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Measurement of the Basic Strength of Weak Bases in Glacial Acetic Acid[1]

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The thermodynamic constants, pK_a, of three indicators useful in the study of weak bases have been evaluated; they are -1.4 for 2-nitro-4-chloro-N-methylaniline, -0.1 for 2,6-dichloro-4-nitro-N,N-dimethylaniline, and $+0.3$ for 2,4-dinitro-N,N-diethylaniline. The indicator method of determining the basic strength of weak bases has been extended to solutions in acetic acid, and has been found applicable for bases having pK_a values between -4.5 and 1.1. Thermodynamic constants pK_a, have been calculated, as follows: acetonitrile, -4.2; dioxane, -4; *p*-toluenesulfonamide, -3.2; water, -2.3_5; acetanilide, -0.9; acetamide, $+0.1$; urea, $+0.5$. The constants of acetone, acetophenone, benzophenone, ethylene diacetate, dibutyl ether, cyclohexene and 3-hexyne do not exceed -4.5 and those of diphenylamine and *o*-chloroaniline exceed 1.1; all these lie outside the range of study by this method. The relationship between the thermodynamic constant, pK_a, of a base and its ionization constant, K_a^s, in acetic acid and in the presence of perchloric acid in concentrations up to 0.2 M is accurately expressed by $pK_a - pK_a^s = -3.88$.

Introduction

The high activity of hydrogen ion in glacial acetic acid solutions of strong acids makes this solvent a useful medium for studying the basic strengths of weak bases. Hall[3] investigated the strengths of a large number of weak bases in acetic acid by conductometric titration with perchloric acid. Hammett and Deyrup[4] determined the basic strengths of water and propionitrile by means of an indicator method, with formic acid as the solvent and benzene–sulfonic acid as the strong acid. Hall and Spengeman[5] established the constants of certain indicators in acetic acid in order that the indicator method might be used in this solvent. In the present paper are presented the results of measurements of a number of indicators in glacial acetic acid and the constants of some weak bases obtained by means of these indicators.

The constants evaluated and the symbols used are shown in Equations 1, 2 and 3, where bracketed expressions are activities (concentration–activity coefficient products), expressions in parentheses are the actual concentrations in glacial acetic acid, B represents an uncharged base and BH^+ its conjugate acid. When the base is colored, *i.e.*, an indicator, these last two are replaced by I and IH^+, respectively. The superscript s stands for solvent, in this case glacial acetic acid.

$$K_a = [B][H^+]/[BH^+] \qquad (1)$$

$$K_a^s = (B)(H^+)/(BH^+) \qquad (2)$$

$$H_0 = \log (B)/(BH^+) + pK_a \qquad (3)$$

The thermodynamic constant K_a is defined in Equation 1. It is the thermodynamic acid constant of BH^+, the conjugate acid of the base. The ionization constant, K_a^s, in a solvent, s, is given by Equation 2. The validity of this equation, with K_a^s constant, depends on the fact that H^+/BH^+ is a ratio so that the ionic activity coefficients cancel because both ions are subjected to similar ion atmospheres in the same medium, and on the fact that γ_B can be taken as unity in dilute solution. The acidity function,[4] H_0, is given by Equation 3. With this equation it is possible to calculate the thermodynamic constant of a base from measurements made in non-aqueous media.

A relation between pK_a and pK_a^s is obtained by adding log (H^+) to Equation 3 and combining with Equation 2.

$$pK_a - pK_a^s = H_0 + \log (H^+) = Q \qquad (4)$$

Since pK_a is a constant, and since pK_a^s is also a constant, subject perhaps to small concentration effects, Q (Equation 4) will also be a constant, and it can be evaluated from observations made on solutions containing a strong acid and an indicator.[6] H_0 can be evaluated readily.[4] The value of (H^+) can be obtained by subtracting from the total concentration of perchloric acid the concentrations of any species containing the proton in combination. The value of (IH^+) is obtained accurately from the known concentrations of total indicator and free indicator in the presence of acid, as determined by the spectrophotometric readings. It is assumed that none of the proton is combined with perchlorate ion.[7] Some of the data are shown in Table II. The result is expressed by Equations 5 and 6.

$$H_0 + \log (H^+) = -3.88 \qquad (5)$$

$$pK_a - pK_a^s = -3.88 \qquad (6)$$

The thermodynamic constant of a base may be calculated with Equation 6 from constants obtained in glacial acetic acid.

