Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

THE FREE ENERGY, ENTHALPY AND ENTROPY CHANGES OF THE DISSOCIATION OF DIPROTONATED DIAMINES

H. S. CREYF and L. C. VAN POUCKE
Department of General and Inorganic Chemistry, University of Ghent, Ghent (Belgium)
(Received February 15th, 1972)

ABSTRACT

The ΔG, ΔH and ΔS values of the dissociation of a number of diprotonated diamines were determinated by potentiometric and calorimetric methods, in $1M$ KNO_3, at 25°C. The results are discussed in terms of solvent effects, the theory of Kirkwood and Westheimer, and microscopic constants.

INTRODUCTION

Since direct calorimetric measurements of the reaction heat in solution has been made possible by commercially available precision calorimeters, much attention has been given to the thermodynamic functions of organic acids. In this study, ΔG, ΔH and ΔS values for the deprotonation of some diamines were determined, so that they may be used for the calculation of the thermodynamic functions of related metal complexes. The influence of substitution of methyl groups on the basic properties of the nitrogen atom was checked, to gain more insight into the donor properties of the different amino bases compared to the metal ion.

EXPERIMENTAL

Apparatus

pa_H measurements were performed with a digital pH meter (Radiometer PHM 52) equipped with a glass electrode (G 202 C) and a saturated calomel electrode. The pH meter was calibrated against a $0.01M$ borax solution which, according to Bates[1], gives a pa_H value of 9.180 at 25°C. Calorimetric measurements were carried out with an LKB 8700-2 titration calorimeter.

Reagents

Ethylenediamine (Fluka) and the other diamines (Koch-Light) were converted into their dinitrate salts. A dilute solution of the diamine was mixed with two equivalents of nitric acid at 0°C. The solution was evaporated in vacuum until all the liquid had disappeared. Ethylenediamine (en), *N*,*N*′-dimethylethylenediamine (s dimen), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tetramen), piperazine (pip), *N*-

methylpiperazine (mpip), and *N*,*N'*-dimethylpiperazine (dimpip) all crystallised out during the evaporation. The others, *N*-methylethylenediamine (men), *N*,*N*-dimethylethylenediamine (a dimen), and *N*,*N*,*N'*-trimethylethylenediamine (trimen), remained as a heavy syrup, which was stored in a dessicator under high vacuum. It took several days before the latter compounds crystallised out. The products obtained in this way were highly hygroscopic. All salts were purified by repeated crystallisation from 90% ethanol.

pa_H *measurements*

For the determination of the acidity constants two series of titrations were performed. In the first series, 50 ml (0.02 moles) of the dinitrate salts in 1*M* KNO_3 were put into a thermostated cell and titrated with 0.2116*M* KOH in 1*M* KNO_3. In the second series, the same titration was repeated with 100 ml (0.01 moles) of the dinitrate salts.

Calorimetric measurements

A solution of the dinitrate salt (25 ml, 0.2 moles), double-distilled water (20 ml) and 2*M* KNO_3 (45 ml) were pipetted into the reaction vessel of the calorimeter. This solution was titrated with 0.9862*M* KOH in 1*M* KNO_3 using a "Tacussel elektroburap" piston buret, equipped with a "Unité de présélection", in portions of 0.5 ml.

With the piston buret, it was possible to regulate the addition speed so that the addition time was almost equal to the heating time in the calibration experiment. At least twenty points were used for the calculation of the reaction heat for each amine.

