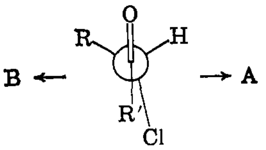
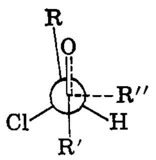
The diastereomeric product ratio A/B in XXVI is about 4/1 ($G_A^{\ddagger} - G_B^{\ddagger} = -800$ cal/mole) when R is methyl or ethyl.[5] On the basis of the dipolar model

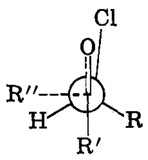


XXVI

XXVI this ratio should increase when R is changed to isopropyl or *t*-butyl. From consideration of XXVII and XXVIII, however, the opposite conclusion is reached. Since XXVII is experimentally favored over XXVIII by 800 cal/mole when R is methyl, it should be favored only by 400 cal/mole when R is isopropyl. The diastereomeric product ratio should therefore



XXVII



XXVIII

decrease from 4/1 to about 2.5/1. Even more striking is the case when R is *t*-butyl, as XXVIII should now be the more stable of the two by about 300 cal/mole. The major diastereomer should thus be B, the diastereomeric product ratio A/B being 0.5/1.

Acknowledgment. The author thanks the National Science Foundation for a Senior Postdoctoral Fellowship, 1965–1966, and the Department of Chemistry, University of California, Berkeley, for its generous hospitality.

Equilibrium Constants and Substituent Effects in the Ionization of Aniline as a Base and the Ion-Pair Dissociation of Anilinium Acetate in Glacial Acetic Acid[1]

Gary W. Ceska and Ernest Grunwald

Contribution from the Lecks Chemical Laboratories, Brandeis University, Waltham, Massachusetts 02154.
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Abstract: This paper shows that in the analysis of substituent effects, it is scientifically fruitful to divide base dissociation into two steps: ionization to form an ion pair, and dissociation of the ion pair into free ions. Equilibrium constants, K_i and K_d, for the separate steps are reported for a series of aromatic amines in acetic acid. For *meta*- and *para*-substituted anilines, substituent effects on K_i are typical of aromatic side-chain reactions: $\delta_R \log K_i$ is proportional to Hammett's σ. Substituent effects on K_d are qualitatively different from those on K_i but resemble those reported by others for K_d of quaternary ammonium salts in aprotic solvents. The relative ion-pair dissociating power of substituents is approximately alkyl or phenyl > methoxy or CH_3OCH_2 > haloalkyl or halogen. This paper also reports values of K_i and K_d for several N,N-dialkylanilines and for pyridine, and compares acetic acid and cyanoacetic acid as proton donors in ionization.

Glacial acetic acid is a good medium for the study of substituent effects on base strength in solution because one can measure separately the equilibrium constants for ionization (eq 1) and dissociation (eq 2).[2–5] In this paper we report measurements of both

$$\mathrm{B + HAc \rightleftharpoons B\cdot HAc} \tag{1a}$$

$$\mathrm{B\cdot HAc \rightleftharpoons BH^+\cdot Ac^-} \tag{1b}$$

$$K_i = [\mathrm{BH^+\cdot Ac^-}]/([\mathrm{B}] + [\mathrm{B\cdot HAc}]) \tag{1c}$$

$$\mathrm{BH^+\cdot Ac^- \rightleftharpoons BH^+ + Ac^-} \tag{2a}$$

$$K_d = [\mathrm{BH^+}][\mathrm{Ac^-}]/[\mathrm{BH^+\cdot Ac^-}] \tag{2b}$$

K_i and K_d for a series of substituted anilines and pyridine. According to eq 1, K_i is a complex quantity since it depends on two equilibria, 1a and 1b. However, because HAc is the solvent, we may assume that the equilibrium in 1a lies far to the right, and K_i is then a close approximation to the equilibrium constant for the elementary proton transfer step, 1b. K_d is simply the equilibrium constant for the dissociation step, 2a.

We find for *meta*- and *para*-substituted anilines that $\log K_i$ varies linearly with the Hammett substituent constant σ,[6] with a correlation coefficient of 0.996. On the other hand, we find that $\log K_d$ is correlated only partially with σ; the correlation coefficient is 0.78. It follows, of course, that substituent effects on K_i are *not* analogous to those on K_d, and that the plot of $\log K_i$ *vs.* $\log K_d$ is *not* a linear free energy relationship.

We also find, from the effect of added cyanoacetic acid on the ionization of substituted anilines in acetic acid, that the relative basicity of acetate ion and cyanoacetate ion is quite close to the ratio of K_B for these carboxylate ions in water.[7]

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(1) This work was supported by the National Science Foundation under Grant GP-3921.

(2) I. M. Kolthoff and S. Bruckenstein, *J. Am. Chem. Soc.*, **78**, 1 (1956).

(3) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 10 (1956).

(4) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 2974 (1956).

