Determination of Ion−Solvent Equilibria in the Gas Phase. Hydration of Diprotonated Diamines and Bis(trimethylammonium) Alkanes

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Abstract: Many ions of interest in condensed phase chemistry cannot be produced in the gas phase by conventional methods. This is particularly the case for multiply charged inorganic and bio-organic ions. However, these species can be produced by electrospray, which is a method with which electrolyte ions present in a solution can be transferred to the gas phase. An ion-source reaction chamber was developed with which the equilibrium constants of ion−molecule equilibria and their temperature dependence can be determined, where the ions involved are produced by electrospray. The hydration equilibria $M^{z+}(H_2O)_{n-1} + H_2O = M^{z+}(H_2O)_n$ were determined for $M^{z+} = Na^+, K^+$, $n\text{-}C_3H_7NH_3^+, n\text{-}C_6H_{13}NH_3^+$. The $\Delta G^\circ_{n-1,n}$, $\Delta H^\circ_{n-1,n}$, and $\Delta S^\circ_{n-1,n}$ were found to be in good agreement with previous determinations where these ions were produced by conventional techniques. Equilibria determinations were also obtained for the diprotonated α,ω-alkyldiammonium ions: $H_3N(CH_2)_pNH_3^{2+}$ where $p = 5, 6, 7, 8, 9, 10, 12$. The ΔH° values obtained for these ions show that the hydration proceeds by water molecules occupying sequentially first the α charge site and then the other site, ω. It is found that the $\Delta H^\circ_{0,1} \approx \Delta H^\circ_{1,2}$ and $\Delta H^\circ_{2,3} \approx \Delta H^\circ_{3,4}$ where the second pair of enthalpies are slightly lower. The equality of the paired enthalpies is due to the large distance between the two charged sites. The entropy $\Delta S^\circ_{n-1,n}$ values also support alternate occupation of the α and ω charge sites. Equilibria were determined also for the methylated analogues: $(CH_3)_3N(CH_2)_pN(CH_3)_3^{2+}$, $p = 2, 3, 4, 6$. The hydration interactions for these ions is much weaker, as expected from previous work on the hydration of $(CH_3)_4N^+$ by Meot-Ner and Deakyne. The observed entropy changes suggest a possible scheme of consecutive charged sites occupation which is different from that observed for the $H_3N(CH_2)_pNH_3^{2+}$ compounds. This different scheme is consistent with structure and energy predictions for the $(CH_3)_4N^+$ hydrates due to Meot-Ner and Deakyne.

Introduction

Determinations of gas-phase equilibria involving singly charged ions and solvent molecules such as H_2O (see eq 1, $z = 1$) or other ligands were initiated some 30 years ago.[1,2] The sequential free energies, $\Delta G^\circ_{n-1,n}$ enthalpies, $\Delta H^\circ_{n-1,n}$, and entropies, $\Delta S^\circ_{n-1,n}$, resulting from these measurements have provided a wealth of data[2,3] on ion−solvent and ion−ligand interactions for positive and negative ions.

$$M^{z+/-}(H_2O)_{n-1} + H_2O = M^{z+/-}(H_2O)_n \qquad (n-1, n) \quad (1)$$
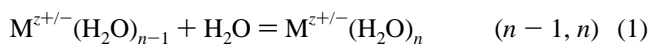
Many ions of great interest in condensed phase chemistry and biochemistry could not be produced in the gas phase by conventional methods.[1−3] Electrospray mass spectrometry (ESMS)[4] is a method whereby electrolyte ions present in solution can be transferred to the gas phase.[5] With ES it is possible to obtain in the gas phase multiply charged ion−ligand complexes,[6] multiply protonated peptides and proteins,[7] and multiply deprotonated nucleic acids.[9] Most of these ions could not be obtained in the gas phase by conventional methods.[2]

Previously we described[10] an ion source reaction chamber with which ion−molecule equilibria involving ES produced ions could be determined. This reaction chamber could only be operated at a single temperature, $T = 293$ K, such that only free energy changes, $\Delta G^\circ_{n-1,n}$, could be obtained.[10−13] In the present work we describe briefly a variable-temperature source with which $\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$ values can also be obtained. The first results obtained with this apparatus are a study of the hydration of diprotonated diamines $H_3N(CH_2)_pNH_3^{2+}$ and the doubly charged $(CH_3)_3N(CH_2)_pN(CH_3)_3^{2+}$ methylammonium ions.

The results obtained for the above diammonium ions provide a good illustration of the changes in the interactions with water when the length of the alkyl chain $(CH_2)_p$ is decreased and the two charged centers come closer to each other. The charged

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(1) Hogg, A. M.; Haynes, R. N.; Kebarle, P. *J. Am. Chem. Soc.* **1966,** *88,* 28.

(2) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977,** *28,* 455.

(3) Keesee, R. G.; Castleman, A. W. *J. Phys. Chem. Ref. Data* **1986,** *15,* 1011.

(4) Yamashita, M.; Fenn, J. B. *J. Phys. Chem.* **1984,** *88,* 4451. Fenn, J. B.; Mann, M.; Meng, C. K.; Wong, S. F.; Whitehouse, C. M. *Science* **1985,** *246,* 64.

(5) Kebarle, P.; Tang, L. *Anal. Chem.* **1993,** *65,* 272A.

(6) Blades, A. T.; Jayaweera, P.; Ikonomou, M. G.; Kebarle, P. *J. Chem. Phys.* **1990,** *92,* 2900. Blades, A. T.; Jayaweera, M. G.; Kebarle, P. *J. Chem. Phys.* **1990,** *102,* 251.

(7) Bruins, A. P.; Covey, T. R.; Henion, J. D. *Anal. Chem.* **1987,** *59,* 2642.

(8) Blades, A. T.; Kebarle, P. *J. Am. Chem. Soc.* **1994,** *116,* 10761.

