as reaction series B, the parameters θ, β_A, and β_B were calculated by a multiple parameter least-squares regression method. The calculated values are $\theta = 2.46 \pm 0.15$, $\beta_A = 640 \pm 69°$, and $\beta_B = 190 \pm 39°$. Bolton and Hall have reported the following values for these two systems: $\theta = 1.63 \pm 0.17$; $\beta_A = 413 \pm 146°$; and $\beta_B = 240 \pm 17°$. Their calculations, however, were based upon only 11 substituents. The β_B value derived from this study is approximately the same as that of Bolton, whereas the β_A and θ values are substantially different, indicating that this treatment is extremely sensitive to slight changes in the anilinium ion data. Furthermore, because of the small entropy changes in the ionization of anilinium ions, the value of β_A used to calculate ΔH_{int} is not very important. Bolton and Hall, using $\beta_A = 413°$ to calculate ΔH_{int}, have reported that a plot of ΔH_{int} *vs.* σ for 12 anilinium ions has a slope of -4053 and a correlation coefficient of 0.9969. Using the value of $\beta_A = 640°$ obtained in this study, a plot of the resulting ΔH_{int} values *vs.* σ for 20 anilinium ions has a slope of -5051 and a correlation coefficient of 0.9931.

An interesting result of this treatment is the observed difference between θ and the ratio of the Hammett ρ values for the reaction series A and B. The former represents the ratio of the substituent induced internal enthalpy changes (eq 8) while the latter represents the ratio of the respective free-energy changes in aqueous solution (eq 9). According to Hepler's theory, θ also represents the ratio of the respective free energy changes in the gas phase for reaction series A and B.

$$\theta = \frac{(\Delta H_{\text{int}})_A}{(\Delta H_{\text{int}})_B} = 2.46 \qquad (8)$$

$$\frac{\rho_A}{\rho_B} = \frac{\Delta G_A°(\text{aq})}{\Delta G_B°(\text{aq})} = 1.3 \qquad (9)$$

From this analysis, anilinium ions show a greater susceptibility to substituent effects relative to phenols in the gas phase than in the aqueous phase. While free energy changes in aqueous solution result from both enthalpy and entropy changes, Gibbs free-energy changes in the gas phase are almost completely due to internal enthalpy changes. If both an acid and its conjugate base are stabilized relative to a reference acid by a substituent, the overall effect of that substituent is minimized; however, if an acid is destabilized while its conjugate base is stabilized, or *vice versa*, the effect of the substituent is maximized. Since anilinium ions exemplify the latter case, gas-phase free energies of ionization should show larger substituent effects for anilinium ions than for phenols.

Free Energy–Entropy Correlations. If it is assumed that the Gibbs free-energy changes for reactions such as 4 may be divided into a temperature independent internal term (nonelectrostatic term) and a temperature dependent external term (electrostatic term), it may be shown that

$$\Delta G°/\Delta S° = \left(1 + \frac{\Delta G_{\text{nonel}}}{\Delta G_{\text{el}}}\right)(\partial \ln \epsilon/\partial T)^{-1} \qquad (10)$$

where ϵ is the dielectric constant of the pure solvent if the Bjerrum electrostatic model is employed or the "effective" dielectric constant if the Kirkwood–Westheimer cavity model is used. In aqueous solution, the Bjerrum model predicts a value of approximately $-218°$ for $(\partial \ln \epsilon/\partial T)^{-1}$ whereas the Kirkwood–Westheimer approach predicts a more negative value since the latter model takes into account the polarizable molecular framework as well as the bulk solvent in calculating the effect of the medium on the work required to remove the proton from the acid.

Table III. Kirkwood–Westheimer Treatment of Substituted Anilinium Ions

Substituent[a]	Cavity volume, Å^3	Focal radius, Å	$(\partial \ln \epsilon/\partial T)^{-1}$		$(\Delta G°/\Delta S°)$
			Spherical model	Ellipsoidal model	Experimental
p-CH_3 (min)	164	2.7712	−1938	−2086	−838
p-CH_3 (max)	164	3.1460	−775	−1116	
p-Cl	155	2.6610	−2145	−2280	−3458
p-Br	162	2.6985	−2165	−2291	−7462
p-I	168	2.7635	−2039	−2179	−2409
p-CN (min)	155	2.8935	−1301	−1525	
p-CN (max)	155	3.2585	−358	−808	−1108
p-NO_2 (min)	158	2.7363	−1923	−2070	
p-NO_2 (max)	158	3.0838	−822	−1149	−926

[a] In polyatomic substituents (Ph-X-Y) such as p-CH_3, p-CN, and p-NO_2 the point dipole is located either at one-half of the maximum extension of the group as projected on the C–X bond axis (min) or in the middle of the X–Y bond (max).

