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Dissociation Constant of Piperidinium Ion From 0° to 50° C and Related Thermodynamic Quantities

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The acidic dissociation constant, K_a, of piperidinium ion has been determined at 5-degree intervals from 0° to 50° C from measurements of the electromotive force of hydrogen-silver chloride cells without liquid junction. The results are given by the equation

$$-\log K_a = \frac{2105.6}{T} - 6.3535 - 0.0076865T,$$

where T is the temperature on the Kelvin scale. Appreciable ion-pair formation between piperidinium ion and chloride ion was postulated in order to explain the mode of variation of the apparent dissociation constant with ionic strength.

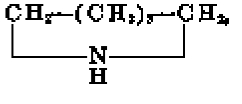
The changes of heat content, entropy, and heat capacity for the dissociation reaction have been calculated from the temperature coefficient of the dissociation constant. For the acidic dissociation of piperidinium ion at 25°, the following values were obtained: $\Delta H^\circ = 53{,}390$ j mole^{-1}, $\Delta S^\circ = -33.9$ j deg^{-1} mole^{-1}, and $\Delta C_p^\circ = 88$ j deg^{-1} mole^{-1}. The corresponding values for the basic dissociation of piperidine at 25° are $\Delta H^\circ = 3{,}170$ j mole^{-1}, $\Delta S^\circ = -44.3$ j deg^{-1} mole^{-1} and $\Delta C_p^\circ = -283$ j deg^{-1} mole^{-1}.

1. Introduction

Although the dissociation and related thermodynamic constants for many uncharged weak acids and dipolar ions (ampholytes) have been the subject of extensive investigations, very little is known concerning the ionization behavior of uncharged weak bases or their conjugate acids of charge +1. This is evident from the summaries given by H. S. Harned and B. B. Owen [1] and by R. A. Robinson and R. H. Stokes [2].[1] The temperature variation of pK_a for 31 uncharged or negatively charged acids in water and for both modes of dissociation of 19 ampholytes is found in the recent list of Robinson and Stokes, yet data for only five weak bases studied with the same degree of care and thoroughness are given.

These bases are ammonia, the three methylamines, and ethanolamine. Two others, ethylenediamine and hexamethylenediamine, have been added by the work of Everett and Pinsent [3], but the list is still too brief and restricted to justify any correlation of dissociation behavior with structure.

The strongest of the seven uncharged bases for which the thermodynamic properties are presently available (namely, dimethylamine) is only 34 times as strong as ammonia. Unlike these seven, piperidine,



$$\mathrm{CH_2{-}(CH_2)_3{-}CH_2}$$ with both end groups joined to $\mathrm{N{-}H}$

is a cyclic base and is about 75 times as strong as ammonia. The acidic dissociation constant of piperidinium ion, that is, the equilibrium constant for the reaction $C_5H_{10}NH_2^+ \rightleftharpoons C_5H_{10}NH + H^+$, has now been determined at 5-deg intervals from 0° to 50° C by measurement of the electromotive force of cells of the type

$$\text{Pt; } H_2(\text{g, 1 atm}),\ C_5H_{10}NH{\cdot}HCl\ (m_1),\ C_5H_{10}NH\ (m_2),\ AgCl;\ Ag.$$

The changes of heat content, entropy, and heat capacity for the dissociation of piperidinium ion have been calculated from the temperature variation of the dissociation constant.

2. Experimental Procedures

The method used was essentially that of Harned and Ehlers [4], with certain modifications made necessary by the volatility of the solute, the formation of complexes between silver chloride and the base, and the rather extensive dissociation of piperidine in water.[2]

The partial pressure of piperidine from its 0.107-M aqueous solution was measured by the dynamic method and found to be 1.2 mm at 25° and 2.1 mm at 50° C. The volatility was thus sufficient to require the use of the triple saturators in series with the cells [5]. However, if the presence of piperidine in the vapor phase were not taken into account in correcting the emf values to 1 atm of hydrogen, an error of only 0.05 mv would be incurred for the most concentrated solution (m_2=0.09678) at the highest temperature (50° C). The small corrections were calculated, where applicable, with the aid of Henry's law, on the assumption that the constant of this law varies linearly with temperature between 25° and 50° C.