(5) For a general theoretical discussion, see J. N. Brønsted, *Z. Physik. Chem.*, **A169**, 52 (1934).

(6) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter 7; (b) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

On comparing the base strength of primary and tertiary aromatic amines in acetic acid, we obtain the sequence of K_i values, $(n\text{-Pr})_2NPh > (CH_3)_2NPh >$ aniline > pyridine. The sequence, aniline > pyridine, is opposite to that of K_B in water. The sequence, $(CH_3)_2NPh >$ aniline, is opposite to that of K_B in methanol but the same as that of K_B in water.[8,9]

The most relevant recent studies of base strength in acetic acid are those of Kolthoff and Bruckenstein[2-4] and of Shkodin and co-workers.[10] Results reported by these two groups are in poor agreement; over-all dissociation constants differ by as much as two orders of magnitude. Where direct comparison is possible, our results support those of Kolthoff and Bruckenstein.

Results

Spectrophotometric Determination of K_i. In the presence of 10^{-3} to 10^{-2} *M* sodium acetate, dissociation of $BH^+ \cdot Ac^-$ to free ions (eq 2) is repressed,[11] and K_i can be derived from the optical absorbance of the solution at an appropriate wavelength (eq 3). Here *A*

$$K_i = (\epsilon_B c - A)/(A - \epsilon_{BH^+Ac^-} c) \qquad (3)$$

is the absorbance of a solution prepared by adding *c* formula weights of pure B per liter of *ca.* 10^{-2} *M* sodium acetate in acetic acid, and ϵ_B and $\epsilon_{BH^+Ac^-}$ are the respective molar extinction coefficients.

It was convenient to work at wavelengths close to, and including, λ_{max} of the so-called B band in the spectrum of the unprotonated aromatic amine.[12,13] This band is centered at 280 mμ for aniline, 260 mμ for pyridine, and 280–310 mμ for substituted anilines. Acetic acid is quite transparent in this region, and $\epsilon_{BH^+Ac^-}$ is small compared to ϵ_B near λ_{max} of the B band for most of our substrates.[14]

To obtain $\epsilon_{BH^+Ac^-}$, we converted the aromatic amine to the perchlorate salt by adding excess perchloric acid and measured $\epsilon_{BH^+ClO_4^-}$. According to Kolthoff and Bruckenstein,[2,3] $\epsilon_{BH^+ClO_4^-}$ is a good approximation to $\epsilon_{BH^+Ac^-}$.

To obtain ϵ_B, we measured the spectrum of the aromatic amines not only in acetic acid but also in 95:5 water–methanol ("water") and in pure methanol. In the latter solvents proton transfer to the aromatic amines is negligible. We found that, in the absence of proton transfer, the B band has some interesting properties. Solvent effects on ϵ_{max} at the band maximum are small, and the small changes that do take place are correlated perfectly with accompanying changes in λ_{max}. Table I lists our data for three substituted anilines that are too weakly basic to be protonated appreciably even in glacial acetic acid. The monotonic relationship shown here between λ_{max} and ϵ_{max} evidently includes glacial acetic acid.

Table I. Correlation of Solvent Effects on λ_{max} and ϵ_{max} for Substituted Anilines[a]

Substituent	Solvent	λ_{max}, mμ	ϵ_{max}
2-Nitro	H_2O[b]	283	5310
	MeOH	277	4910
	HAc	276	4860
2-CF_3, 4-F	MeOH	310	3090
	HAc	306	2810
	H_2O[b]	298	2670
4-CF_3	MeOH	287	1780
	HAc	282	1400
	H_2O[b]	279	1370

[a] Data at 25°. [b] Water–methanol (95:5, wt %).

For all primary anilines for which we report K_i measurements, λ_{max} for the B band in acetic acid coincides with λ_{max} in "water." We therefore equated ϵ_B to ϵ_{max} as measured in "water." For the N-dialkylanilines, λ_{max} in acetic acid coincides with λ_{max} in methanol, and we therefore identified ϵ_B with ϵ_{max} in methanol. For pyridine we identified ϵ_B with ϵ_{max} in "water."[14b] Within experimental error, ϵ_{max} was independent of the temperature between 20 and 40°.

Results for K_i, $\Delta H_i°$, and $\Delta S_i°$. In the K_i measurements, aniline concentrations ranged from 10^{-2} to 10^{-4} *M*, being chosen so that *A* (eq 3) fell between 0.1 and 1.0 where it could be measured with good precision. The validity of eq 3 was tested for each substrate by confirming that K_i is independent of *c* over a two- to sixfold variation. Average results at three temperatures are listed in Table II. The reproducibility of these K_i values is about ±1%, except for the smaller values, especially those for $m\text{-}F_3CC_6H_4NH_2$, where the reproducibility deteriorates to ±5%, and for *p*-methoxyaniline and pyridine.

