

[CONTRIBUTION FROM THE DEPARTMENT OF SANITARY ENGINEERING, GRADUATE SCHOOL OF ENGINEERING, HARVARD UNIVERSITY]

Equilibrium Studies on N-Chloro Compounds. II. The Base Strength of N-Chloro Dialkylamines and of Monochloramine¹

BY IRA WEIL AND J. CARRELL MORRIS

A knowledge of the possible basic or acidic nature of the chlorine substitution products of ammonia, monochloramine (NH₂Cl), and dichloramine (NHCl₂) is of great importance in analyzing the behavior of these compounds in water solution. Moreover, such information is of theoretical interest, since it would provide a knowledge of the change in acid or base strength produced by the substitution of a chlorine atom for a hydrogen on an ammonia-type molecule. This paper presents the results of an attempt to evaluate the base strength of the monosubstituted compound, NH₂Cl, and of its alkyl homologs.

In the water system, substitution of a chlorine for a hydrogen has a strong acidifying effect which is roughly comparable to that produced by substitution of an acetyl group. Thus, the acid ionization constant of HOCl is 3×10^{-8} and that of CH₃COOH is 2×10^{-5} , as compared with 2×10^{-16} for water itself. The effect of the acetyl group in this case is accentuated by the large amount of resonance in the acetate ion. In the ammonia system the acetyl group has a base-weakening effect of the same order of magnitude, for the base strength of CH₃CONH₂ is only $(3 \times 10^{-15})^2$ whereas that of ammonia is 2×10^{-5} . By analogy one might predict roughly that NH₂Cl and its alkyl homologs should also be very weak bases with ionization constants in the neighborhood of 10^{-15} .

Unfortunately a direct measurement of an ionization constant of this magnitude for monochloramine appears impossible, since the basic properties would be manifested to a measurable extent only in very acid solutions, and monochloramine disproportionates very rapidly under such conditions. However, by working with the N-chlorodialkylamines it has been possible to eliminate this side reaction and to obtain a direct measurement of the base strengths of N-chlorodimethylamine and N-chlorodiethylamine. From these, reasonable estimates of the base strength of monochloramine can be made.

The method employed for the direct determinations was to measure the ultraviolet absorption spectra of the N-chlorodialkylamines in solutions of varying acid concentration. It was observed that as the acid concentration of solutions of these substances is increased above 0.01 M the characteristic absorption bands for the N-chlorodialkylamines are increasingly diminished in intensity.

These changes in the absorption spectra are not accompanied by any changes in the oxidizing-chlorine titers, and the absorption bands can be made to appear and disappear rapidly by alternate addition of alkali and acid. Consequently, the observed spectral changes were attributed to ionization processes, and the quantitative measurements are based upon this interpretation.

Experimental

Materials.—The distilled water and the acid and base solutions used in the determinations were all made "chlorine-demand-free"³ to insure that no reducing materials remained.

Stock chlorine solutions were obtained by bubbling gaseous chlorine into distilled water and diluting the solution until the desired strength was obtained, approximately 1.3×10^{-3} molar. The solutions were checked daily by addition of potassium iodide followed by titration with sodium thiosulfate.

Dimethylammonium chloride and diethylammonium chloride (Eastman Kodak Company) were dried and weighed to prepare stock solutions which contained 7×10^{-3} mole per liter. The concentrations of these solutions were checked by Kjeldahl nitrogen determinations, which gave values within 0.5% of those obtained from the weights of the salts.

Perchloric acid and sodium hydroxide solutions were standardized with reagent-grade potassium acid phthalate.

Procedure.—Equivalent quantities of the chlorine and amine solutions at 25° were mixed at a pH of 10.7 to form the N-chlorodialkylamine. At this pH, the time for 99% reaction is less than one minute.⁴ Fifty ml. of the resulting solution, which was approximately 4×10^{-4} molar, was diluted with perchloric acid and sodium hydroxide to obtain the desired acid concentration and ionic strength and was then made up to 100 ml. in a volumetric flask. One portion of this solution was placed in the quartz cell of the spectrophotometer and a second portion was titrated to obtain the exact concentration of N-chlorodialkylamine.

The absorption data were obtained with a Beckman ultraviolet spectrophotometer, Model DU. In all the determinations 10-cm. quartz cells which had been calibrated against one another were used. In place of the conventional cell holder there was substituted a cell block which permitted the cells to be kept at a constant temperature of $25.0 \pm 0.3^\circ$ by the circulation of water from a constant temperature bath.