It is generally assumed that the nonelectrostatic contribution to the free energy change is negligible in symmetrical proton transfer processes,[24] so the ratio of $\Delta G°$ to $\Delta S°$ should equal $(\partial \ln \epsilon/\partial T)^{-1}$. While benzoic acids $[(\Delta G°/\Delta S°) = -205°]$[4] and, to a lesser extent, phenols $[(\Delta G°/\Delta S°) = -350°]$[2] tend to support the assumption that $\Delta G_{\text{nonel}} = 0$, anilinium ions $[(\Delta G°/\Delta S°) = -900°]$ deviate markedly from the theoretical predictions.

From the point of view of electrostatic theory, there are at least two possible explanations for the deviation from simple electrostatic theory which is exhibited by anilinium ions. Kirkwood–Westheimer electrostatic theory assigns considerable importance to the size and shape of the molecular cavity which an acid occupies in solution. Since phenols, benzoic acids, and anilinium ions may be expected to occupy cavities of similar size and shape in aqueous solution, the results predicted by the Kirkwood–Westheimer theory are about the same for all three acid types.

Using the Kirkwood–Westheimer approach, $(\partial \ln \epsilon/\partial T)^{-1}$ values have been calculated for a variety of para-substituted anilinium ions, employing both spherical and oblate ellipsoidal cavities. The cavity volume for a particular para-substituted anilinium ion was determined from the partial molar volume of p-nitroaniline (95.0 ml/mol)[25] in combination with Traube's rule for the various para substituents. The focal radii were calculated from literature bond lengths.[26] The "effective" dielectric constants were calculated at 25 and 50° by means of the equations developed by Kirkwood and Westheimer[27] for the spherical cavity and by Sarmousakis[28] for the oblate ellipsoidal cavity using a temperature-independent dielectric constant of 2.0 for the cavity and the experimental dielectric constant of water at the respective temperatures.[22] From the experimental data for substituted anilinium ions, substituent induced changes in Gibbs free energy and entropy of ionization were calculated according to eq 4. Then the experimental value of $(\Delta G°/\Delta S°)$ for eq 4 was calculated for each anilinium ion. The results in Table III indicate that although the calculated slope is extremely sensitive to the location of the point dipole, both the spherical and ellipsoidal models give values for $(\Delta G°/\Delta S°)$ which are in good agreement with the observed values. The difference between these values and the corresponding slope of −900° for a plot of $\Delta G°$ *vs.* $\Delta S°$ for all the anilinium ions included in this study is clearly reflected in the deviation of the para substituents from the least-squares slope for the plot of $\Delta G°$ *vs.* $\Delta S°$ which is shown in Figure 2.

While the results for anilinium ions agree with the predictions of the Kirkwood–Westheimer electrostatic theory, phenols and benzoic acids are in much closer agreement with the predictions of simple electrostatic theory. When a proton is removed from an anilinium ion, the cavity containing the conjugate base is uncharged, so that the work of the proton transfer for the symmetrical reaction 4 is totally determined by the magnitude of the difference of the dipole moments of the neutral anilines. Since charge-dipole forces decrease with the inverse square of the charge-dipole separation, most of the work of the proton transfer will be expended while the proton is still close to the molecular cavity. This system is adequately represented by the Kirkwood–Westheimer model, and thus the predicted $(\Delta G°/\Delta S°)$ ratios agree quite well with the experimental values for substituted anilinium ions.