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] The changes in experimental techniques, as well as the corrections for volatility of the base and for solubility of the electrode, have been described in two earlier papers [5, 6].

The solubility of silver chloride in a 0.1–M solution of the base was determined as formerly [6] and found to be about 46 percent as large as in an equally concentrated solution of ammonia. The figure calculated from the stability constants given by Bruehlman and Verhoek [7] is 48 percent. The correction for complex-ion formation could therefore be safely omitted.[3] Furthermore, transfer of silver ion to the hydrogen electrode took place so slowly that the large stopcocks separating the electrode compartments [5, 6] were also dispensed with.

Three samples of piperidine were prepared by purification of commercial material graded "CP" and "Purified." *Sample 1:* The base was distilled from sodium hydroxide pellets and then redistilled with rejection of the first and last tenths of the distillate. *Sample 2:* A portion of the first sample was partially frozen and the last 5 percent of liquid rejected. The piperidine obtained in this way was redistilled. *Sample 3:* A portion of the second sample was twice redistilled, with rejection of the first and last fractions.

Aqueous solutions of these three preparations of piperidine showed absorption peaks at 260 mμ, indicative of the presence of small amounts of pyridine. If all of the absorption at this wavelength was due to pyridine, with a molar absorption index of 3,160 [8], the three samples contained 0.6, 0.6, and 0.3 percent, respectively, of pyridine. As the strength of this base is only 1/10^6 that of piperidine, pyridine can be regarded as an inert impurity at high pH values. The concentration of piperidine in the stock solutions was determined by titration with standard acid to the end point of phenol red, pH about 7.2. At this pH, only about 1 percent of the pyridine impurity would be neutralized; hence, the pyridine present could cause an error of not more than 0.01 percent in the concentration of piperidine determined by titration.

The preparation of the electrodes has been described elsewhere [9]. The solutions in the cells were made from analyzed stock solutions prepared from piperidine, twice-distilled hydrochloric acid, and water that had been de-aerated with nitrogen. Seventeen different solutions were studied.

The emf of the cells was measured initially at 25° C before the temperature of the water bath was lowered to 0° C for the beginning of the 0° to 25° series of measurements. Most of the cells were refilled before the measurements from 25° to 50° C were begun, giving two "initial" emf values at 25° C for 11 of the 17 solutions. The mean difference between the duplicates was 0.08 mv. Although each series of measurements was completed in 8 hr, a comparison of initial and final values at 25° C usually revealed a decrease of emf, most pronounced at the high temperatures and with the relatively dilute buffer solutions. Corrections were applied when this irreversible change exceeded 0.1 mv. In the four extreme cases, the correction amounted to 0.40, 0.57, 0.57, and 0.80 mv at 50° C.

3. Results and Calculation of the Dissociation Constant

The corrected values of the emf, E, for a partial pressure of 760 mm of hydrogen are summarized in table 1.

The cell reaction is

$$\tfrac{1}{2}H_2(g)+AgCl(s)=Ag(s)+H^+(aq)+Cl^-(aq).$$

Production of electrical work by the cell is therefore accompanied by the formation of hydrogen and chloride ions in the aqueous piperidine buffer solution. Taking into account the reaction of piperidine with water, one may write the following expression for K_a, the thermodynamic constant for the acidic dissociation of piperidinium ion:

$$-\log K_a' = -\log K_a - \beta\mu' = pw\mathrm{H} + \log\frac{m_1+m'_{\mathrm{OH}^-}}{m_2-m'_{\mathrm{OH}^-}} - \frac{2A\sqrt{\mu'}}{1+Ba^*\sqrt{\mu'}}, \qquad (1)$$

in which A and B are constants of the Debye-Hückel equation, a^* is the ion-size parameter, and the prime marks indicate "apparent" values that become exact in the limit of infinite dilution, $\mu=0$.[4] The quantity pwH is defined by

$$pw\mathrm{H} \equiv \frac{E-E^\circ}{2.3026RT/F} + \log m_{\mathrm{Cl}^-}, \qquad (2)$$