CALCULATIONS

The determination of the acidity constants

In studying the addition of potassium hydroxide to a solution of the protonated form of the diamines, the following reaction equilibria must be considered

$$H_2L^{2+} + OH^- \rightleftharpoons HL^+ + H_2O \tag{1}$$

$$HL^+ + OH^- \rightleftharpoons L + H_2O \tag{2}$$

The protonation function $\bar{n}_H$, can be defined as

$$\bar{n}_H = \frac{2c_L - c_B - [H^+] + [OH^-]}{c_L} = \frac{K_2' a_H + 2K_1'K_2' a_H^2}{1 + K_2' a_H + K_1'K_2' a_H^2} \tag{3}$$

where c_L is the total concentration of the diamine and c_B is the concentration of added base in the reaction vessel. Furthermore,

$$\frac{1}{K_1'} = K_1 = \frac{a_H[HL^+]}{[H_2L^{2+}]}$$

and

$$\frac{1}{K_2'} = K_2 = \frac{a_H[L]}{[HL^+]}$$

However, since $[OH^-]$ and $[H^+]$ are unknown, the following procedure[2] was preferred for the determination of $\bar{n}_H$. Two titrations were performed with a different degree of dilution of the protonated diamines. It can be shown that, at the same pa_H values in each titration, $\bar{n}_H$ is given by

$$\bar{n}_H = \frac{2C_L - C_L' - (C_B - C_B')}{C_L - C_L'} \tag{4}$$

where the prime indicates the more dilute solutions. Eqn. (3) can then be solved for K_1' and K_2' by a systematic search for those values which minimize Eqn. (5)

$$\sum_i \left(\bar{n}_H - \frac{K_2' a_H + 2K_1' K_2' a_H^2}{1 + K_2' a_H + K_1' K_2' a_H^2}\right)^2 = \sum_i \varepsilon_i^2 \tag{5}$$

Therefore, a computer program NET was written in FORTRAN IV, applying the method proposed by Unwin *et al.*[3].

Determination of the heat of reaction

The total heat of reaction after each addition can be expressed by:

$$-Q = -\sum_i Q_i = \Delta H_i'([L]+[HL^+]) + \Delta H_2'[L] \tag{6}$$

where Q_i is the heat of reaction observed by the addition of the ith portion of potassium hydroxide. $\Delta H_1'$ and $\Delta H_2'$ are the enthalpy changes accompanying reactions (1) and (2), respectively.

[L] and $[HL^+]$ can be calculated from the acidity constants, C_L, C_B and pa_H. Instead of measuring the pa_H values, it was preferred to solve Eqn. (7)

$$C_B a_H^3 + (C_B K_1 - K_w - C_L K_1) a_H^2 + (C_B K_1 K_2 - K_w K_1 - 2K_1 K_2 C_L) a_H - K_w K_1 K_2 = 0 \tag{7}$$

As the hydrogen ion concentration is negligible over the whole range used in these experiments, $K_w = a_H[OH^-]$ was obtained by minimizing Eqn. (8), *i.e.*

$$\sum_i \left(\frac{2C_L - C_B + K_w/a_H}{C_L} - \frac{K_2' a_H + 2K_1' K_2' a_H^2}{1 + K_2' a_H + K_1' K_2' a_H^2}\right)^2 = \sum_i \varepsilon_i^2 \tag{8}$$

for the experimental data of ethylenediamine, by a systematic search for the values of the parameters K_w, K_1' and K_2' corresponding to the minimal value of $\sum \varepsilon_i^2$, using the computer program, KUBUS. pK_w was found to be 13.688.

From known a_H values, [L] and [HL^+] could be calculated for the different experimental points, and Eqn. (6) was solved in the same way as Eqn. (3), by minimizing the expression

$$\sum_i (-Q - \Delta H'_1([L]+[HL^+]) - \Delta H'_2[L])^2 = \sum_i \varepsilon_i^2 \quad (9)$$

The total calculation, *i.e.* solution of Eqn. (6) and minimizing of Eqn. (9), was performed using the computer program, ENTAL.

RESULTS AND DISCUSSION

The acidity constants of the various diamines are given in Table I.