(9) Limbach, P. A.; Crain, P. F.; McCloskey, J. A. *J. Am. Soc. Mass Spectrom.* **1995,** *6,* 27. Smith, R. D.; Lou, J. A.; Edonds, C. G.; Barinaga, C. J.; Udseth, H. R. *Anal. Chem.* **1990,** *62,* 882.

(10) Klassen, J. S.; Blades, A. T.; Kebarle, P. *J. Am. Chem. Soc.* **1994,** *116,* 12075.

(11) Klassen, J. S.; Blades, A. T.; Kebarle, P. *J. Am. Chem. Soc.* **1995,** *99,* 15509.

(12) Blades, A. T.; Klassen, J. S.; Kebarle, P. *J. Am. Chem. Soc.* **1995,** *117,* 10563.

(13) Blades, A. T.; Ho, Y.; Kebarle, P. *J. Phys. Chem.* **1996,** *100,* 2443.

(14) Dzidic, I.; Kebarle, P. *J. Phys. Chem.* **1970,** *7,* 1466.

(15) Tang, I. N.; Lian, M. S.; Castleman, A. W., Jr. *J. Chem. Phys.* **1976,** *65,* 4022.

(16) (a) Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1984,** *106,* 1265. (b) Meot-Ner (Mautner), M.; Deakyne, C. A. *J. Am. Chem. Soc.* **1985,** *107,* 469.
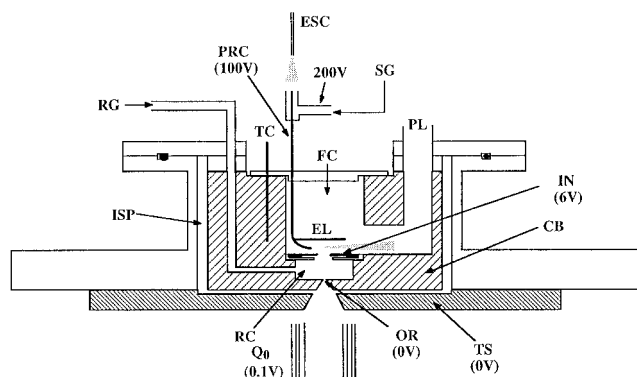
Figure 1. Ion source for determining ion—molecule equilibria involving electrospray generated ions. ESC = electrospray capillary. SG = pipe and sleeve through which N_2 gas is supplied which reduces inflow of solvent vapor into pressure reducing capillary, PRC. Forechamber = FC, at 10 Torr; EL = electrode attached to PRC. CB = copper block housing of FC and reaction chamber, RC. Thermocouple = TC. Evacuated space for thermal insulation = ISP. Interface = IN with 4-mm orifice. RG supply of reagent gas to reaction chamber. PL = pumping lead. TS = thermal shield; reduces radiative heating of cryopump surfaces of vacuum chamber. Q_0 AC only Brubacker lens. Q_0 is followed by the triple quadrupole assembly Q_1, Q_2, and Q_3, not shown in this figure.

groups selected in the two compound series $-NH_3^+$ and $-N(CH_3)_3^+$ represent two extremes, *i.e.* a strongly hydrogen bonding and a very weakly hydrogen bonding species, and the results obtained for these contrasting compounds are of additional interest.

Experimental Section

The variable-temperature ion source is shown in Figure 1. It is of very similar design to the room temperature source described previously,[10] except for the following changes. The forechamber, FC, and the reaction chamber, RC, are now housed in a solid cylindrical copper block, CB. The copper block has four wells for cartridge heaters (wells not shown in the figure) and a narrow well for the thermocouple, TC, with which the temperature was measured.

The ion source operates on the same principles as the previous source.[10] The electrospray generating capillary, ESC, produces a fine spray of very small charged droplets. The evaporation of solvent from the droplets leads ultimately to the formation of gas phase ions.[4,5] This stage occurs at atmospheric pressure. Some of the ions and surrounding gases are drawn into the pressure reducing capillary, PRC, which leads to the forechamber, FC. Inside FC the ions drift toward the reaction chamber, RC, under the influence of an electric field imposed between the electrode, EL (which is connected to PRC), and the interface plate, IN. Some ions enter RC through a 3-mm orifice in IN. Reagent gas, consisting of nitrogen at 10 Torr and water vapor at 1—80 mTorr, is supplied to the reaction chamber via the channel RG. The pressure in RC and FC is maintained at the desired magnitude (10 Torr) by the pumping lead, PL. Ion hydration equilibria establish in RC, through which the ions drift at near thermal velocities. The ions in RC are then sampled by allowing for gas flow through the orifice, OR, and into a vacuum chamber which houses the triple quadrupole mass spectrometer.

The present reaction chamber was somewhat longer, 8 mm, compared to 5 mm with the previous design,[10] and the potential drop between IN and OR was smaller, 6 versus 10 V. The drift field used in the present source is thus 2.7 times lower. The ion residence time in RC is correspondingly longer and conditions for achieving thermal and reaction equilibrium are better than was the case for the previous source. Duplicate equilibrium constant determinations with the two sources led to essentially identical results.

Other typical potentials used with the present apparatus were the following: SG = 200 V; PRC = EL = 100 V; IN = 6 V; CB = OR = 0 V; $Q_0 = -0.1$ V; $Q_1 = -5$ V; $Q_2 = -10$ V. The design of the ion source was much simplified by choosing ground potential for CB
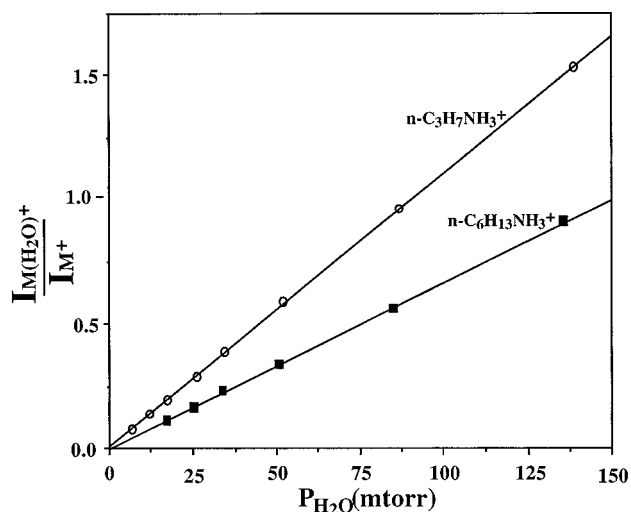