The absorption for each sample was measured from 220 to 300 mμ, against a blank which contained the same quantities of acid and base as the chloramine sample. Transmission values near the absorption maximum were measured three or four times on each sample and were found to check within an average deviation of ± 0.002 in terms of optical density. Readings were taken at 5 mμ intervals with band widths varying from 0.3 to 1.4 mμ.

The absorption spectra of the N-chlorodialkylamine bases were determined on solutions prepared at pH 10.7. Three concentrations, 1×10^{-4} , 2×10^{-4} and 3×10^{-4} M were employed. Values of the molar extinction coefficients for the three concentrations, calculated from the transmission data, agreed within 2 to 3 units at practically

(1) This paper is based on work performed under Contract No. W-44-009 eng-463 for the Engineer Research and Development Laboratories.

(2) Euler and Ölander, *Z. physik. Chem.*, **131**, 107 (1928)

(3) Butterfield, Wattie, Megregian and Chambers. *Pub. Health Reports*, **58**, 1837 (1943).

(4) Weil and Morris, *THIS JOURNAL*, **71**, 1664 (1949)

all wave lengths. Absorption spectra of the acidified solutions were determined at a total chloramine concentration of $2 \times 10^{-4} M$.

The reliability of the dissociation constant values calculated from the spectra depends largely on the accuracy of differences in the extinction coefficient values, as shown by equation (5). On the basis of the estimated errors in the individual extinction coefficient values, the largest error in any one value of K_a is 14%, the minimum error, about 3%. The final average values of K_a are believed to be accurate to $\approx 5\%$.

Results and Discussion

Absorption Spectra.—Values of ϵ , the molar extinction coefficient, for N-chlorodimethylamine and N-chlorodiethylamine in the region 220 to 300 $m\mu$ are shown as the upper curves in Figs. 1 and 2, respectively. These were computed from the transmission data on solutions at pH 10.7 by means of the usual formula, $\epsilon = (1/lM) \log I_0/I$, l being in cm. and M in moles per liter. N-Chlorodimethylamine has an absorption maximum at $263 \pm 2 m\mu$ and N-chlorodiethylamine shows one at $262 \pm 2 m\mu$. Determinations of the ionization constants were based on measurements at 265 $m\mu$ for N-chlorodimethylamine and at 260 $m\mu$ for N-chlorodiethylamine. At these wave lengths the molar extinction coefficients, which are very close to the maximum values, are 366 ± 3 and 312 ± 3 , respectively.⁵

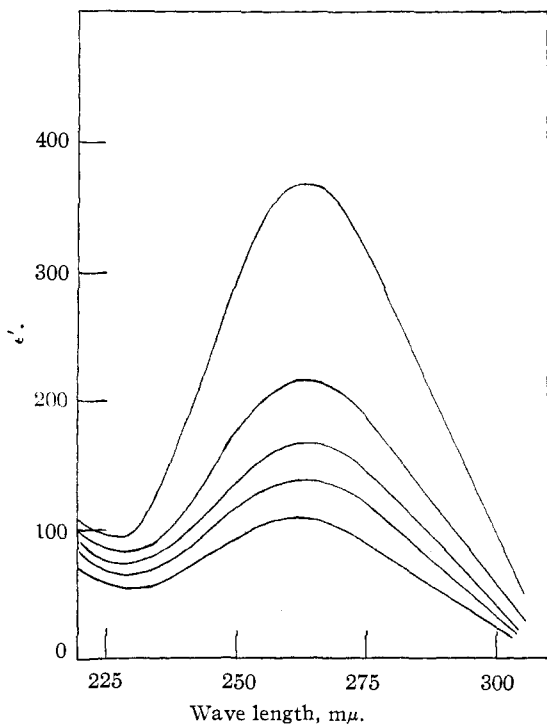


Fig. 1.—Absorption spectra of N-chlorodimethylamine at different acid concentrations. The uppermost curve is at a pH of 10.7. For the others in descending order, $[H^+] = 0.125, 0.224, 0.322,$ and 0.519 , respectively.

(5) Metcalf, *J. Chem. Soc.*, 148 (1942), gives $\lambda_{max} = 263 m\mu$ and $\epsilon_{max} = 300$ for both substances.