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[2] Wyandotte Chemicals Corporation, Wyandotte, Michigan.

[3] N. F. Hall, THIS JOURNAL, **52**, 5115 (1930).

[4] L. P. Hammett and A. J. Deyrup, *ibid.*, **54**, 2721, 4239 (1932).

[5] N. F. Hall and W. F. Spengeman, *ibid.*, **62**, 2487 (1940).

(6) Throughout these investigations the acid used, except as noted in footnote seven, was perchloric acid and the indicators, I, were substituted nitroanilines of the type used by previous investigators.[4,5] They are colored and their conjugate acids, IH^+, are colorless.

(7) The assumption that perchloric acid is completely ionized in acetic acid may not be completely justified, even though Q has a constant value of -3.88 over a two thousand fold range of concentration of perchloric acid, namely, 7.6×10^{-5} M to 0.14 M. Presumably at the lowest concentrations the solutions have become so dilute that extrapolation to zero concentration would produce little further change in Q. However, solutions of sulfuric acid also show a constant value of Q in solutions in acetic acid up to 0.4 M, from observations made in the present investigation and from earlier work,[5] but the value of Q is different in this case, namely, about -2.55. On the basis of constancy of Q sulfuric acid also could be considered to be completely ionized, but it is evident that its concentration must be twenty times that of perchloric acid to produce a solution of equal acidity. It appears, therefore, that constancy of Q cannot be considered proof of complete ionization.

The referee has pointed out that in a solvent of low dielectric constant there may be an apparent compensation of neglected activity coefficient and ion association effects and that this may explain the behavior of the two acids. For this reason there may be some uncertainty in the method of obtaining (H^+). To the extent that the calculated value of (H^+) is in error, the values given for pK_a^s, will deviate from the true ionization constants, and the values given for pK_a will deviate from the true thermodynamic constants.

TABLE I

INDICATOR CONSTANTS

Soln. no.	Indicator name	Concn., $M \times 10^4$	Absorp. max., mμ	Molar extinct. coefficient at absorp. max.	pK_a Lit.[a]	K^s_a $\times 10^3$	pK_a Eq. 4
IA	4-Chloro-2-nitroaniline	5.81	410	4470	−0.91	1.22	−0.97
IB		5.53		4700		1.33	−1.00
ICa		5.52		4840		1.08	−0.91
ICb		5.52		4620		1.08	−0.91
ID		5.75		4930		0.97	−0.87
IIA	4,6-Dichloro-2-nitroaniline	5.40	408	4540	−3.67	701	−3.73
IIIA	4-Chloro-2-nitro-N-methylaniline	4.93	437	5560		3.08	−1.37
IVB	2,6-Dichloro-4-nitro-N,N-dimethylaniline	6.78	[b]			0.172	−0.11
VA	2,4-Dinitro-N,N-diethylaniline	3.18	375	15,700		0.0655	+0.30

[a] Reference five and references therein. [b] Absorption maximum of Indicator IV was at about 380 mμ. Readings were made at 420 mμ to avoid interference from absorption by the conjugate acid of this indicator.

Experimental

Preparation of Materials.—Acetic acid, C.P., was fractionally distilled through a 90-cm. column of glass helices surrounded by an electrically heated jacket and provided with a total-reflux partial-take off still head.[8] Batch lots of 2.5 liters were distilled and initial cuts of 0.5 to 0.7 liter were discarded. The melting point of the main cut was always 16.6°, and this value remained constant throughout the weeks of use.