Figure 2. Determination of equilibrium constants: Plot of ion intensity ratio $I_{M(H_2O)^+}/I_{M^+}$ for hydration equilibrium: $M^+ + H_2O = M(H_2O)^+$, (0, 1), versus P_{H_2O}, pressure of water vapor in the ion source reaction chamber, at a temperature $T = 382$ K for $M^+ = n\text{-}C_3H_7NH_3^+$ (O), and $n\text{-}C_6H_{13}NH_3^+$ (■). The slope of straight lines observed corresponds to the equilibrium constant $K_{0,1}$. The equilibrium expression eq 2 requires also that the straight line goes through the origin, as is the case in the present plots.

and OR, which could be directly silver soldered to the flange which is bolted to the vacuum housing. The IN electrode is electrically insulated from CB with a disk of machinable ceramic. Mass resolution was obtained with the third quadrupole Q_3, which was operated at an offset potential of -10 V. Corrections for the mass dependent transmission of the quadrupole were made with a procedure detailed in the previous work.[11]

The solution flow rate through the electrospray capillary was $1-2$ μL/min with methanol as the solvent. The ammonium ions were obtained from the ammonium salts, either the chlorides or iodides, at $\sim10^{-4}$ M concentrations.

Results and Discussion

(a) Determination of the Equilibrium Constants and $\Delta G°$, $\Delta H°$, $\Delta S°$ Values. Comparison with Some Data from the Literature. The equilibrium constants $K_{n-1,n}$ were obtained from the ion intensities I_n and I_{n-1} of the corresponding hydrates, determined at a known partial pressure of water vapor p_{H_2O}. Plots of the intensity ratio, I_n/I_{n-1}, versus p_{H_2O} are shown in Figure 2 for the n-propyl and n-hexylammonium ions. Good straight lines passing through the origin are observed. According to eq 2,

$$K_{n-1,n} = I_n/I_{n-1}p_{H_2O} \qquad (2)$$

the slope of the straight line should be equal to the equilibrium constant $K_{n-1,n}$.

Equilibrium constants determined at different temperatures are then used in van't Hoff plots to obtain $\Delta H°_{n-1,n}$ and $\Delta S°_{n-1,n}$, while the free energy can be obtained at any temperature from $-\Delta G°'_{n-1,n} = RT \ln K_{n-1,n}$. van't Hoff plots for the n-propyl- and n-hexylammonium ions as well as the α,ω hexane diammonium ion are given in Figure 3. These plots illustrate very directly the stronger hydration present for the doubly charged ion. Thus, the (0, 1) line for the doubly charged ion is very much higher, which signals a much higher exoergicity, and the slope of the line is steeper, which signals a higher exothermicity.

van't Hoff plots for the sequential hydration of the α,ω dodecane diammonium ion are shown in Figure 4. These $(n-1, n)$ plots show a very interesting pattern with n which will be examined further in the discussion. The van't Hoff plots for
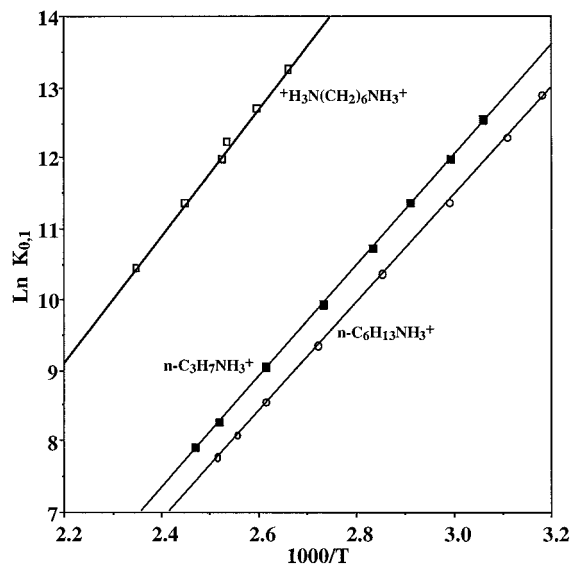
Figure 3. van't Hoff plots of ln $K_{0,1}$ vs reciprocal absolute temperature for hydration of n-$C_3H_7NH_3^+$ (■), n-$C_6H_{13}NH_3^+$, (○), and $NH_3(CH_2)_6$-NH_3^{2+} (□). The much stronger hydration of the doubly charged ion is indicated by the much larger equilibrium constant values $K_{0,1}$, which corresponds to a larger exoergicity, $-\Delta G_{0,1}^\circ = RT \ln K_{0,1}$, and by the steeper slope of the straight line obtained, which corresponds to a larger exothermicity, $-\Delta H_{0,1}^\circ$.
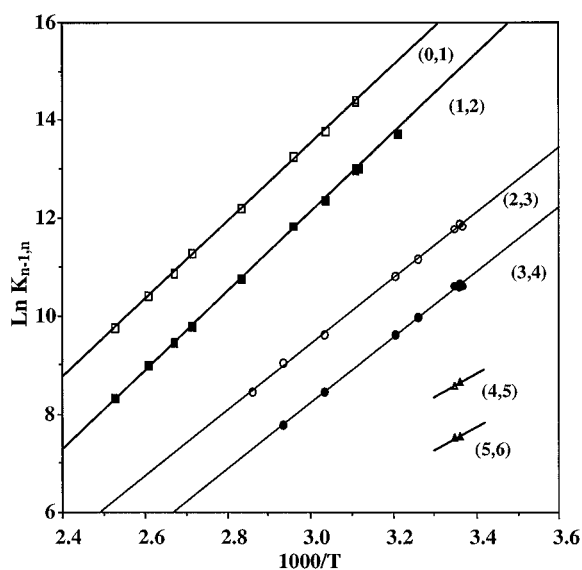