where E° is the standard potential of the cell [10] and R, T, and F have their usual significance. The apparent concentration of hydroxide ion in terms of pwH and K_w, the ion-product constant for water, is

$$\log m'_{\mathrm{OH}^-} = \log K_w + pw\mathrm{H}, \qquad (3)$$

and the apparent ionic strength is

$$\mu' = m_1 + m'_{\mathrm{OH}^-}. \qquad (4)$$

It is expected that a plot of the values of $-\log K_a'$ obtained by eq (1) as a function of ionic strength will be a straight line easily extended to $\mu=0$, if the proper choice of a^* is made. For strong electrolytes, the value of this parameter exceeds 3.5 A, and lower values suggest incomplete dissociation. When $a^*=4$ was used in eq (1), the plot of $-\log K_a'$ as a function of ionic strength had the definite curvature shown by the dashed line in figure 1. The curve remained concave downward for all values of a^* exceeding -2, at which point approximate linearity was reached. The unusually small values of a^*, decreasing as the basic molecule becomes larger, found for other nitrogen bases may indicate that the hydrochlorides of these bases are present partly as ion pairs even in

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[3] The correction is less than 0.03 mv at 25° C.

[4] Thus, eq (3) gives the true molality of hydroxide ion only if the activity coefficients of chloride and hydroxide ions are equal. Likewise, the last term of eq (1) is a reliable representation of the activity coefficients only at low concentrations. However, both log m'_{OH^-} and log K_a' are expected to vary linearly with ionic strength.

TABLE 1. *Electromotive forces of the cells* Pt; H_2 (*g, 1 atm*), $C_5H_{10}NH \cdot HCl$ (m_1), $C_5H_{10}NH$ (m_2), AgCl; Ag *from 0° to 50° C*

m_1	m_2	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
0.09803	0.09678	0.95081	0.95144	0.95194	0.95223	0.95230	0.95220 .95212	0.95177	0.95126	0.95049	0.94962	0.94829
.09803	.09678	.95116	.95175	.95226	.95251	.95259	.95237	.95196	.95141	.95064	.94967	.94847
.09337	.09211	.95200	.95288	.95354	.95414	.95421	.95404 .95417	.95389	.95349	.95276	.95189	.95082
.08884	.08690	.95309	.95443	.95499	.95530	.95580	.95530 .95531	.95505	.95459	.95392	.95306	.95202
.08352	.08170	.95423	.95494	.95544	.95572	.95585	.95576	.95542	.95495	.95428	.95339	.95222
.07291	.07260	.95711	.95793	.95862	.95889	.95903	.95900 .95899	.95869	.95810	.95776	.95688	.95573
.06668	.06542	.95843	.95913	.95973	.96016	.96036	.96039	.96007	.95967	.95904	.95824	.95726
.06179	.06170	.96030	.96104	.96164	.96203	.96226	.96246 .96240	.96224	.96173	.96142	.96060	.95963
.05159	.04992	.96276	.96361	.96432	.96489	.96513	.96512 .96504	.96497	.96467	.96416	.96347	.96253
.05182	.05167	.96249	.96422	.96502	.96549	.96575	.96582 .96555	.96570	.96538	.96492	.96410	.96309
.04447	.04440	.96649	.96737	.96814	.96863	.96896	.96909 .96909	.96905	.96881	.96833	.96774	.96693
.03206	.03195	.97174	.97263	.97345	.97403	.97441	.97466	.97471	.97450	.97408	.97332	.97251
.02890	.02887	.97415	.97514	.97596	.97657	.97679	.97733 .97744	.97754	.97745	.97718	.97670	.97605
.02149	.02146	.97995	.98100	.98169	.98259	.98311	.98343 .98341	.98356	.98352	.98330	.98279	.98214
.017764	.017376	.98269	.98371	.98471	.98545	.98610	.98644	...	...	...	...	...
.013907	.013867	.98737	.98854	.98954	.99030	.99091	.99134	...	...	...	...	...
.009693	.009666	.99355	.99501	.99606	.99687	.99759	.99815 .99819	.99865	.99882	.99867	.99840	.99794

these rather dilute solutions. For example, a value of +2 has been found for ammonium ion [5], +1 for ethanolammonium ion [6] and tris(hydroxymethyl)ammonium ion [11], and −2 for triethanolammonium ion [12].