Solutions of perchloric acid in acetic acid were prepared by mixing in anhydrous acetic acid the appropriate quantities of 60% aqueous perchloric acid and acetic anhydride. Standardizations were made in two ways: (1) on the original aqueous perchloric acid, by dilution with water, then titration against standard aqueous iodide–iodate,[9] and (2) on the final acetic acid solution by titration against a standard solution of recently distilled aniline in acetic acid with crystal violet as the indicator. There was exact agreement between the results of the two methods.

The indicators, if available, were purified, and if not, were prepared by standard methods. **4-Chloro-2-nitroaniline** (I) (Eastman Kodak Co.) was crystallized from hot water, m.p.[10] 116.0°. Chlorination of *o*-nitroaniline in concentrated hydrochloric acid[11] gave **4,6-dichloro-2-nitroaniline** (II) which after crystallization from ligroin (90–127°) had m.p.[12] 100.7–101.0°.

Recrystallized I was heated with dimethyl sulfate at 100° for one hour. The solid resulting from the addition of aqueous sodium hydroxide was recrystallized successively from ligroin, water and ligroin; product, **4-chloro-2-nitro-N-methylaniline** (III), m.p.[13] 106.0–106.5°. Nitration of dimethylaniline[14] followed by stepwise chlorination[15] gave **2,6-dichloro-4-nitro-N,N-dimethylaniline** (IV), crystals from ethyl alcohol, m.p.[16] 105–107°. Diethylamine and 2,4-dinitrochlorobenzene in 1-butanol reacted spontaneously and the solution became hot. On the addition of water **2,4-dinitro-N,N-diethylaniline** (V) separated. This was crystallized twice from alcohol, reprecipitated from its solution in hydrochloric acid by sodium bicarbonate and recrystallized from alcohol; m.p.[17] 78.5–79.0°.

The colorless bases, in addition to water, which was laboratory distilled water, were the best grade of commercially available products. They were subjected to additional purification. *Acetonitrile* was dried with phosphorus pentoxide and distilled, $n^{25}\mathrm{D}$ 1.3409. *Dioxane* was refluxed five hours over sodium hydroxide and five hours over metallic sodium and then distilled, $n^{25}\mathrm{D}$ 1.4195. *Acetamide* was crystallized from freshly distilled isopropyl ether, m.p. 80.0–80.8°, *acetanilide* from water, m.p. 113–114°, and *p-toluenesulfonamide*, m.p. 138–138°, and *urea*, m.p. 132.2–133.5°, were crystallized from ethyl alcohol.

Measurement of Basic Strength. (1) **Indicators.**—Stock solutions of the indicators were prepared in glacial acetic acid in concentrations of about 0.0005 *M*. The optical densities of diluted solutions of each stock solution were determined with a Beckman spectrophotometer in 1.000-cm. Corex cells. Readings were taken at a specified wave length, usually an absorption maximum. Solutions of indicators that were strong enough bases to react appreciably with the solvent (those having a pK_a greater than −1.0) were diluted with acetic acid containing aniline or potassium acetate. Concentrations were chosen for both the neutral and the basic (last two) solutions and also for the test solutions containing perchloric acid, so that the observed optical densities were usually between 0.200 and 0.400. Different dilutions of the same stock solution were found to obey Beer's law in the range in which observations were made. The observed readings were divided by the fraction by which the concentration of the indicator had been diminished (called the dilution factor) so as to convert all readings to the same basis, which would be the optical density of the original stock solution if Beer's law held. It is immaterial for these calculations whether or not Beer's law holds up to the concentrations of the stock solutions, because the readings are made at approximately the same concentration of the colored form of the indicator.