Plots of log K_i *vs.* T^{-1} are straight lines, within experimental error, leading to values of $\Delta H_i°$ and $\Delta S_i°$ as listed in Table II. The precision of $\Delta H_i°$ ranges from ±0.2 to 1.0 kcal and that of ΔS_i from ±0.7 to 3.0 gibbs.

We have also measured the equilibrium constant for proton transfer between substituted anilines and cyanoacetic acid (HX) in acetic acid solution. Following previous practice[15] we define K_i^{HX} by eq 4, where [B] and $[BH^+X^-]$ denote molar concentrations, and N_{HX} is the (formal) mole fraction (formula weight fraction) of cyanoacetic acid in the solvent. Since

$$K_i^{HX} = [BH^+X^-]/[B]N_{HX} \qquad (4)$$

values of N_{HX} ranged up to 0.10, we further allowed for the changing activity of acetic acid with N_{HX} by assuming that $[BH^+Ac^-]/[B] \approx K_i(1 - N_{HX})$. On this basis, and neglecting ion-pair dissociation, we obtained eq 5. It follows from eq 5 that a plot of $(\epsilon_B c - A)/$

$$-\frac{A - \epsilon_B c}{A - \epsilon_{BH^+} c} = \frac{[BH^+X^-] + [BH^+Ac^-]}{[B]} = K_i + (K_i^{HX} - K_i)N_{HX} \qquad (5)$$

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(7) F. S. Feates and D. J. G. Ives, *J. Chem. Soc.*, 2798 (1956).

(8) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworth and Co., Ltd., London, 1965.

(9) H. Goldschmidt and E. Mathiesen, *Z. Physik. Chem.*, **A119**, 439 (1926).

(10) (a) A. M. Shkodin, N. A. Izmailov, and L. I. Karkuzaki, *Ukr. Khim. Zh.*, 27, 155 (1960); (b) A. M. Shkodin and L. P. Sadovnichaya, *ibid.*, 30, 773 (1964); (c) A. M. Shkodin and L. P. Sadovnichaya, *Izv. Vysshykh. Uchebn. Zavedenii, Khim. i Khim. Tekhnol.*, 7, 568 (1964).

(11) $[BH^+]/[BH^+Ac^-] = ([Na^+]/[Na^+Ac^-])(K_d/K_d^{Na^+Ac^-})$. $[Na^+]/[Na^+Ac^-] \leqslant (4 \times 10^{-7})[Na^+Ac^-]^{-1/2}$; the K_d ratio is of the order of unity. $[BH^+Ac^-]$ is less than 0.001 *M* in our experiments.

(12) A. E. Gillam and E. S. Stern, "Ultraviolet Absorption Spectroscopy," 2nd ed, E. Arnold Publishing Co., London, 1957, p 140.

(13) This band probably involves charge transfer from the amino group to the aromatic π system. We are indebted to Dr. L. Goodman for a helpful discussion.

(14) (a) In fact, $\epsilon_{BH^+Ac^-} c$ could be neglected relative to *A* in all K_i measurements except those for pyridine and the methoxy-substituted anilines. (b) On the other hand, $\epsilon_B c$ in eq 3 could not be neglected relative to *A* near λ_{max} of the B band for any of the bases studied. The neglect of this term in previous work on pyridine in acetic acid accounts for the discrepancy between our K_i value for pyridine (Table II) and that reported previously.[3]

(15) E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **86**, 4517 (1964).

Table II. Thermodynamic Quantities for the Ionization of Substituted Anilines in Acetic Acid

Aniline	Optical data[a]		K_i at			$\Delta H_i°$,	$\Delta S_i°$,
	λ, mμ	ϵ_B	20°	30°	40°	kcal	gibbs
p-OCH_3	298	1975	...	32.8	...	...	...
m-OCH_3	282[b]	1980	6.50	4.71	3.43	−5.8	−16.0
3,5-Di-OCH_3	272[b]	709	...	2.23	...	...	...
p-CH_3	288	1450	26.9	19.2	13.7	−6.2	−14.5
m-CH_3	282	1400	...	9.56	...	...	...
3,5-Di-CH_3	285	1295	20.5	14.0	9.87	−6.6	−16.5
H	280	1412	9.77	7.10	5.30	−5.6	−14.6
p-Cl	290	1353	...	1.24	...	...	...
m-Cl	287	1650	0.505	0.415	0.326	−4.2	−15.6
p-Br	291	1265	...	0.944	...	...	...
p-I	288	1455	0.863	0.690	0.559	−3.9	−13.6
p-F	288	1780	6.19	4.66	3.43	−5.5	−15.0
m-CF_3	289	1832	0.280	0.240	0.197	−2.1	−9.8
N,N-Di-CH_3	299[c]	1950[c]	14.9	11.4	8.67	−5.0	−11.6
N,N-Di-C_3H_7-n	305[c]	2310[c]	...	28.6	...	...	...
Pyridine	260[b]	1720	...	1.88	...	...	...
Butter yellow	534[b]	d	...	0.0984	...	...	...