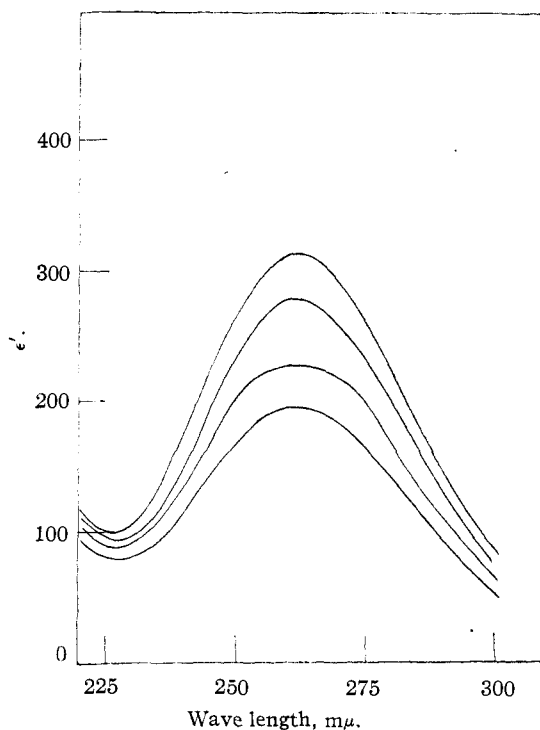


Fig. 2.—The absorption spectra of N-chlorodiethylamine at different acid concentrations. The uppermost curve is at a pH of 10.7. For the others in descending order, $[H^+] = 0.0100, 0.0298,$ and 0.0495 , respectively.

The other curves in Figs. 1 and 2 depict typical absorption spectra for acidified solutions of these chloramines. The curves have been computed from the transmission data in terms of "apparent molar extinction coefficients," ϵ' , defined as $\epsilon' = (1/lM_0) \log I_0/I$, M_0 being the total chloramine concentration, whether present as base or ion. The decreasing absorption with increasing acidity is evident.

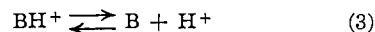
Concentration Dissociation Constants.—For a solution containing both free base and ion the Beer-Lambert law becomes

$$(1/l) \log I_0/I = \epsilon_B [B] + \epsilon_{BH^+} [BH^+] = \epsilon' M_0 \quad (1)$$

Combination of this expression with the relation $M_0 = [B] + [BH^+]$ gives for the ratio of the molarity of chloramine to that of chlorammonium ion

$$[B]/[BH^+] = (\epsilon' - \epsilon_{BH^+})/(\epsilon_B - \epsilon') \quad (2)$$

At constant ionic strength the dissociation constant or acidity for the reaction



may be expressed in terms of concentrations as

$$K_a = [H^+][B]/[BH^+] \quad (4)$$

Combination of this with equation (2) then gives

$$K_a = [H^+] (\epsilon' - \epsilon_{BH^+})/(\epsilon_B - \epsilon') \quad (5)$$

Values of ϵ_B and ϵ' for substitution in this equation were taken from the data at 265 $m\mu$ for N-

chlorodimethylamine and at 260 $m\mu$ for N-chlorodiethylamine. However, direct evaluation of the ϵ_{BH^+} terms was not practical and so an indirect technique was used. Rearrangement of equation (5) gives the expression

$$\epsilon_{BH^+} = \epsilon' - K_a(\epsilon_B - \epsilon')/[H^+] \quad (6)$$

Consequently, evaluation of ϵ_{BH^+} may be accomplished by plotting values of ϵ' for a constant ionic strength against the function $(\epsilon_B - \epsilon')/[H^+]$ and determining the intercept of the straight line drawn through the points.

Determination of ϵ_{BH^+} in this way for both N-chlorodialkylammonium ions is shown in Fig. 3. The intercepts give $\epsilon_{BH^+} = 30 \pm 5$ for N-chlorodimethylammonium ion at 265 $m\mu$ and $\epsilon_{BH^+} = 15 \pm 5$ for N-chlorodiethylammonium ion at 260 $m\mu$.

Tables I and II show values of K_a for N-chlorodimethylamine and N-chlorodiethylamine obtained by means of equation (5) with the preceding values for ϵ_{BH^+} . At fixed ionic strength the figures are constant within the experimental error, but vary with the ionic strength of the solutions.

