Thermodynamics of Protonation of Aqueous Triethylenediamine

JOHN W. LARSON, GARY L. BERTRAND, and LOREN G. HEPLER
Carnegie Institute of Technology, Pittsburgh, Pa.

Calorimetric determinations of heats of solution of solid triethylenediamine in water and in aqueous acid at 25° C. lead to the following: $NR_3NH^+(aq) = H^+(aq) + NR_3N(aq)$; $\Delta H^\circ = 7.21$ kcal. per mole and $^+HNR_3NH^+(aq) = 2H^+(aq) + NRN(aq)$; $\Delta H^\circ = 10.18$ kcal. per mole. Combination of these ΔH° values with ΔG° values from ionization constants leads to $\Delta S^\circ = -15.2$ and $\Delta S^\circ = -18.8$ cal. deg.$^{-1}$ mole^{-1} for the two ionization reactions indicated above.

AS PART of a larger program of thermodynamic investigation of basicities of various organic amines, calorimetric measurements have been made on triethylenediamine to obtain ΔH° values for ionization of the mono- and diprotonated species of this substance in aqueous solution. Triethylenediamine is of particular interest because of its chemical and structural relations to such compounds as ethylenediamine and triethylamine, and also because of recent interest in this compound as a ligand in complexes of transition elements.

EXPERIMENTAL

The calorimeter used is patterned after one described previously (*3*), except that a Leeds and Northrup Mueller G-2 bridge and HS galvanometer were used with a nickel resistance thermometer. Also, the thermometer and calibration heater were contained in a glass spiral filled with mineral oil. All of the work reported here was carried out with 950 ml. of aqueous solution in the calorimeter at 25.0° ± 0.2° C.

Triethylenediamine, given to us by the Houdry Co., was purified by either vacuum sublimation or recrystallization from diethyl ether and stored in a vacuum desiccator with P_2O_5. Samples prepared in these ways were thermochemically indistinguishable.

RESULTS

Heats of solution of triethylenediamine, represented by NR_3N, were determined in dilute NaOH solution to repress hydrolysis to NR_3NH^+. Small corrections (0.01 to 0.05 kcal. per mole to the observed heats were made with the hydrolysis constant and an approximate value for the heat of hydrolysis to yield the results given in Table I for the principal calorimetric reaction as in Equation 1.

$$NR_3N(c) = NR_3N(aq) \tag{1}$$

A second series of measurements was made in which an excess of $NR_3N(c)$ was dissolved in dilute aqueous HCl. Part of the $NR_3N(c)$ dissolved according to Equation 1, and part reacted with $H^+(aq)$ as in Equation 2:

$$NR_3N(c) + H^+(aq) = NR_3NH^+(aq) \tag{2}$$

The experimental results are given in Table II along with the derived values of ΔH_2. These derived values of ΔH_2 were calculated from the experimental heats by means of the equation

$$Q/n = f_1\Delta H_1 + f_2\Delta H_2 + f_4(\Delta H_2 + \Delta H_w) \tag{3}$$

in which f_1, f_2, and f_4 represent the fractions of the $NR_3N(c)$ that react according to Equations 1, 2, and 4.

Table I. Heats of Solution of $NR_3N(c)$ in Dilute Base

Moles NR_3N/950 Ml.^{a}	NaOH^a	$-\Delta H_1$, Kcal. Per Mole
5.929	2.5	6.22
7.071	2.5	6.24
7.143	0.5	6.20
7.910	2.5	6.26
8.173	5.0	6.21

$\Delta H_1^\circ = -6.23 \pm 0.03$ kcal. per mole

$^a \times 10^{-3}$.

Table II. Heats of Solution of $NR_3N(c)$ in Dilute Acid

Moles HCl/950 Ml.^{a}	n, Moles NR_3N^a	$-Q/n$, Kcal. Per Mole	$-\Delta H_2$, Kcal. Per Mole
2.315	7.128	8.64	13.46
2.315	3.356	11.27	13.42
3.762	6.862	10.17	13.42
3.810	3.812	13.43	13.43
4.703	5.576	12.26	13.38
5.173	5.505	12.97	13.40
8.935	9.126	13.25	13.40

$\Delta H_2^\circ = -13.44 \pm 0.10$ kcal. per mole

$^a \times 10^{-3}$.

$$NR_3N(c) + H_2O = NR_3NH^+(aq) + OH^-(aq) \tag{4}$$

ΔH_w represents the heat of ionization of water (*1*, *5*). In calculating the f values, pK = 8.60 (*2*) was used for the ionization Reaction 5 with activity coefficients estimated from the extended Debye equation.

$$NR_3NH^+(aq) = H^+(aq) + NR_3N(aq) \tag{5}$$

The indicated uncertainty in ΔH_1° includes contributions from the uncertainties in values of f_1, f_2, f_4, ΔH_1, and ΔH_w used in Equation 3, along with uncertainties in the measured Q values and the extrapolation by least squares to zero concentration.

Combination of our ΔH_1° and ΔH_2° values leads to $\Delta H_5^\circ = +7.21 \pm 0.10$ kcal. per mole for the ionization reaction represented by Equation 5. From pK = 8.60 one may calculate $\Delta G_5^\circ = 11.74$ kcal. per mole and, thence, by combination with ΔH_5°, obtain $\Delta S_5^\circ = -15.2$ cal. deg.$^{-1}$ mole^{-1} for the ionization Reaction 5.