Figure 4. van't Hoff plots for the sequential hydration $(n-1, n)$ of $NH_3(CH_2)_{12}NH_3^{2+}$. Determinations for $(n-1, n) = 4, 5$ and $5, 6$ could be obtained only at the lowest temperature, i.e. $T = 298$ K.

the (0, 1) hydration of the doubly protonated $H_3N(CH_2)_pNH_3^{2+}$ with increasing value of p are given in Figure 5 and the same type of plots but for $(CH_3)_3N(CH_2)_pN(CH_3)_3^{2+}$ are given in Figure 6. The ΔH°, ΔG°, and ΔS° values resulting from these plots are summarized in Table 1−3.

Table 1 gives data for which previous determinations have been reported in the literature. The data from the present work for the sodium and potassium ions, given in Table 1, were obtained from van't Hoff plots but these plots are not shown. Comparison of the present values with the literature results[14−16] shows agreement within 1 kcal/mol for the ΔH° and ΔG° values and 2 cal/(deg mol) for the ΔS° results, which is as good as can be expected considering previously observed consistency within ion-equilibria determinations.[17,18]

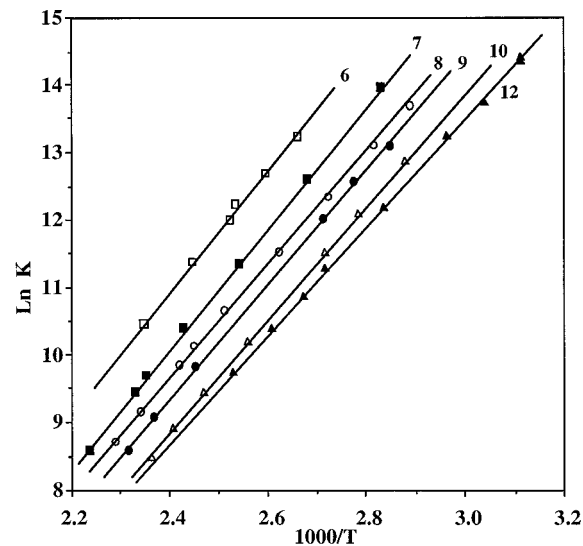(17) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445.

Figure 5. van't Hoff plots of the equilibrium constant K for the monohydration $(0, 1)$ of several diprotonated diamines $NH_3(CH_2)_p$-NH_3^{2+}, versus the reciprocal temperature. Value of p is shown beside each plot.

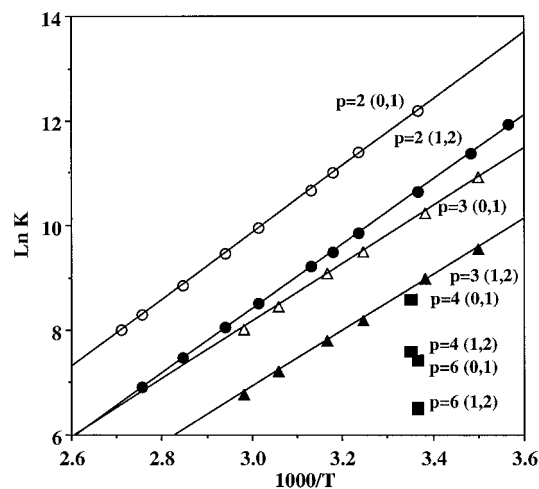**Figure 6.** van't Hoff plots for the $(0, 1)$ and $(1, 2)$ hydration of $(CH_3)_3N(CH_2)_pN(CH_3)_3^{2+}$. Values of p are given beside each plot. The hydration of the ions with $p > 3$ was weak at temperatures above $T = 298$ K and equilibrium constant determinations for these compounds could be obtained only for the lowest temperature, $T = 298$ K.

(b) Sequential Hydration of a Doubly Protonated Diamine. The van't Hoff plots for the sequential hydration of $H_3N(CH_2)_{12}$-NH_3^{2+} are shown in Figure 4, and the resulting thermodynamic data are given in Table 2. The $\Delta H_{n-1,n}^\circ$ values follow an interesting pattern: $\Delta H_{0,1}^\circ = \Delta H_{1,2}^\circ = -15.7$ kcal/mol, then a drop in exothermicity occurs, $\Delta H_{2,3}^\circ = \Delta H_{3,4}^\circ = -13.5$ kcal/mol. This pattern is very different from the gradual decrease of $\Delta H_{n-1,n}^\circ$ with increase of n observed for singly charged ions.[17,18] This difference is easily understood. Since the charges in the diammonium ion are separated, the strongest interactions occur when the sequential water molecules go to different charged sites. Furthermore, because in the dodecane the two charged sites are very widely separated, the interaction of the second water molecule with the second site is essentially identical to the first with the first site.

The hydration of alternate charged sites by sequentially added water molecules is also fully in accord with the observed $\Delta S_{n-1,n}^\circ$ changes, Table 2. Thus, the observed values:

(18) Keesee, R. G.; Castleman, A. W. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1011.