TABLE I

DISSOCIATION CONSTANT DATA FOR N-CHLORODIMETHYLAMMONIUM ION

Temperature 25°; absorption measurements at 265 $m\mu$;
 $\epsilon_B = 366$; $\epsilon_{BH^+} = 30$

[H ⁺]	Ionic strength, μ	$M_0 \times 10^3$, (mol/l.)	ϵ'	K_a , mole/l.
0.0380	0.039	1.96	327	0.294
.0250	.104	1.89	338	.278
.0644	.104	1.99	301	.270
.0841	.104	1.97	285	.268
.1039	.104	1.99	275	.276
.1730	.174	2.03	227	.244
.3460	.347	2.10	151	.196
.1250	.520	2.02	217	.156
.2240	.520	1.98	169	.159
.3220	.520	1.91	141	.158
.4210	.520	2.04	122	.158
.5190	.520	1.98	108	.157
.6920	.693	2.10	80	.123

TABLE II

DISSOCIATION CONSTANT DATA FOR N-CHLORODIETHYLAMMONIUM ION

Temperature 25°; absorption measurements at 260 $m\mu$;
 $\epsilon_B = 312$; $\epsilon_{BH^+} = 15$

[H ⁺]	Ionic strength, μ	$M_0 \times 10^4$, mole/l.	ϵ'	K_a , mole/l.
0.0173	0.018	1.94	265	0.092
.0346	.036	1.99	227	.086
.0100	.070	1.91	278	.076
.0298	.070	2.01	229	.077
.0495	.070	2.01	196	.076
.0692	.070	2.06	171	.077
.1039	.104	2.03	139	.073
.1730	.174	2.10	98	.067

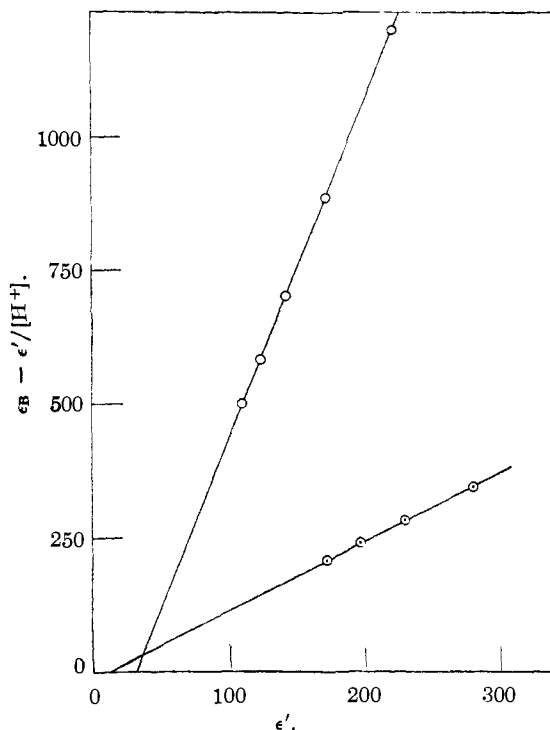


Fig. 3.—Plots of $(\epsilon_B - \epsilon')/[H^+]$ vs. ϵ' for N-chlorodimethylamine (O) and for N-chlorodiethylamine (O), at constant ionic strength.

Activity Dissociation Constants.—Evaluation of the true acidity constant defined as

$$K_a = ([H^+]f_{H^+}[B]f_B)/([BH^+]f_{BH^+}) = K_c f_B f_{H^+}/f_{BH^+} \quad (7)$$

requires a knowledge of or method of estimation for the activity coefficient ratio, $f_B f_{H^+}/f_{BH^+}$. The high ionic concentrations make it impossible to use the Debye-Hückel limiting law. Previous investigators⁶ have made the assumption that f_B/f_{BH^+} is independent of the base employed, and have made corrections on that basis, although it is readily apparent from a consideration of the extended forms of the Debye-Hückel equation that this is only an approximation. However, the assumption should have increased validity if it is applied to bases of essentially the same nature and size. Hence in the present case it was assumed that the activity coefficient ratios for the N-chlorodialkylamines are the same as those for trimethylamine, which have been determined by Harned and Robinson,⁷ and their values were used in the calculation of ionic strength corrections for the chloramines.

The data reported by Harned and Robinson are in the form $(f_B/f_{BH^+} f_{OH^-})^{1/2}$. These values were squared and then multiplied by the activity coefficient product of water⁸ to yield $f_B f_{H^+}/f_{BH^+}$. The values so obtained were then plotted against the ionic strength and correction factors for the

(6) Hammett and Deyrup, *THIS JOURNAL*, **54**, 2721 (1932).