[a] Unless otherwise indicated, λ is λ_{max} and ϵ_B is ϵ_{max} for the "B band" of the aromatic amine, as measured in water-methanol (95:5). See text. [b] At this λ, $\epsilon_{BH^+Ac^-}$ is not negligible. Values are: m-OCH_3, 630; 3,5-di-OCH_3, 2042; pyridine, 4040; butter yellow, 4.50×10^5. [c] Same as footnote a, but measured in pure methanol. [d] ϵ_{BC} can be neglected.

Table III. Equilibrium Constants for Proton Transfer between Cyanoacetic Acid and Substituted Anilines in Acetic Acid at 30°

Substituent	K_i^{HX}, eq 4	K_i^{HX}/K_i
p-Cl	115	93
m-Cl	44	106
m-CF_3	24	100

$(A - \epsilon_{BH^+}c)$ *vs.* N_{HX} should give a straight line, with slope equal to $(K_i^{HX} - K_i)$ and intercept equal to K_i. Since we have previously measured K_i, only the slope is needed to measure K_i^{HX}. Experimentally, such a plot showed cuvature at low concentrations of cyanoacetic acid ($N_{HX} < 0.03$), followed by a straight-line relationship at higher concentrations. The magnitude of the deviations from the straight-line relationship at low N_{HX} varied uncontrollably with the batch of acetic acid used; it was independent of the batch of cyanacetic acid. However, the slope of the straight-line portion above $N_{HX} = 0.03$ was reproducible and independent of solvent batch. We take these observations to imply the presence of an impurity in variable amount, whose perturbing effect goes to completion at $N_{HX} \approx 0.03$. We tried to remove possible impurities by various methods (see Experimental Section) but could not remedy the problem. We finally decided to ignore the curved portion of the plots and deduce K_i^{HX} from the reproducible slopes above $N_{HX} \approx 0.03$. Values obtained in this way are summarized in Table III. K_i^{HX}/K_i is consistently ≈100, independent of the substituent. For comparison, K_A^{HX}/K_A^{HAc} is 193 in water[7] and 85 in m-cresol.[16]

Results for K_d. To obtain K_d it was convenient to measure over-all dissociation constants,[2] K_B (defined in eq 6), and to calculate K_d by means of eq 7, using K_i as listed in Table II. Since we were interested primarily in substituent effects on K_d, we used a method that would give accurate *ratios* of K_B (and therefore of K_d) for the various aromatic amines, although the *absolute* K_B values are considerably less accurate. This method, which employs a color indicator to measure the concentration of free acetate ion, was first reported by Bruckenstein and Kolthoff,[3] whose paper should be consulted for details and derivations. As indicator we used butter yellow (p-dimethylaminoazobenzene), whose ionization constant ($K_i^I = 0.0984$ at 30°) and absorption spectrum in the acid and base form in acetic acid are suitable. Our results for butter yellow are in good agreement with results reported by Bruckenstein and Kolthoff[3] for an indicator called DMAAB (p,p'-dimethylaminoazobenzene, by mistake), and Dr. Bruckenstein has informed us that DMAAB and butter yellow are in fact the same substance.[17]

$$K_B = \frac{[BH^+][Ac^-]}{[B] + [BH^+Ac^-]} = \frac{K_iK_d}{1 + K_i} \tag{6}$$

$$K_d = K_B(1 + K_i)/K_i \tag{7}$$

To obtain K_B we measured the absorbance at 534 mμ for a series of solutions containing a fixed concentration of indicator and various concentrations, c_B, of added aromatic amine. The absorbance, which is due almost entirely to the acid form of the indicator, coupled with data for ε and K_i^I enabled us to evaluate [I], the concentration of unprotonated butter yellow, and [IH+], that of its free conjugate acid ion. K_B for the aromatic amine was then obtained from the slope and intercept of the data plotted according to eq 8.

$$[I]/[IH^+]^2 = (K_i^IK_d^I)^{-1} + (K_i^IK_d^I)^{-2}K_Bc_B/[I] \tag{8}$$

Equation 8 assumes that thermodynamic activities are equal to concentrations for all solutes because of the very low concentrations and ionic strengths used. In order to minimize any errors that might nevertheless arise from this assumption on the *ratio* of K_B for different anilines, we kept the indicator concentration constant at 3×10^{-5} M in all experiments and varied c_B for each aniline such that $[IH^+]$ varied from 3×10^{-6} to 1×10^{-6} M. In this way all K_B determinations refer to the same range of ionic strengths, from 3×10^{-6} to 8×10^{-6} M.

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(16) J. N. Bronsted, A. Delbanco, and A. Tovborg-Jensen, *Z. Physik. Chem.*, **A169**, 361 (1934).

(17) We found that authentic p,p'-dimethylaminoazobenzene gives a green color in pure acetic acid, which changes to red on acidification with perchloric acid.