In the ionization of phenols and benzoic acids, the conjugate base which occupies the cavity bears a unit negative charge which is primarily localized at the reaction center (O^-, COO^-). Molecular orbital theory suggests that the magnitude of the charge at the reaction center will depend on the electron-donating or -withdrawing properties of the substituent. The assumption of Kirkwood and Westheimer that the charges on the reaction centers are identical in a symmetrical reaction appears to be incorrect for phenols and benzoic acids. The incomplete cancellation of the charge–charge interaction would yield an additional term in the work required to effect the proton transfer. Because this additional interaction is a charge–charge interaction, which is inversely related to the proton-charge separation, a larger percentage of the overall electrostatic interaction would be expected to occur through the bulk solvent than in the ionization of anilinium ions. Therefore,

(24) (a) N. Bjerrum, *Z. Phys. Chem. (Frankfurt am Main)*, **106**, 219 (1923). (b) It has been pointed out by one of the referees that "the $\Delta G_{\text{nonel}} = 0$ idea (ref 24) is reasonable for carboxylic acids, but not so for anilines or phenols, particularly those that are para substituted with substituents for which resonance interactions may be substantial. This is consistent with present experimental results, previous results of ref 2, and general experience with Hammett substituent parameters:" L. D. Hansen and L. G. Hepler, *Can. J. Chem.*, **50**, 1030 (1972).

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the increased role of the solvent in the ionization of phenols and benzoic acids causes the ($\Delta G°/\Delta S°$) ratio to approach that of simple electrostatic theory.

A second possible explanation for the deviation of anilinium ions from the predictions of simple electrostatic theory lies in the assumption that nonelectrostatic Gibbs free-energy changes are negligible for symmetrical proton transfer processes. It has been shown in the above discussion that internal enthalpy changes and, hence, internal Gibbs free-energy changes are expected to be larger for anilinium ions than for phenols or benzoic acids. Thus, anilinium ions would be expected to show a greater deviation from simple electrostatic theory than either phenols or benzoic acids.

Recently Taft and coworkers[29] have determined the gas-phase acidities of several 4-substituted pyridinium ions, a system which is expected to be quite similar to anilinium ions. The results of their work clearly show that internal free energy changes are not equal to zero, but rather they are larger than the corresponding free energy changes in aqueous solution. When data are available on gas-phase acidities of anilinium ions, it will be possible more clearly to interpret the results obtained in this study for the ionization of anilinium ions in aqueous solution.

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Ion Pairing Effects on Electron Transfer Rate Constants by Electron Spin Resonance Fast Exchange Line-Width Studies. Application to Tri-*p*-tolylamine and Phenothiazine Cation System

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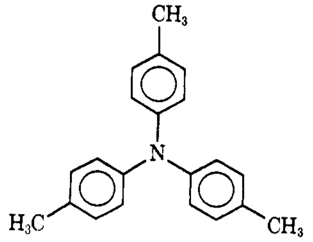
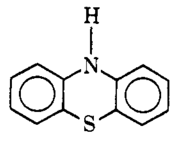
Abstract: The rates of electron transfer between radical cations and their parent molecules for tri-*p*-tolylamine and phenothiazine systems have been obtained in various chloroform–acetonitrile mixed solvents in the fast exchange limit, using electrolytic oxidation and chemical oxidation with iodine. The second-order rate constants obtained were solvent dependent, except for the iodine-oxidized tri-*p*-tolylamine systems. The rate constant dependence on the dielectric constant of the solvent was attributed to ion pairing between the organic aromatic cation and the inorganic anion. The solvent independence of the rate constant in the iodine-oxidized tri-*p*-tolylamine systems was attributed to steric factors which prevent various types of ion pair formation. Anomalous activation energies were obtained for systems having extensive ion pairing and were attributed to a shift in equilibria between various types of ion pairs with temperature. The results have obvious significance for reaction mechanism studies in which ion pairs are postulated as intermediates.

Electron spin resonance (esr) provides a convenient method to determine electron transfer rates in organic radical systems. The second-order rate constants for electron transfer in anion and cation exchanging systems have been calculated in the fast exchange region,[2–10] slow exchange region,[10–21] and the intermediate region[8] of exchange. Studies in the fast and slow exchange regions are possible by applying limiting conditions to the full line-shape function for an N site exchanging system.[22] Studies in the intermediate region of exchange are possible by using computer techniques to simulate the esr spectra.[8]

The (esr) hyperfine spectrum of the tri-*p*-tolylamine (TPTA) (I) and phenothiazine (PTAZ) (II) cation sys-



I



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[1] Taken in part from the Ph.D. thesis of S. P. Sorensen, submitted to the Graduate Faculty of the University of Nebraska, 1972.

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