TABLE I

ACIDITY CONSTANTS IN 1*M* KNO_3 AT 25°C

Diamine	pK_1	pK_2
en	7.536	10.225
men	7.473	10.280
s dimen	7.525	10.258
a dimen	6.925	9.834
trimen	6.827	9.979
tetramen	6.357	9.450
pip	6.044	10.007
mpip	5.199	9.317
dimpip	4.630	8.539

The values (in kcal/mole) of $\Delta H'_1$ and $\Delta H'_2$ as defined before, are given in Table II.

TABLE II

VALUES OF $\Delta H'_1$ AND $\Delta H'_2$ ACCOMPANYING REACTIONS (1) AND (2)

Diamine	$\Delta H'_1$ *(kcal/mole)*	$\Delta H'_2$ *(kcal/mole)*
en	2.14	1.29
men	2.62	2.25
s dimen	3.30	2.96
a dimen	4.88	3.29
trimen	5.83	3.75
tetramen	6.32	6.00
pip	5.44	3.08
mpip	7.89	4.38
dimpip	9.05	7.27

Taking into account that ΔH for the reaction $H^+ + OH^- \rightleftharpoons H_2O$ equals -13.47 kcal/mole in $1M$ KNO_3, the thermodynamic functions ΔG (kcal/mole), ΔH (kcal/mole) and ΔS (cal/mole.deg) for the reactions

$$H_2L^{2+} \rightleftharpoons HL^+ + H^+ \tag{10}$$

$$HL^+ \rightleftharpoons L + H^+ \tag{11}$$

have been calculated. The results are given in Table III.

TABLE III

THERMODYNAMIC FUNCTIONS ACCOMPANYING THE DEPROTONATION OF THE DIAMINES

Diamine	ΔG_1 *(kcal/mole)*	ΔH_1 *(kcal/mole)*	ΔS_1 *(cal/mol.deg)*	ΔG_2 *(kcal/mole)*	ΔH_2 *(kcal/mole)*	ΔS_2 *(cal/mol.deg)*
en	10.28	11.33	+3.5	13.94	12.18	−5.9
men	10.19	10.85	+2.2	14.02	11.22	−9.4
s dimen	10.26	10.17	−0.3	13.99	10.51	−11.7
a dimen	9.44	8.59	−2.8	13.41	10.19	−10.2
trimen	9.31	7.64	−5.6	13.61	9.72	−13.0
tetramen	8.67	7.15	−5.0	12.89	7.47	−13.1
pip	8.24	8.03	−0.7	13.64	10.40	−10.9
mpip	7.09	5.58	−5.0	12.70	9.09	−12.1
dimpip	6.31	4.42	−6.3	11.64	6.21	−18.2

The acidic strength of protonated amines as a function of the substitution of the methyl group on the nitrogen atom is expected to follow the sequence[4,5], $CH_3NH_3^+ > (CH_3)_2NH_2^+ > (CH_3)_3NH^+$. In aqueous solution, due to solvent effects, this sequence becomes $CH_3NH_3^+ \sim (CH_3)_2NH_2^+ < (CH_3)_3NH^+$. As can be seen from the second column in Table I, the latter sequence is followed fairly closely for symmetric diamines only.

From Table III it can be seen that, in general, ΔG values vary less than the corresponding ΔH and $T\Delta S$ values. This has also been mentioned by previous workers[6,7]. The "stiffening" of the aliphatic chains of di-protonated molecules[7] can, therefore, be an explanation. When losing a hydrogen ion, the possibility of rotation and vibration of the molecule increases, so that both enthalpy and entropy increase. Otherwise, the loss of a hydrogen ion is accompanied by a decreasing number of free water molecules, the entropy decreases but the enthalpy decreases also, due to hydratation energy of the monoprotonated diamines, the unprotonated diamines, and the hydrogen ions, respectively.

Still considering the symmetric diamines, Table II shows that the decrease of ΔH as a function of the substitution on the nitrogen atoms by methyl groups is not entirely compensated by the term $T\Delta S$ for the tertiary amines. Therefore, solvent effects seem to be the main cause, since it may be assumed that by the stiffening effect the gain in enthalpy is compensated by the gain in entropy.