(7) Harned and Robinson, *ibid.*, **50**, 3157 (1928).

(8) Harned and Mannweiler, *ibid.*, **57**, 1873 (1935).

desired ionic strengths were read from the smooth curve drawn through the points.

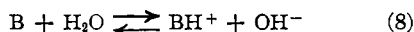
Table III shows the application of these corrections to the K_c data to obtain values for K_a . The consistency of the figures indicates that the procedure employed is a suitable one. A weighted average, which takes into account the number of determinations and the estimated error at each ionic strength, gives for N-chlorodimethylammonium ion, $K_a(25^\circ) = 0.345$, and for N-chlorodiethylammonium ion, $K_a(25^\circ) = 0.095$ mole/liter.

TABLE III

ACTIVITY DISSOCIATION CONSTANTS FOR N-CHLORODIALKYLAMMONIUM IONS AT 25°

Ionic strength, μ	K_c , mole/l.	$f_B f_{H^+} / f_{BH^+}$	K_a , mole/l.
A. N-Chlorodimethylammonium ion			
0.039	0.294	1.14	0.335
.104	.273	1.29	.352
.174	.244	1.44	.351
.347	.196	1.81	.355
.520	.158	2.13	.336
.693	.123	2.52	.310
	Weighted average		0.345 \pm 0.015
B. N-Chlorodiethylammonium ion			
0.018	0.092	1.07	0.098
.036	.086	1.13	.097
.070	.077	1.22	.095
.104	.073	1.29	.094
.174	.067	1.44	.096
	Weighted average		0.095 \pm 0.003

Basic Ionization Constants.—The basic ionization constants, K_b , corresponding to the process



are related to K_a by the equation $K_b = K_w / K_a$, in which K_w is the activity product for water. Application of this expression gives for N-chlorodimethylamine, $K_b(25^\circ) = 2.9 \times 10^{-14}$ and for N-chlorodiethylamine, $K_b(25^\circ) = 1.06 \times 10^{-13}$.

By comparison of the basic ionization constants of the dialkylamines with those of the N-chlorodialkylamines, an estimate of the decrease in basicity resulting from substitution of a chlorine on a nitrogen atom can be obtained. The change in ionization constant produced by chlorine substitution for dimethylamine is from $6.0 \times 10^{-4(9)}$ to 2.9×10^{-14} or a factor of 5×10^{-11} ; for diethylamine it is from $1.3 \times 10^{-8(10)}$ to 1.06×10^{-13} or a factor of 8×10^{-11} . It may reasonably be assumed that the basic ionization constant of NH_2Cl is smaller than that of ammonia by a similar factor. Since K_b for ammonia is 1.8×10^{-5} , the basic ionization constant for monochloramine should be approximately 1×10^{-15} .

Acknowledgment.—The authors wish to express their appreciation for the help of Miss Frances R. Tibbetts and Miss Alice E. Ozanian in obtaining the data for this paper.

Summary

Basic ionization constants for N-chlorodimethylamine, $(CH_3)_2NCl$, and N-chlorodiethylamine, $(C_2H_5)_2NCl$, have been determined from measurements of the ultraviolet absorption spectra of acidified solutions of these compounds. The values obtained for the activity ionization constants at 25° are $K_b = 2.9 \times 10^{-14}$ for N-chlorodimethylamine and $K_b = 1.06 \times 10^{-13}$ for N-chlorodiethylamine.

On the assumption that substitution of a chlorine for a hydrogen on the nitrogen atom has the same effect on base strength for ammonia as for the N-chlorodialkylamines, it has been estimated that $K_b = 1 \times 10^{-15}$ for monochloramine, NH_2Cl .

The ultraviolet absorption spectrum of N-chlorodimethylamine has a maximum at 263 m μ with a molar extinction coefficient, $\epsilon = 370$; that for N-chlorodiethylamine has a maximum at 262 m μ with $\epsilon = 315$.

CAMBRIDGE, MASS.

RECEIVED APRIL 4, 1949

(9) Everett and Wynne-Jones, *Proc. Roy. Soc. (London)*, **A177**, 499 (1941).

(10) Hall and Sprinkle, *THIS JOURNAL*, **54**, 3469 (1932).