Table 1. Hydration Energies of Some Singly Charged Ions

ion	$(n-1, n)$	$-\Delta G_{298}^{\circ}$, kcal/mol	$-\Delta H^{\circ}$, kcal/mol	$-\Delta S^{\circ}$, cal/(deg mol)
Na^+	(2, 3)	9.5	16.1	22.0
		(9.3)[a]	(15.8)[a]	(21.9)[a]
		(8.7)[b]	(14.9)[b]	(20.8)[b]
	(3,4)	6.1	12.7	22.0
		(6.3)[a]	(13.0)[a]	(22.5)[a]
		(5.5)[b]	(12.6)[b]	(23.7)[b]
K^+	(2, 3)	6.3	13.0	22.5
		(6.3)[a]	(13.2)[a]	(23.0)[a]
$n\text{-}C_3H_7NH_3^+$	(0, 1)	8.8	15.6	22.8
		(8.7)[c]	(15.1)[c]	(21.5)[c]
$n\text{-}C_6H_{13}NH_3^+$	(0, 1)	8.4	15.2	22.8
$(CH_3)_4N^+$	(0, 1)[a]	(2.6)[d]	(9.0)[d]	(21.5)[d]

[a] Dzidic Kebarle.[14]   [b] Tang, Lian, Castleman.[18]   [c] Meot-Ner (Mautner).[16a]   [d] Meot-Ner and Deakyne.[16b]

Table 2. Sequential Hydration of $H_3N(CH_2)_{12}NH_3^{2+}$

$n-1, n$	$-\Delta G_{298}^{\circ}$, kcal/mol	$-\Delta H^{\circ}$, kcal/mol	$-\Delta S^{\circ}$, cal/(deg mol)
0, 1	9.7	15.7	20.1
1, 2	8.8	15.7	23.2
2, 3	7.0	13.4	21.5
3, 4	6.3	13.6	24.5
4, 5	5.1		
5, 6	4.4		

Table 3. Hydration of α,ω-Diammonium Alkanes and Dimethylammonium Alkanes

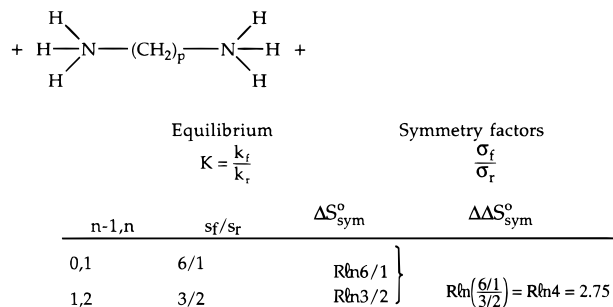| p	$-\Delta G_{298}$, kcal/mol		$-\Delta H$, kcal/mol		$-\Delta S$, cal/(deg mol)	
	(0, 1)	(1, 2)	(0, 1)	(1, 2)	(0, 1)	(1, 2)
	$H_3N(CH_2)_pNH_3^{2+}$					
12	9.7	8.8	15.7	15.7	20.1	23.2
10	10.3	9.3	16.8	16.8	22.8	25.2
9	10.3	9.3	16.5	16.3	20.8	23.4
8	10.5	9.7	16.9	16.8	21.5	23.8
7	11.1	9.8	17.8	17.2	22.6	23.7
6	11.5	10.4	17.8	17.3	21.0	23.1
5	(12.2)[a]	(11.3)[a]	(18.6)[a]	(18.4)[a]	(21.5)[a]	(23.9)[a]
	$(CH_3)_3N(CH_2)_pN(CH_3)_3^{2+}$					
6	4.4	~3.8				
5						
4	5.1	4.5	(10.0)[b]		(16.5)[b]	
3	6.1	5.0	11.0	10.7	16.5	19.0
2	7.0	6.4	12.7	12.2	19.3	19.8

[a] Due to low yield of doubly protonated $p = 5$ ion obtained with electrospray, measurements of equilibria at only one temperature were feasible. These led to $-\Delta G_{0,1}^{\circ} = 10.1$ kcal/mol and $-\Delta G_{1,2}^{\circ} = 8.9$ kcal/mol at $T = 398$ K. The values given in the table were obtained by assuming $-\Delta S_{0,1}^{\circ} = 21.5$ cal/(deg mol) and $-\Delta S_{1,2}^{\circ} = 23.9$ cal/(deg mol). These values correspond to averages obtained for the longer chain length ($p > 5$) diammonium ion. [b] ΔH° was obtained assuming $-\Delta S_{0,1}^{\circ} = 16.5$ cal/(deg mol).

$$\Delta\Delta S_{0,2}^{\circ} = \Delta S_{0,1}^{\circ} - \Delta S_{1,2}^{\circ} = 3.1 \text{ cal/(deg mol)}$$

$$\Delta\Delta S_{0,2}^{\circ} = \Delta S_{0,1}^{\circ} - \Delta S_{1,2}^{\circ} = 3.0 \text{ cal/(deg mol)}$$

can be predicted by considering the expected statistical factor ratios for the forward and reverse rates k_f/k_r of the given $(n-1, n)$ equilibrium. This procedure is detailed in Scheme 1 for the 0, 1 and 1, 2 equilibria.

The ratio of 6/1 for the (0, 1) equilibrium comes about from the six equivalent hydrogen bonding positions on the diammonium ion for an incoming water molecule in the forward process and a single water molecule available to leave the monohydrate of the diammonium ion in the reverse. In deducing the ratio 3/2 for the (1, 2) equilibrium one takes into account that only 3 hydrogen bonding positions (those on the second charged site)

Scheme 1. Evaluation of ΔS_{sym}° for Hydration of

n-1,n	s_f/s_r	ΔS_{sym}°	$\Delta\Delta S_{sym}^{\circ}$
0,1	6/1	$R\ln 6/1$	
1,2	3/2	$R\ln 3/2$	$R\ln\left(\frac{6/1}{3/2}\right) = R\ln 4 = 2.75$

are available for the second incoming water molecule, while two equivalent water molecules can leave the dihydrate of the ion in the reverse reaction. We assume that only three hydrogen bonding positions and not five are available for the second incoming molecule because the other two positions on the already singly occupied ammonium site form significantly weaker bonds. The energy difference can be estimated to be $\sim$2.2 kcal/mol, on the basis of the difference between $\Delta H_{0,1}^{\circ} = \Delta H_{1,2}^{\circ} = -15.7$ kcal/mol and $\Delta H_{2,3}^{\circ} = \Delta H_{3,4}^{\circ} = -13.5$ kcal/mol, see Table 2. An energy difference of 2.2 kcal/mol is sufficient to "shut down" the singly occupied site; the maximum $T\Delta S$ term contribution favoring this site will be only $\sim$0.55 kcal/mol (evaluated from: $\Delta S = R\ln(5/2)$ and $T \approx 300$ K and assuming all hydrogens are equivalent).