The indicator constant K^s_a was determined by mixing known amounts of indicator solution, perchloric acid solution, and, usually, extra acetic acid. The optical density of such a test solution was determined and the value so obtained was divided by the dilution factor. The quotient is called the calculated optical density of the test solution. The value of K^s_a was then calculated with Equation 7, where *T* is the calculated optical density of the test solution, *S* is the calculated optical density of the stock indicator solution, *A* is the total perchloric acid concentration in the test solution and *C* is the total indicator concentration in the test solution.

$$K^s_a = \frac{(\mathrm{I})(\mathrm{H}^+)}{(\mathrm{IH}^+)} = \frac{(T)\{A - C(S - T)/S\}}{(S - T)} \tag{7}$$

(2) **Colorless Bases.**—The constants of colorless bases were determined from data on test solutions containing known amounts of indicator, perchloric acid, and colorless base. The calculated optical density of a test solution was obtained as before. The ionization constant was then calculated with Equation 8, where K_{aI} is the ionization constant of the indicator and B_t is the sum of the concentration of the colorless base and its conjugate acid. The value of pK^s_a from Equation 8, when inserted in Equation 6 gives

$$K^s_a = \frac{(\mathrm{B})(\mathrm{H}^+)}{(\mathrm{BH}^+)} = \frac{\{B_t - A + C(S - T)/S + K^s_{a1}(S - T)/T\}K^s_{a1}(S - T)/T}{A - C(S - T)/S - K^s_{a1}(S - T)/T} \tag{8}$$

the thermodynamic constant of the weak base.

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[8] F. Todd, *Ind. Eng. Chem., Anal. Ed.*, **17**, 185 (1945).

[9] I. M. Kolthoff, THIS JOURNAL, **48**, 1447 (1926).

[10] Previous value 116.2°, F. Swartz, *Rec. trav. chim.*, **35**, 131 (1916).

[11] A. E. Holleman and F. E. van Haeften, *ibid.*, **40**, 67 (1921).

[12] Previous value,[11] 101–102°.

[13] Previous value, 108°, H. Behrens, *Rec. trav. chim.*, **21**, 269 (1902).

[14] J. B. Tingley and F. C. Blanck, THIS JOURNAL, **30**, 1395 (1908).

[15] N. L. Drake, *et al.*, *ibid.*, **68**, 1602 (1946).

[16] Previous value,[15] 104–105°.

[17] Previous value, 80°, J. J. Blanksma and H. H. Schreinemachers, *Rec. trav. chim.*, **52**, 428 (1933).

TABLE II

TYPICAL VALUES OF H_0 + LOG (H^+) FOR VARIOUS SOLUTIONS CALCULATED FROM LITERATURE VALUES OF pK_a

Indicator soln. No.	(H^+), M × 10^5	(I), M × 10^5	(IH^+), M × 10^5	pK_a^s	pK_a	H_0	H_0 + log (H^+)
IA	128	4.25	5.4	+3.00	−0.91[a]	−1.02	−3.91
IB	95.4	6.27	4.6	+2.89	− .91[a]	− .78	−3.80
ICa	50.4	6.64	3.1	+2.97	− .91[a]	− .58	−3.88
ID	50.1	6.52	3.4	+3.02	− .91[a]	− .63	−3.92
II	9340	9.5	1.3	+0.16	−3.67[a]	−2.80	−3.83

[a] Reference five and references therein.

Results and Discussion

Indicators.—The properties of some solutions of the indicators, and the indicator constants are shown in Table I. Four different solutions of indicator I, *i.e.*, IA, IB, IC and ID, were made, IA and IB from one crystallization but five weeks apart, IC and ID from two other crystallizations. Precautions were taken to exclude air from the product of the last crystallization. It is believed to be the purest. The solutions underwent a slow change but this was not significant except in the case of IC, for ICb represents data taken three weeks after ICa.