Although a negative value of a^* does not preclude an accurate extrapolation to $-\log K_a$, it seemed desirable to allow for the presence of ion pairs. This was done by fixing a^* at 4 in eq (1) and choosing by trial a value of K_i, the dissociation (instability) constant of piperidinium chloride, that would yield a straight-line plot of $-\log K'_a$. The computation was thus essentially an evaluation of the true molalities of chloride and piperidinium ions, m_{Cl^-} and m_{HP^+}, for use in eq (2) and in place of the stoichiometric m_1 in eq (1) and (4).

From the mass-law expression for the ion-pair equilibrium,

$$m_{Cl^-} = m_{HP^+} = \sqrt{2km_1 + k^2} - k, \qquad (5)$$

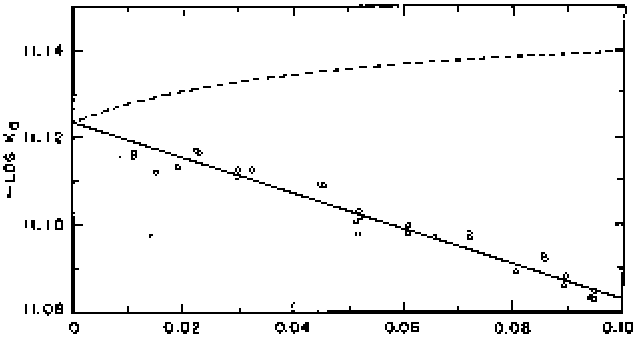

FIGURE 1. *Plot of* $-\log K'_a$ *as a function of ionic strength at 25° C.*

........, Without correction for ion pairs in piperidinium chloride solutions. ○ and ———, with ion-pair correction.

where k is written for $\frac{1}{2} K_i/f^2$. The activity coefficient, f, of an "average" univalent ion was estimated by the Debye-Hückel expression with an ion-sized parameter of 4, and that of the ion pair was taken to be unity. It was necessary to use the method of successive approximations to obtain m_{Cl^-} by eq (5), as a value for the ionic strength is needed to evaluate k.

The value of $-\log K'_a$ was found to be a linear function of the ionic strength when K_i was given the following values: 0° to 25° C, 0.8; 30°, 0.7; 35° and 40°, 0.6; 45°, 0.5; and 50°, 0.4. The circles and lower line in figure 1 are a plot of the data at 25° C. The values of $-\log K_a$ given in table 2 were determined from large-scaled plots of this type. The constant, K_b, for the basic dissociation of piperidine, $P + H_2O = HP^+ + OH^-$, is also listed in the table. It is K_w/K_a, where K_w is the ion-product constant for water [1]. An accuracy of ±0.005 in $\log K_a$ and $\log K_b$ is estimated. The values of $-\log K_a$ at 15° and 25° C are higher by about 0.06 unit than those found by Wynne-Jones and Salomon [13] (11.38 and 11.06, respectively), whereas that at 25° C (11.123) is in excellent agreement with 11.13 cited by Hall and Sprinkle [14].

4. Heat Content, Entropy, and Heat Capacity of the Dissociation Reaction

The values of $-\log K_a$ at temperatures (T) from 273.16° to 323.16° K (0° to 50° C) given in table 2 can be represented by the equation

$$-\log K_a = \frac{2105.6}{T} + 6.3535 - 0.0076865T \qquad (6)$$

with a standard deviation of 0.002. By application of the usual thermodynamic formulas, therefore,