A successful theory about symmetric dibasic acids in terms of pure electrostatic interactions has been presented by Kirkwood and Westheimer[8]. This theory can be expressed by the following relationship

$$\Delta(\Delta G) = \Delta G_2 - \Delta G_1 = \frac{Ne^2}{D_E r} + RT \ln \sigma$$

where σ is a symmetry factor and is equal to 4, D_E is the effective dielectric constant, and r is the distance between the two positive charges. For the five symmetric dibasic acids, the following $\Delta(\Delta G)$ values were obtained: en, 3.66; s dimen, 3.73; tetramen, 4.22; pip, 5.40; and dimpip, 5.33 kcal/mole.

$\Delta(\Delta G)$ values of the ethylenediamine derivatives are clearly lower than the piperazine derivatives. As pointed by Paoletti *et al.*[9], this effect is due to the larger distance between the charges in the protonated ethylenediamine molecule compared to those in the piperazine molecule. The somewhat large value for tetramen must be due to a larger value of D_E, since r is roughly constant for all the ethylenediamine derivatives. This larger value of D_E is due to the so called "space-filling" effect of the methyl groups[4,9]. However, this "space-filling" effect is not encountered in dimpip. A possible explanation could be found in the shape and rigidity of the piperazine molecule.

In the course of this investigation an interesting paper has been published by Paoletti *et al.*[9], who consider the basic properties of the asymmetric diamines in terms of the microscopic constants. An asymmetric diamine consists of a more- and a less-substituted nitrogen atom.

α is defined as the fraction of monoprotonated diamine with the hydrogen ion on the less-substituted nitrogen atom. Paoletti *et al.*[9] give two methods for the calculation of α, the first one from enthalpy changes, and the second from dissociation constants.

Using the first method, α can be calculated from the equation

$$\Delta H_1 = (1-\alpha)\Delta H^{l}_1 + \alpha \Delta H^{m}_1$$

and from

$$\Delta H_2 = \alpha \Delta H^{l}_2 + (1-\alpha)\Delta H^{m}_2$$

ΔH^{l} and ΔH^{m} represent the ΔH values of the corresponding symmetric diamines with the less- and the more-substituted nitrogen atoms, respectively.

A mean value of $\alpha = 0.42$ for men, and $\alpha = 0.62$ for a dimen is in good agreement with the values reported by Paoletti *et al*[9]. For mpip, $\alpha = 0.68$ and for trimen, $\alpha = 0.79$. For men and mpip, the two equations give the same result, for the two others the agreement was reasonable. This means that the secondary amino function is a slightly stronger base than the primary amino function; and the primary is a much stronger base than the tertiary amino function.

ACKNOWLEDGMENT

The authors thank Prof. Dr. Z. Eeckhaut for his kind interest shown in this work and his helpful discussions.

REFERENCES

1 B. G. Bates, *Determination of pH*, John Wiley and Sons, New York, 1964, p. 89.
2 G. F. Thiers, L. C. van Poucke and M. A. Herman, *J. Inorg. Nucl. Chem.*, 30 (1968) 1543.
3 E. A. Unwin, R. G. Beimer and Quintus Fernando, *Anal. Chim. Acta*, 39 (1967) 95.
4 E. J. King, *Acid–Base Equilibria*, Pergamon Press, 1965, p. 151.
5 F. Trotman-Dickenson, *J. Chem. Soc.*, (1949) 1293.
6 R. Barbucci, P. Paoletti, and A. Vacca, *J. Chem. Soc.* (*A*), (1970) 2202.
7 J. J. Christensen, R. M. Izatt, D. P. Wrathall and L. D. Hansen, *J. Chem. Soc.* (*A*), (1969) 1212
8 J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, 6 (1938) 506.
9 P. Paoletti, R. Barbucci, A. Vacca and A. Dei, *J. Chem. Soc.* (*A*), (1971) 310.