Heats of solution of $NR_3N(c)$ were also determined in acid of sufficient concentration that the principal solution reaction can be represented by Equation 6:

Table III. Heats of Solution of NR_3N(c) in Excess Acid

Moles HCl/950 Ml.[a]	n, Moles NR_3N[b]	$-Q/n$, Kcal. Per Mole	$-\Delta H_6$ Kcal. Per Mole
1.04	3.902	16.61	16.64
1.05	3.568	16.50	16.54
2.12	3.792	16.73	16.76
2.96	3.144	16.94	16.96
3.00	4.330	17.02	17.02
4.23	4.255	17.14	17.14
4.31	3.413	17.24	17.25
4.31	5.027	17.18	17.18

$\Delta H^\circ_6 = -16.4 \pm 0.3$ kcal. per mole

[a] $\times 10^{-1}$. [b] $\times 10^{-3}$.

$$NR_3N(c) + 2\,H^+(aq) = {}^+HNR_3NH^+(aq) \qquad (6)$$

Although most of the NR_3N(c) dissolved according to Equation 6, some dissolved according to Equation 2, so it was necessary to correct the observed heats (Q/n values in Table III) for this secondary process by means of ΔH_2 and extent of reaction calculated from pK = 11.55 (*2*) for

$${}^+HNR_3NH^+(aq) = 2\,H^+(aq) + NR_3N(aq) \qquad (7)$$

The derived values of ΔH_6 are listed in Table III with the experimental data. The estimated uncertainty in ΔH°_6 includes contributions from calculations and extrapolations, along with calorimetric uncertainties.

Combination of our ΔH°_1 and ΔH°_6 values leads to $\Delta H^\circ_7 = 10.2 \pm 0.3$ kcal. per mole for the ionization represented by Equation 7. Further combination of $\Delta G^\circ_7 = 15.77$ kcal. per mole from pK = 11.55 with ΔH°_7 gives $\Delta S^\circ_7 = -18.8$ cal. deg.$^{-1}$ mole^{-1}.

There are no data in the literature that are directly comparable to the standard state thermodynamic data reported here. Paoletti, Stern, and Vacca (*4*) have made calorimetric measurements on triethylenediamine in 0.1*M* KCl as solvent and have reported results that lead to $\Delta H_5 = 7.30$ kcal. per mole (the authors' $\Delta H^\circ_2 = 7.21$) and $\Delta H_7 = 10.31$ kcal. per mole (the authors' $\Delta H^\circ_7 = 10.2$). The small differences between the present results and those of Paoletti, Stern, and Vacca (*4*) should probably be attributed mostly to differences in the solvent systems (water *vs.* 0.1*M* KCl) used in the two investigations.

ACKNOWLEDGMENT

We thank the National Institutes of Health for support of this research and the Houdry Co. for samples of triethylenediamine and helpful correspondence.

LITERATURE CITED

(1) Hale, J., Izatt, R.M., Christensen, J.J., *J. Phys. Chem.* **67**, 2605 (1963).
(2) Houdry Co., Bulletin, "Triethylenediamine"; personal communication from A. Farkas, Houdry Co.
(3) O'Hara, W.F., Wu, C.H., Hepler, L.G., *J. Chem. Educ.* **38**, 512 (1961).
(4) Paoletti, P., Stern, J.H., Vacca, A., *J. Phys. Chem.* **69**, 3759 (1965).
(5) Vanderzee, C.E., Swanson, J.A., *Ibid.*, **67**, 2608 (1963).

RECEIVED for review March 14, 1966. Accepted May 20, 1966.

Electromotive Force Measurements of the Free Energy of Formation of Molten LeadChloride

K. HAGEMARK and D. HENGSTENBERG
North American Aviation Science Center, Thousand Oaks, Calif.

The e.m.f. of a formation cell of molten $PbCl_2$ has been measured at 500° to 620° C. The data obtained may be represented by e.m.f. (volt) = $1.2471 - 602 \times 10^{-6}$ (t − 550° C.); agreement with some of the reported e.m.f. data is good. The estimation of the free energy of formation of molten $PbCl_2$ given in thermochemical tables has not included values for molten $PbCl_2$ obtained by direct e.m.f. methods. A new expression for the free energy of formation of molten $PbCl_2$ $\Delta G_f = 86{,}630 + 94.90\,T - 8.860\,T \ln T$, has been obtained by a best fit to the present data for the molten state and the previous data for the solid. These measurements lend support to the previous estimates and show that molten salt formation cells can be a reliable and valuable source of data on free energies of formation.

A LARGE NUMBER of e.m.f. measurements of the formation cell of molten $PbCl_2$ have been reported in the literature. References to most of the previous work may be found in a paper by Delimarskiĭ and Roms (*2*). The agreement among the published data has not been too good, except for the two recent investigations by Lantratov and Alabyshev (*7*) and Markov, Delimarskiĭ, and Panchenko (*8*). Attempts to assess the e.m.f. data, however, are beyond the scope of this paper.

The thermodynamic properties for molten $PbCl_2$ are estimated in the JANAF tables (*4*) by using the data for the solid state, the values for the heat of fusion, the melting point, and a heat capacity value for the liquid. No measurements directly yielding the free energy of formation of the molten salt were included.

The data on pure molten $PbCl_2$ presented here are part of a more extensive study of ternary systems consisting of $PbCl_2$ and alkali metal chlorides. In order to evaluate the solution properties of the ternary systems, separate e.m.f. measurements have been made of the formation cell

$$C,Pb(l)\,|\,PbCl_2\,|\,Cl_2(1\text{ atm.}), C$$