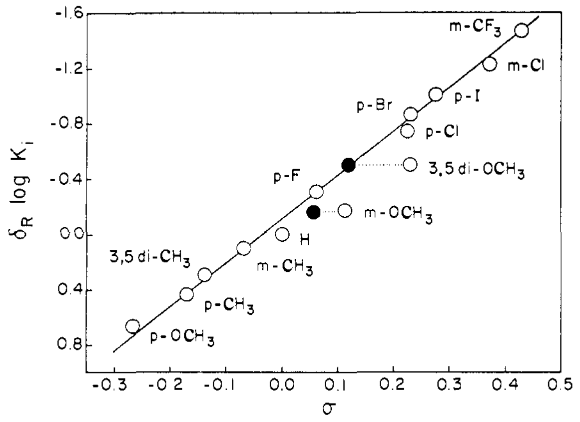

Figure 1. Substituent effects on K_i for aniline in acetic acid at 30°. The abscissa is the Hammett substituent constant σ; ○, σ values from ref 18; ●, special σ value for m-OCH_3 in nonaqueous solvents as given in ref 20.

In view of the difficulty to remove all traces of water or basic impurities from the solvent, the preceding experimental design has another important advantage: in the plot of the data according to eq 8, the *slope* is virtually independent of the presence of small amounts of basic impurities in the solvent; the impurities affect the intercept. To show this, suppose that the solvent contains an impurity B′ at concentration c_B' in addition to the substrate B and the indicator I. Then I behaves according to eq 9, which is a more general version of eq 8. Now [IH$^+$], in spite of its relatively large

$$[I]/[IH^+]^2 = (K_i^IK_d^I)^{-1} + (K_i^IK_d^I)^{-2}(K_Bc_B + K_B'c_B')/[I] \qquad (9)$$

variation with c_B, is always a small fraction of the total concentration of indicator, so that [I] varies by less than 8% in all experiments. Thus, if a single solvent batch is used throughout the series of measurements, $c_B'/[I]$ will be virtually constant as c_B is changed. That is to say, in the plot according to eq 8 the intercept will be larger than $(K_i^IK_d^I)^{-1}$ but the slope will be substantially correct.

Table IV. Ion-Pair Dissociation Constants for Substituted Anilinium Acetates and Related Salts in Acetic Acid at 30°

Substituent	Slope × 10^{-5}, eq 8	$K_d \times 10^7$
m-CF_3	2.48	2.02
p-Cl	7.53	2.14
m-Cl	6.13	3.29
p-F	23.7	4.5
H	30.6	5.5
p-OCH_3	38.4	6.3
3,5-Di-OCH_3	28.5	6.5
m-OCH_3	38.8	7.4
m-CH_3	48.3	8.4
N,N-Di-C_2H_5	...	16[a]
Pyridinium Ac	...	12[b]
NaAc	24.6	3.9[c]
IH Ac[d]	...	41[e]

[a] $K_i = 20$; $K_B = 1.6 \times 10^{-6}$ at 25°.[4] [b] $K_i = 1.88$; $K_B = 7.9 \times 10^{-7}$ at 25°.[3] [c] Reference 4 reports 2,6 on the basis of emf measurements at 25°. [d] Acetate salt of butter yellow. The average intercept in eq 8 (after applying a small corrrection for *ca.* 0.03 M water in the solvent, using data of ref 3) for all salts is (25 ± 5) × 10^5. K_i^1 is 0.0984. [e] Reference 3 reports 50 at 25°.

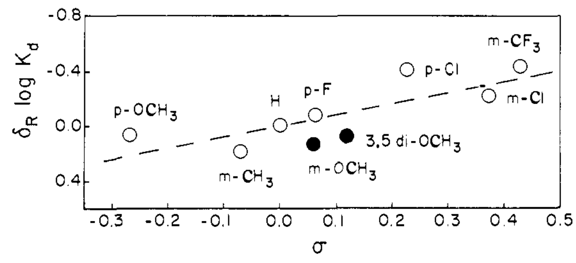

Figure 2. Substituent effects on K_d for anilinium acetate in acetic acid at 30°. For further details see caption of Figure 1.

The relevant results are summarized in Table IV. The second column lists the slopes of the plots *vs.* c_B/[I], which are reproducible to 5% or better. The third column lists "best values" for K_d, which are based on these slopes, on K_i values as listed in Table II, and on an average *intercept* of (25 ± 5) × 10^5 for all substrates. We believe that the *ratio* of any two K_d values for substituted anilines is accurate to 10%. The *absolute* values are uncertain by about 50%, on the basis of the precision of the intercept. In the two cases where our K_d values can be compared with previous determinations by Bruckenstein and Kolthoff[3,4] the agreement is well within the 50% figure (see Table IV).

Discussion

From a chemist's point of view there is a marked difference between ionization to form an ion pair and dissociation of the ion pair to free ions. The ionization step is a genuine chemical reaction in which covalent bonds are broken and formed. The dissociation of an ion pair is a physical process, involving the physical separation of the ions. Ordinary covalent bonds are not broken or formed; nonbonded electrostatic interactions dominate, modified perhaps by hydrogen bonds with small amounts of covalent character. We shall see that this difference in the two processes is reflected in a lack of analogy between substituent effects on K_i and K_d.