The values of the indicator constants, pK_a, varied as follows: for indicator II, −3.74 to −3.61; III, −1.48 to −1.37; IV, −0.17 to −0.04; and V, +0.26 to +0.38. Whenever an indicator solution was being used for determining the basic strength of a colorless base, the values of the optical density and ionization constant were redetermined weekly. From the ionization constants of indicators I and II and literature values of the thermodynamic constants of these same indicators it has been possible to calculate the value of H_0 + log (H^+) Equation 5, as given in Table II.

Colorless Bases.—The data leading to the determination of the strength of seven weak bases are shown in Table III. The values for acetonitrile were obtained from two solutions of separately purified material, the first four from one, and the last five from the other. The values of pK_a were but very little affected by a three hundred-fold change in the acid concentration. This result is partial justification for neglecting the effect of

TABLE III

THE DETERMINATION OF THE STRENGTH OF WEAK BASES

Base	Indicator solution (Table I) No.	Indicator solution (Table I) Opt. dens.	Indicator dilution factor	Test solution $HClO_4$ total concn. M × 10^3	Test solution Base total concn. M × 10^3	Optical density obsd.	Basic strength K_a'	Basic strength pK_a
Acetonitrile	IB	2.60	1/4	1.250	951	0.400	2.15	−4.21
			1/5	1.000	381	.318	2.96	−4.35
			5/28	0.536	680	.355	2.66	−4.30
			1/8	.625	476	.235	2.50	−4.28
	ICb	2.55	5/28	.536	680	.3325	2.42	−4.26
			1/4	1.250	951	.361	2.14	−4.21
	IIA	2.452	1/5	186.8	761	.4085	2.17	−4.22
			1/6	78.2	633	.379	1.47	−4.05
			1/5	93.4	381	.442	1.69	−4.11
Dioxane	ID	2.836	1/5	1.000	556	.313	2.74	−4.32
			1/5	1.000	840	.325	2.66	−4.31
			1/5	1.000	280	.3035	2.30	−4.24
			5/23	1.087	183	.315	1.73	−4.12
p-Toluenesulfonamide	ID	2.836	1/5	1.000	149	.362	0.200	−3.18
			1/5	1.000	44.2	.309	.263	−3.30
			5/23	1.087	28.8	.320	.202	−3.19
Water	IA	2.60	1/6	1.67	100	.326	.0319	−2.38
			1/7	2.14	85.7	.250	.0328	−2.40
			1/4	2.50	50.0	.369	.3000	−2.36
	IIIA	2.742	5/28	0.893	119	.465	.0266	−2.31
Acetanilide	IB	2.60	1/5	1.00	1.86	.3865	.00121	−0.96
			1/4	1.25	0.820	.400	.00103	−0.89
			1/5	1.00	.620	.3315	.00153	−1.06
			1/8	0.625	.410	.2375	.00123	−0.97
	IIIA	2.742	1/6	.833	.940	.395	.000885	− .83
			1/6	.833	.470	.377	.00126	− .98
			5/28	.893	.302	.394	.00111	− .93
Acetamide	ICa	2.67	1/8	.625	1.802	.3125	.000166	− .10
			1/6	.833	1.202	.384	.000146	− .04
			5/23	1.087	0.941	.435	.000125	+ .06
			1/8	0.625	1.470	.307	.000169	− .10
			1/6	0.833	0.982	.363	.000174	− .11
			5/23	1.087	.769	.4135	.000113	+ .07
Urea	ICa	2.67	1/9	0.556	.791	.279	.04436	.48
			1/9	.556	.791	.2775	.04478	.44
			1/9	.556	.648	.4445	.04408	.51
			5/28	.536	.635	.3665	.04316	.62
			5/33	.455	.443	.2725	.04355	.57