TABLE 2. *Dissociation constants of piperidinium ion (K_a) and piperidine (K_b)*

Temperature	$-\log K_a$	$-\log K_b$
°C		
0	11.963	2.980
5	11.786	2.948
10	11.613	2.922
15	11.443	2.903
20	11.280	2.887
25	11.123	2.873
30	10.974	2.859
35	10.818	2.862
40	10.670	2.865
45	10.526	2.870
50	10.384	2.878

the following expressions for the standard changes of heat content ($\Delta H°$), of entropy ($\Delta S°$), and of heat capacity (ΔC_p°) for the dissociation reaction are obtained:

$$\Delta H° = 2.3026R \quad (2105.6 + 0.0076865T^2), \tag{7}$$

$$\Delta S° = 2.3026R \quad (0.015373T - 6.3535), \tag{8}$$

$$\Delta C_p^\circ = 2.3026R \quad (0.015373T). \tag{9}$$

To obtain the figures given in table 3, R was taken to be 8.31439 j mole^{-1}; the results are accordingly in joules. The corresponding quantities for the basic dissociation of piperidine at 25° C are $\Delta H° =$ 3,170 j mole^{-1}, $\Delta S° = -44.3$ j deg^{-1} mole^{-1}, and $\Delta C_p^\circ = -283$ j deg^{-1} mole^{-1}.

TABLE 3. *Thermodynamic quantities for the acidic dissociation of piperidinium ion from 0° to 50° C*

Temperature	$\Delta H°$	$\Delta S°$	ΔC_p°
°C	j mole^{-1}	j deg^{-1} mole^{-1}	j deg^{-1} mole^{-1}
0	51,290	−41.3	80
5	51,700	−39.8	82
10	52,110	−38.3	83
15	52,530	−36.8	85
20	52,960	−35.4	86
25	53,390	−33.9	88
30	53,830	−32.4	89
35	54,280	−31.0	91
40	54,740	−29.5	92
45	55,210	−28.0	94
50	55,680	−26.5	95

5. Discussion

It has been shown [15] that the method used here cannot usually furnish accurate values for the dissociation constants of acids with $K_a > 0.005$, as a consequence of the uncertainty in establishing the hydrogen-ion concentration and, hence, the buffer ratio. A determination of the strengths of very weak acids (moderately strong bases) encounters a similar difficulty in establishing the hydroxide-ion concentration. It is noteworthy, however, that this restriction may be less important for moderately strong bases than for moderately strong acids. This is because the estimation of m_{OH^-} depends upon a ratio of the activity coefficients of two univalent anions (see footnote 4), a quantity that may be nearly unity even at ionic strengths well above the Debye-Hückel region. On the other hand, the necessity of selecting arbitrarily an ion-size parameter for the computation of m_{H^+} limits severely the accuracy with which K_a can be established when more than 10 percent of the acid is dissociated.

The dissociation of singly charged cation acids is an isoelectric process, and the thermodynamic constants for these reactions are accordingly of unusual interest. The heat content change for the dissociation of piperidinium ion differs by only slightly more than 1,000 j mole^{-1} from that for ammonium ion and by less than 3,000 j from that for ethanolammonium ion. That the entropy change (−34 j deg^{-1} mole^{-1}) is larger than that found for any other base yet studied suggests that the cyclic structure of the piperidinium ion interferes with extensive solvent orientation.

The heat-capacity change for an isoelectric process might be expected on electrostatic grounds to be quite small, and indeed ΔC_p° for ammonium ion [5, 16] and ethanolammonium ion have been found to be nearly zero. Nevertheless, the values found for the methyl-substituted ammonium ions [17] are positive and rise with increasing substitution of methyl groups from 33 j deg^{-1} mole^{-1} for monomethylammonium to 183 j deg^{-1} mole^{-1} for trimethylammonium. Other acids of this charge type have given the following positive values: ethylenediammonium ion, 73 j [3]; hexamethylenediammonium ion, 34 j [3]; and piperidinium ion, 88 j (this investigation). The highest of these values is about as large as that found for many uncharged acids, but is of opposite sign.

Orientation of the solvent molecules by the ions should affect both $\Delta S°$ and ΔC_p° in the same sense, and the contrary variation of these two quantities is evidence that the dissociation cannot be explained on a simple electrostatic basis even when solvent orientation is considered [18]. It is evident that charge type, the interaction of ions and molecules with the solvent, and electrostatic, steric, and statistical effects must all be taken into account in any interpretation of the thermodynamics of acidic dissociation [3, 18]. For all but the simplest reactions, even qualitative predictions remain unsatisfactory at the present time.

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