***meta*- and *para*-Substituted Anilines.** To compare our data with substitutent effects in other chemical reactions of *meta*- and *para*-substituted benzene derivatives, it is convenient to test the Hammett equation (10), which applies to a wide variety of reactions.[6]

$$\delta_R \log K \equiv \log (K/K^\circ) = \rho\sigma \qquad (10)$$

Here and throughout this Discussion we use the operator δ_R to denote the substituent effect on whatever function follows it. In (10), K° pertains to the substrate without a *meta* or *para* substituent; ρ and σ are parameters characteristic of the reaction and the substituent.[6] Required values of σ were taken from the compilation of Taft.[18] It should be noted that the substituents chosen for study in this work are such that electron-removing resonance (+R effect)[19] is relatively small, and we need not distinguish between σ and (in Jaffé's terminology)[6b] σ^-.

Figures 1 and 2 show plots of $\delta_R \log K_i$ and δ_R log

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(18) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13, p 571.

(19) L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963, pp 416-417.

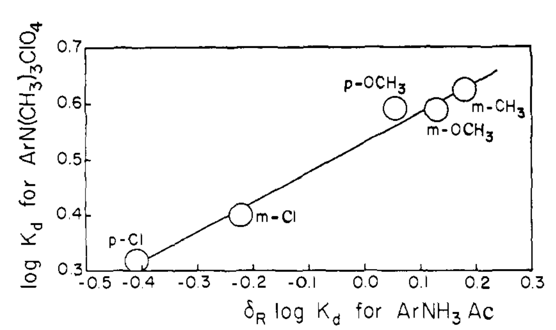

Figure 3. Log K_d for substituted phenyltrimethylammonium perchlorates in ethylene dichloride at 25° plotted *vs.* δ_R log K_d for substituted anilinium acetates in acetic acid at 30°. The straight line is drawn with slope 0.536.

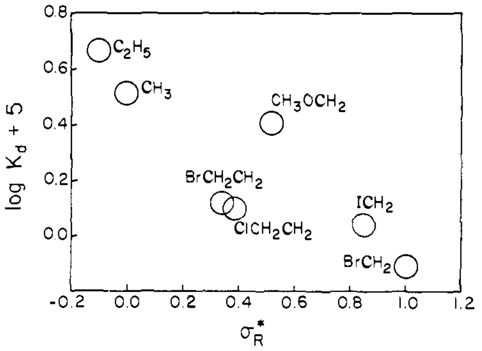

Figure 4. Log K_d for $RN(CH_3)_3$ picrate in ethylene dichloride at 25° *vs.* the Taft substituent constant σ_R^*. The identification marks of the points denote R.

K_d *vs.* σ. The coordinates are drawn on the same scale, to facilitate comparison. The relationship of δ_R log K_i to σ (Figure 1) is very close to a straight line, in agreement with (10). The only points that deviate seriously are those for *m*-OCH_3 and 3,5-di-OCH_3. However, Professor R. W. Taft has pointed out to us that these points become aligned with the others if we allow $\sigma_{m\text{-}OCH_3}$ to have the special value, 0.060, that he has recommended for *m*-OCH_3 in nonaqueous solvents.[20] The straight line drawn in Figure 1 has a slope, $-\rho_i$, of 3.126 and fits the data with a probable error of 0.04 log unit, almost within the combined experimental errors of δ_R log K_i and σ. The correlation coefficient is 0.996. We conclude that with respect to substituent effects, the ionization of aniline is a "normal" and typical aromatic side-chain reaction.

Substituent effects on log K_d are plotted *vs.* σ in Figure 2. The range of K_d is about one-fourth of that of δ_R log K_i. There is a rough trend for log K_d to increase with σ, but the plot shows considerable scatter. The least-squares linear correlation is shown by the dashed line in Figure 2. The slope of the line, $-\rho_d$, is 0.817, and the probable error of fit is 0.09 log unit. The correlation coefficient is 0.78. We regard this correlation as "poor."