The value for $\Delta\Delta S_{2,4}^{\circ} = R\ln(4/1)$ was obtained in an analogous manner from the statistical factor ratios: 4/2 and 2/4 for the (2, 3) and (3, 4) equilibria. An entropy change due to symmetry numbers of $\Delta\Delta S_{4,6}^{\circ} = R\ln(4/1) = 2.75$ cal/(deg mol) can be deduced also. Only single-temperature determinations at 298 K were obtained for the (4, 5) and (5, 6) equilibria, see Table 2 and Figure 4. However, because the $\Delta H_{4,5}^{\circ}$ and $\Delta H_{5,6}^{\circ}$ are expected to be the same, the $\Delta\Delta G_{4,6}^{\circ}$ can be used to obtain the entropy change and this procedure leads to $\Delta\Delta S_{4,6}^{\circ} \approx 2.3$ cal/(deg mol) in fairly good agreement with the symmetry predicted value of 2.75 cal/(deg mol).

(c) Changes of Hydration Thermochemistry with Distance between the Charged Substituents, $H_3N(CH_2)_pNH_3^{2+}$. The ΔG°, ΔH°, and ΔS° values obtained from hydration equilibria determinations (0, 1) and (1, 2) involving the diammonium ions $H_3N(CH_2)_pNH_3^{2+}$ are given in Table 3 for $p = 5-10, 12$. A plot of the enthalpy changes in $\Delta H_{0,1}^{\circ}$, as a function of the chain length p, is given in Figure 7. The $-\Delta H_{0,1}^{\circ}$ values are seen to increase gradually as p decreases. The change, which initially is quite slow, is followed by a somewhat more rapid increase at $p = 6$ and 5. A very rapid increase is expected at still lower p values. Unfortunately, measurements of equilibria were possible only for $p > 4$, because the intensity of doubly protonated ions obtained with $p < 5$ with electrospray was too low.[19]

Since the hydration energy changes with p are driven by changes of Coulombic repulsion, a linear relationship between $-\Delta H_{0,1}^{\circ}$ and the reciprocal distance between the charged centers may be suspected, since the reciprocal distance is proportional to the Coulombic energy. The quantity $p + 2$ may be assumed to be approximately proportional to the distance between the charged centers. A plot of the present enthalpy data, $-\Delta H_{0,1}^{\circ}$

(19) For $p > 6$ the intensities of the doubly protonated ions were very much higher than those of the singly protonated species. However, the intensity of the singly protonated ion became dominant for $p < 6$ and the doubly protonated species disappeared for $p < 4$. With electrospray, multiply protonated ions which are known to be present in the solution may not be observed in the gas phase when the sites of protonation are quite close to each other. The proton loss occurs in the transition from solution to gas phase as the ion is desolvated.
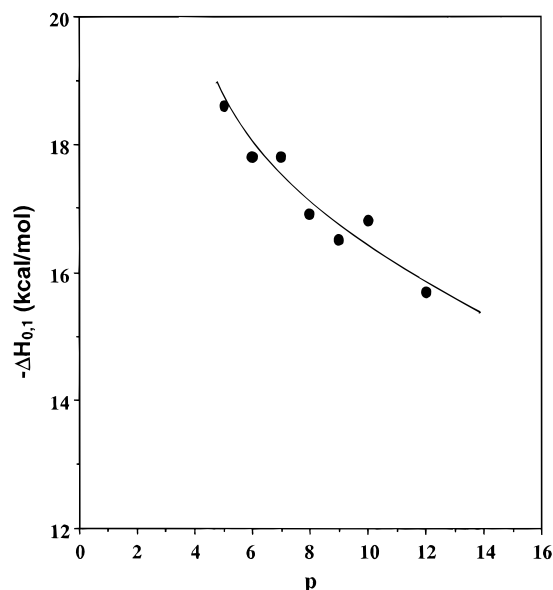
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Figure 7. Enthalpy change, $\Delta H_{0,1}^{\circ}$, for monohydration of $H_3N(CH_2)_p$-NH_3^{2+} as a function of chain length p.

Figure 8. Plot of hydration free energy $\Delta G_{0,1}^{\circ}$ for singly protonated alkyl amines BH^+ versus the gas phase basicity, GB(B), corresponding to free energy change for the reaction: $BH^+ = B + H^+$. The bases B used are identified in the figure. Also shown is the hydration energy of $H_3N(CH_2)_7NH_3^{2+}$ plotted versus the gas phase basicity GB($H_2N(CH_2)_7$-NH_3^+) obtained by Gronert.[20] The diprotonated ion clearly does not fit the linear relationship observed for the singly protonated bases. GB-(B) values are from Lias et al.[25] Hydration free energies of BH^+: n-$C_3H_7NH_3^+$, n-$C_6H_{13}NH_3^+$, present work; $CH_3NH_3^+$, $C_2H_5NH_3^+$, and $CF_3CH_2NH_3^+$, ref 16a.

versus $1/p + 2$ (plot not shown), does indicate the presence of a linear relationship, although the quality of the plot is affected by experimental error in the $\Delta H_{0,1}^{\circ}$ values.