ionic strength when calculating the constants. The best value is -4.2 for pK_a of acetonitrile. Hammett and his co-workers[4,18] found a value of -4.19 for propionitrile. For dioxane, the first value came from 0.926 *M* solution, the other three from 1.40 *M* solution in glacial acetic acid. There is a definite concentration effect. The best value is about -4. For acetamide, the first three values were obtained with one and the last three with a second stock solution. In general, the apparent basicity of the amide increases with an increase in the ratio of acid to base. This observation may be related to the tendency of one mole of strong acid to combine with two moles of acetamide.[19] The best value of pK_a probably is about 0.1, with the acid in excess. Results obtained in aqueous solution[3] average about 0.5. Values for *p*-toluenesulfonamide came from one stock solution, for water from two, and for acetanilide and urea from three solutions of each. The best pK_a values are -3.2 for *p*-toluenesulfonamide, -2.3_5 for water, -0.9 for acetanilide and 0.5 for urea. Previous values are -3.72 for water and -1.89 and -1.74 for acetanilide, all from measurements in formic acid,[4,18] and an average of about -0.5 for acetamide and $+0.1$ for urea, from measurements in aqueous solutions.[3] The greater basicity observed for urea and acetamide in the present work, in comparison with earlier values, may be due in part to the high concentrations necessitated in the earlier studies in aqueous solution.[3]

It was found that constants could not be obtained for a number of other compounds because their constants lie outside the range for which the method is applicable. As a test of the method, *n*-heptane[20] was examined with indicator solutions, IB and IIIA. In concentrations up to 0.9 *M*, $K_b^s = 1/K_a^s$, was found to be 0.00, well within experimental error. Acetone, acetophenone, dibutyl ether, ethylene diacetate, cyclohexene and 3-hexyne failed to show any basic character or else showed so little that the differences from blank readings had little significance. Most of these observations were made with indicator III. Indicator I was unsuitable in solutions containing ketones, probably because these react with formation of Schiff bases. Diphenylamine and *o*-chloroaniline were too strongly basic for the method.

Range of Applicability of the Indicator Method.—The various subtractions necessary in solving Equation 8 limit the range within which reasonably accurate values can be obtained.

Limit for Weak Bases.—If in a test solution the values of *A*, the total acid concentration and of (H^+), the free acid concentration, which equals $K_a^s\ (S - T)/T$, are too close together, the subtraction to give (BH^+) could lead to large errors. If much base is added so as to make (H^+) smaller, the nature of the solution changes and the behavior of the indicator may not be the same as in the dilute solutions. If the maximum value of (B) is taken as 0.5 *M*, and if it is decided that at least 10% of the total acid present, excluding that present as IH^+, should react to form BH^+, then 4.5 is the K_a^s value of the weakest base that can be measured (Equation 9), and -4.5 is the corresponding value of pK_a.

$$K_a^s = (B)(H^+)/(BH^+) = (0.5)(0.9A)/(0.1A) = 4.5 \quad (9)$$

Limit for Strong Bases.—If in a test solution the values of B_t, the concentration of all of the colorless base, and of (BH^+), that of its conjugate acid, are too close together, the subtraction to give (B) could lead to large errors. If, in order to make (BH^+) small, only a small amount of acid is present, the ionization of the solvent will not be suppressed, and the interaction of this with the bases becomes appreciable. If the minimum acceptable value of (H^+) is taken as 0.0001 *M*, and if it is decided that at least 10% of the total base should not react, then 1.1×10^{-5} is the K_a^s value of the strongest base that may be measured (Equation 10) and 1.1 is the corresponding pK_a value.

$$K_a^s = (B)(H^+)/(BH^+) = (0.1B_t)(0.0001)/(0.9B_t) = 1.1 \times 10^{-5} \quad (10)$$

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[18] L. P. Hammett and M. A. Paul, THIS JOURNAL, **56**, 827 (1934).

[19] T. W. J. Taylor, *J. Chem. Soc.*, 2741 (1930), and references therein.

[20] This was a sample of 99% *n*-heptane, kindly supplied by the Phillips Petroleum Company, Bartlesville, Oklahoma.