Pattern of Substituent Effects in Ion-Pair Dissociation. It is of course not surprising that δ_R log K_d in Figure 2 should show at least a rudimentary correlation with σ. Any substituent that acts so as to decrease the electron density of aromatic side chains in chemical reactions ($\sigma > 0$) should also increase the effective positive charge of the NH_3^+ group, thereby stabilizing the anilinium acetate ion pair relative to the free ions. For this reason we had expected at the start of this work that the correlation of log K_d with σ would be quite good. On finding otherwise, we compared our results with previously reported substituent effects on ion-pair dissociation constants. Although the data are scant, they suggest that there is a general pattern of substituent effects in ion-pair dissociation, and that this pattern is quite different from the well-known pattern of substituent effects in chemical reactions.[21]

Denison and Ramsey have reported ion-pair dissociation constants for *o*-, *m*-, and *p*-anisyl-, -tolyl-, and -chlorophenyltrimethylammonium perchlorate in ethylene chloride.[22] For *meta* and *para* substituents their K_d values follow the sequence, *m*-CH_3 ≈ *p*-CH_3 > *m*-OCH_3 ≈ *p*-OCH_3 > *m*-Cl > *p*-Cl, which closely resembles the sequence we report in Table IV. A log-log plot of their K_d values against ours is shown in Figure 3. The linear relationship suggested by the line fits the data well: the probable error of fit is 0.012 log unit, the correlation coefficient is 0.993.

Kraus and co-workers have reported ion-pair dissociation constants for salts of the type $RN(CH_3)_3$ picrate in ethylene chloride[23] and nitrobenzene.[24] The R group is alkyl, phenyl, methoxy, XCH_2, or XCH_2CH_2, where X = Cl, Br, I, or OCH_3. If substituent effects in ion-pair dissociation were analogous to those in chemical reactions, we would expect log K_d to be related linearly to Taft's polar substituent constant σ^*.[18,21] The actual data are plotted in Figures 4 and 5. Again there are rough linear trends, but the correlations are not good. On the other hand, if the substituents are arranged in order of increasing K_d, the sequence that develops appears to be the same in each solvent and very similar to that noted previously for *meta* and *para* substituents in the benzene series: K_d is largest when R is a hydrocarbon radical such as CH_3, C_2H_5, or C_6H_5; it is somewhat smaller when R is methoxy or CH_3OCH_2; and it is still smaller when R is haloalkyl or a halogen atom. This sequence is distinctly different from that of polar substituent effects in chemical reactions, as measured by σ or σ^*.

Concerning Inductive and Field Effects. In physical organic discussions of substituent effects a distinction is sometimes made between two models, called *inductive effects* and *field effects*.[25] Inductive effects can be transmitted efficiently only through covalent bonds. Field effects can be transmitted through any volume element of space, the efficiency of transmission depending on the dielectric properties of the matter in the volume element, in accordance with general laws of electricity. In theory the field effects model includes the inductive effects: one needs only to describe the dielectric properties of each volume element with sufficient precision. In practice one needs to simplify. In the usual approximate theory of field effects one

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[20] R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

[21] See, for example, J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 7.

[22] J. T. Denison and J. B. Ramsey, *J. Am. Chem. Soc.*, **77**, 2615 (1955).

[23] D. J. Mead, J. B. Ramsey, D. A. Rothrock, and C. A. Kraus, *ibid.*, **69**, 528 (1947).

[24] E. G. Taylor and C. A. Kraus, *ibid.*, **69**, 1731 (1947); C. R. Witschonke and C. A. Kraus, *ibid.*, **69**, 2472 (1947).

[25] See, for example, J. D. Roberts and W. T. Moreland, *ibid.*, **75**, 2167 (1953).

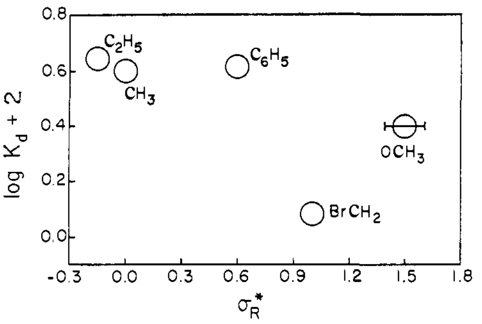

Figure 5. Log K_d for $RN(CH_3)_3$ picrate in nitrobenzene *vs.* the Taft substituent constant σ_R^*. The value of $\sigma_{OCH_3}^*$ was estimated by the authors and is uncertain by ±0.1. The identification marks of the points denote R.

represents the substrate molecule as a small sphere or ellipse containing a fixed set of permanent charges or electric dipoles and filled with an isotropic dielectric fluid, and which is imbedded in a dielectric continuum that represents the solvent.[26]

In terms of this approximate model of field effects, ion-pair dissociation of anilinium acetate is exactly analogous to a displacement reaction in an aromatic side chain: acetate ion leaves and a solvent molecule enters. We would, therefore, expect log K_d to be correlated with substituent parameters that correlate chemical reactivity, such as σ or σ^*. On the other hand, in terms of the model of inductive effects, ion-pair dissociation is *not* analogous to a genuine displacement reaction because there is no change in covalency: the absence of covalent bonds to the entering and leaving groups should make an essential qualitative difference. It is in this sense that the results presented in the preceding section support the model of inductive effects.

Tertiary *vs.* Primary Aromatic Amines. The effect of N-alkyl substitution on the basicity of an amine depends very much on the solvent.[27] We find (Table II) that in acetic acid, K_i is in the sequence $PhNH_2$ < $PhN(CH_3)_2$ < $PhN(n\text{-}C_3H_7)_2$, which is the sequence of increasing electron supply to nitrogen as measured by σ^*.[18] In acetic acid (as in other solvents[24]) N-alkyl substitution also promotes ion-pair dissociation (Table IV).