The increase of the hydration exothermicity with decreasing separation of the two charged centers is easily understood. The presence of a positively charged substituent exerts a Coulombic repulsion on the three protic hydrogens of the other $-NH_3^+$ group which increases their protic character. Better hydrogen bonding with water is expected when the hydrogens involved have a higher partial positive charge.[20,21]

For the dodecane diammonium ion we found that the $\Delta H_{0,1}^{\circ}$ and $\Delta H_{1,2}^{\circ}$ values are essentially the same, see Section b. This result was attributed to the very large distance between the charged groups for this system, $p = 12$. One expects that as p decreases the $-\Delta H_{0,1}^{\circ}$ will become larger than $-\Delta H_{1,2}^{\circ}$, because the hydration of the first functional group induces a small shift of the positive charge on this group away from the nitrogen atom toward the H atom that interacts with the water molecule. This shift has a very small effect when p is large but, should become noticable for low p. The data for $\Delta H_{0,1}^{\circ}$ and $\Delta H_{1,2}^{\circ}$ given in Table 3 show that the two values remain approximately the same down to $p = 7$. For $p = 6$ and 5 there is an indication of a change in the direction $-\Delta H_{0,1}^{\circ} > -\Delta H_{1,2}^{\circ}$; however, the difference observed is small, ~ 0.3 kcal/mol, and essentially within the experimental error.

The Coulombic repulsion between the two charged $-NH_3^+$ substituents has also a strong effect on the gas phase acidity of the doubly protonated diamines. Recent *ab initio* calculations by Gronert[20] for $H_3N(CH_2)_7NH_3^{2+}$ ($=HB_2H^{2+}$) provide a proton affinity for B_2H^+ of 181.6 kcal/mol. This value can be converted to the free energy change, i.e. the gas phase basicity (GB), GB(B_2H^+) $\approx$ 174 kcal/mol, by subtracting the entropy term ($T\Delta S = 7.8$ kcal/mol, $T = 298$ K) for the free proton. The GB for the singly protonated diamine is some 36 kcal/mol lower than that of the neutral diamine B_2. The B_2H^+ was assumed[20] to be in the same extended (noncyclised) structure as the HB_2H^{2+}.

In previous work[21,22] involving measurements of the hydration of singly protonated monobasic nitrogen and oxygen bases it
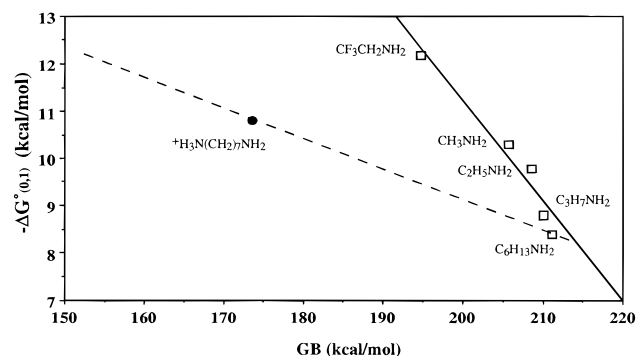
was established that an approximately linear relationship exists between the gas phase basicity of the base B, GB(B), and the hydration energy of BH^+, $-\Delta G_{0,1}^{\circ}(BH^+)$. High GB(B)'s, *i.e.* relatively weak BH^+ acids, where the charge is well stabilized, lead to low hydration exoergicities, $-\Delta G_{0,1}^{\circ}$. A very similar dependence was found also for the enthalpy change counterparts, *i.e.* the proton affinity PA(B) and $-\Delta H_{0,1}^{\circ}(BH^+)$. The relationship involving the free energy changes is illustrated by the plot shown in Figure 8 for the alkylammonium ions, BH^+; a fair straight line relationship is indicated by these data. We were interested in examining whether the diprotonated diamines would fit on the same line. The single point available is for the $p = 7$, i.e. the diammonium ion, $H_2N(CH_2)_7NH_3^+$, for which, as mentioned above, a theoretically evaluated proton affinity was obtained by Gronert.[20] As evident from Figure 8, the diprotonated diamine does not at all fall on the line obtained with the singly protonated amines. In hindsight, this large deviation is not unexpected considering the large difference between a charged and a neutral substituent. The Coulombic repulsion present when the substituent is charged leads to an extension of the $N-H^+$ bond which increases the strength of the hydrogen bond with the water molecule. However, only a small part of the Coulombic energy is used in that process. On the other hand, when the proton is completely removed, the total Coulombic energy is used to reduce the gas phase basicity. Therefore, the decrease of the gas phase basicity by the Coulombic repulsion is expected to be much larger than the increase of the hydrogen bond energy. The direction of the deviation of the diprotonated diamine from the correlation for the singly charged amines, Figure 8, conforms to the above conclusion; the actual gas phase basicity, 174 kcal/mol, is very much lower than the GB value of ~ 202 kcal/mol predicted by the correlation for a neutral base that has the same hydration value, $\Delta G_{0,1}^{\circ} = 11.1$ kcal/mol, as the protonated diamine base. Actually, the value predicted by the correlation may be expected[23] to be closer to the apparent gas phase basicity of B_2H^+, $GB^{app}(B_2H^+)$, as determined by kinetic bracketing proton transfer measurements.[20,24] Gronert's[22] calculations lead to a

(20) Gronert, S. *J. Am. Chem. Soc.* **1996**, *118*, 3525.
(21) Davidson, W. R.; Sunner, J.; Kebarle, P. *J. Am. Chem. Soc.* **1979**, *101*, 1675.
(22) Lau, Y. K.; Kebarle, P. *Can. J. Chem.* **1981**, *59*, 151.

(23) The "expected" closer correspondence with the apparent gas phase basicity follows from an inspection of a reaction coordinate for the proton transfer reaction; see for example Figure 1, 4.2 in Gronert.[22]
(24) Gross, D. S.; Rodriguez-Cruz, S. E.; Bock, S.; Williams, E. R. *J. Phys. Chem.* **1995**, *99*, 4034.

$GB^{app}(B_2H^+)$ of $\sim$192 kcal/mol, compared with the correlation value of $\sim$202 kcal/mol.