Data for the relative basicity of N-dimethylaniline, pyridine, and aniline in a number of solvents[8,9,16,27–29] are summarized in Table V. The values of δ_R log K_B are quite large and range from positive to negative, without showing any obvious pattern. Two remarks are perhaps worth making. (1) It is not justified in this case to single out water as a unique solvent in which substituent effects are characteristically different or complex. (2) There is no strong analogy between δ_R log K_B for N-dimethylaniline and pyridine even though both bases are tertiary aromatic amines.

$\Delta H_i°$, $\Delta S_i°$. Values of $\Delta H_i°$ and $\Delta S_i°$ for ionization in acetic acid are included in Table II. For *meta*- and *para*-substituted anilines the substituent effects appear to be enthalpy controlled: except for *m*-CF_3, all values of $\Delta S_i°$ differ by no more than the experimental error. Our results may be compared with results reported recently by Biggs[30] for base dissociation in water. For the 12 monosubstituted anilines with F, Cl, Br, I, OCH_3, and CH_3 in the *meta* or *para* positions, $\delta_R \Delta H_B°$ varies by more than 2 kcal, $T\delta_R\Delta S_B°$ varies by about 1.3 kcal, and there is no obvious correlation between the two quantities.

Table V. Basicity of N-Dimethylaniline and Pyridine Relative to Aniline in Various Solvents

Solvent	δ_R log K_B[a] $C_6H_5N(CH_3)_2$	C_5H_5N	Ref
H_2O	0.51	0.61	8
CH_3OH	−0.80	−0.46	9, 28
C_2H_5OH	−1.33	. . .	27
CH_3COCH_3	−1.01	−0.15	28
$HCONH_2$	. . .	0.38	29
m-Cresol	1.92	. . .	16
CH_3CO_2H	0.20	−0.58	δ_R log K_i[b]
CH_3CO_2H	0.66	−0.23	δ_R log (K_iK_d)[b]

[a] δ_R log K_B for aniline is 0.00 throughout this table. [b] This work.

Experimental Section

Spectral Measurements. The absorbance of solutions was measured with a Beckman Model DU spectrophotometer equipped with thermospacers which provided constant temperature (±0.05°) in the cell compartment. Optical cells were matched, 1-cm silica cells provided with ground-glass stoppers. Solutions were always prepared fresh from recently purified batches of substrate and solvent. Absorbances were highly reproducible (except in the experiments with added cyanoacetic acid) and did not change over several hours after temperature equilibrium had been established.

Materials. Acetic acid was purified in 5-lb lots by partially freezing in an ice bath until approximately half of the material was frozen, and then discarding the mother liquor. This process was repeated at least twice. The final product still contained *ca.* 0.03 *M* water (by Karl Fischer titration), but was neutral ($<10^{-6}$ *M*) to acid and base and gave stable aniline spectra. By contrast, we found in preliminary experiments that any method of purification that involves distillation of acetic acid at atmospheric pressure as the final step results in a product that gives time-dependent aniline spectra. The spectral changes are consistent with the theory that the solvent, after distillation, contains acetic anhydride which reacts with aniline to give acetanilide. This undesirable interaction of solvent with aniline takes place not only if the solvent is distilled from a pot containing a dehydrating agent such as triacetyl borate or chromium trioxide but also when the pot contains no additive other than a boiling chip. The interaction becomes insignificant if the solvent is distilled below 50° at reduced pressure. Dr. S. Bruckenstein has informed us that he, too, has evidence to indicate that acetic acid disproportionates into anhydride and water when distilled at atmospheric pressure.

As mentioned previously, the solvent purified by several cycles of partial freezing, discarding of the mother liquor, and thawing gives highly reproducible aniline spectra but still contains an impurity in adventitious amount that causes the absorbance in the presence of cyanoacetic acid to be variable with solvent batch by up to 10%. The impurity could not be removed by distillation at reduced pressure, nor could it be removed by treatment with 2,4-dinitrophenylhydrazine followed by distillation at reduced pressure.

The anilines were commercial products of reagent or White Label grade. Solid anilines were recrystallized to analytical purity from water or from ethanol-water mixtures; liquid anilines were distilled under vacuum. All melting and boiling points agreed with values found in the literature.

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(26) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1938).

(27) See, for example, B. Gutbezahl and E. Grunwald, *J. Am. Chem. Soc.*, **75**, 559 (1953).

(28) N. I. Izmailov and T. V. Mozharova, *Zh. Fiz. Khim.*, **34**, 1543, 1709 (1960).

(29) F. H. Verhoek, *J. Am. Chem. Soc.*, **50**, 2577 (1936).

(30) A. I. Biggs, *J. Chem. Soc.*, 2573 (1961).