Now while the single point available for the protonated diamines does not fall on the line for the monoamines, an approximate straight line relationship may still be expected between the $-\Delta G^\circ_{0,1}$ (HB_2H^{2+}) and $GB(B_2H^+)$ values for the diamines. This inverse relationship is reasonable since GB is expected to decrease linearly with increasing Coulombic repulsion between the charge sites, while the hydration energy should increase proportionately with Coulombic repulsion. Unfortunately, only a single GB is available for the B_2H^+ ions, that of $H_2N(CH_2)_7NH_3^+$. Nevertheless, a tentative relationship (shown by the dashed line in Figure 8) can be proposed based on the experimentally determined GB of n-hexylamine. The hexylamine value should be a reasonable approximation for the limiting case where the amino groups on the diprotonated diamine are so remote from one another such that the effect of the Coulombic repulsion is negligible. Hexylamine rather than heptyl- or octylamine was chosen to represent this point, because $\Delta G^\circ_{0,1}$ values are not available for the higher amines. However, the hydration energies and the gas phase basicities are expected to change little for the higher amines. See for example the rather small change between n-propylamine and n-hexylamine in Figure 8. Using this plot, the GB's of the B_2H^+ ions may be estimated on the basis of the measured $-\Delta G^\circ_{0,1}$ values. The estimated values are as follows: ($p = 5$) GB = 158, ($p = 6$) 169, ($p = 8$) 185, ($p = 9, 10$) 187, and ($p = 12$) 197 kcal/mol (note that the $-\Delta G^\circ_{0,1}$ values for the diamines were reduced by 0.4 kcal/mol to account for the effect of the charge site multiplicity (symmetry effect) which is not present in n-hexylamine). Work is currently underway in this laboratory to evaluate theoretically the GB's of the B_2H^+ ions in order to compare them with the present estimates.

(d) Hydration Energies of $(CH_3)_3N(CH_2)_pN(CH_3)_3^{2+}$ Ions. The energies for the (0, 1) and (1, 2) hydration of the bis(trimethylammonium) ions are given in Table 3. Determinations of the hydration enthalpies for $p > 3$, where the hydration interaction becomes quite weak, require equilibration temperatures well below room temperature. These are as yet not accessible with the present ion source. Therefore, only the $-\Delta G^\circ$ values for $p = 4$ and 6 could be determined. Due to the low stability of the hydrates, van't Hoff plots for $p = 3$ and 2 could be obtained only over a narrower temperature range. Therefore, the resulting ΔH° and ΔS° data are expected to be of lower accuracy than the data for the ammonium ions.

The hydration energies for the doubly charged methylammonium compounds are seen to be much lower than those for the ammonium analogues, see Table 3 and Figure 9. For example, $-\Delta G^\circ_{0,1} = 11.5$ kcal/mol for $H_3N(CH_2)_6NH_3^{2+}$ but only 4.4 kcal/mol for $(CH_3)_3N(CH_2)_6N(CH_3)_3^{2+}$. The major reason for this difference is the much poorer H bonding ability of the CH_3 relative to the NH_3 hydrogens. This is due to the lower electronegativity of the N relative to the C atom and for the charged substituents, the longer distance between the N atom and the CH_3 hydrogens. Similar differences in the hydration energies are observed also for the singly charged ions, see Table 1, where $-\Delta G^\circ_{0,1} = 8.8$ kcal/mol for n-$C_3H_7NH_3^+$ and only 2.6 kcal/mol for $N(CH_3)_4^+$.[13b]

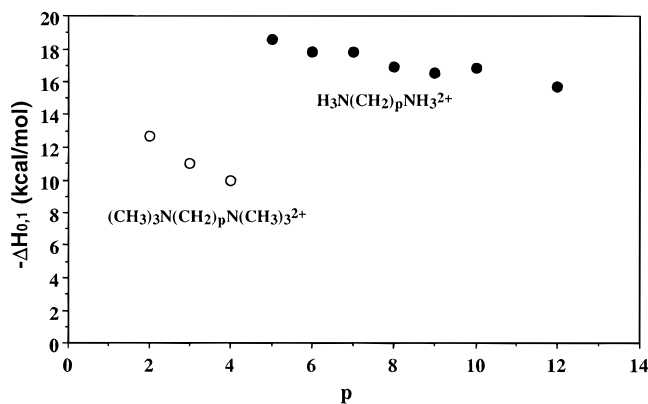The bonding of water and other ligands to singly charged quaternary alkyl ammonium ions has been studied by Meot-

(25) Lias, S. G.; Bartmess, J. E.; Liebman, J. L.; Levine, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

Figure 9. Comparison of enthalpy change for monohydration of $H_3N(CH_2)_pNH_3^{2+}$ and $(CH_3)_3N(CH_2)_pN(CH_3)_3^{2+}$ ions. The $\Delta H^\circ_{0,1}$ value for the methylammonium ion where $p = 3$ was estimated from $\Delta G^\circ_{0,1}$ for this compound, see Table 3.

Ner and Deakyne[13b] by experimental and theoretical methods. The theoretical calculations have shown that the most stable geometry is obtained when the oxygen atom of the water molecule interacts with three C$-$H hydrogens *and* when each of these hydrogens come from a different methyl group. The interaction with the three hydrogens from the different methyl groups is $\sim$6 kcal/mol more stable than the interaction with three hydrogens from the same methyl group (data for $N(CH_3)_4^+$).[13b] Another interesting result was the finding that the second water molecule in a dihydrate interacts preferentially with a hydrogen atom on the first water molecule and that this interaction is equivalent in magnitude to the interaction between the first H_2O and three methyl hydrogens.

The observations of Meot-Ner and Deakyne can be used to predict expected entropy changes for the hydration of the $(CH_3)_3N(CH_2)_pN(CH_3)_3^{2+}$ ions. For $p = 2$, an entropy change, $\Delta\Delta S^\circ_{0,2} = 2.5$ cal/(deg mol), is obtained from the data in Table 3. Proceeding as in Section c, one can evaluate $\Delta\Delta S^\circ$ values on the basis of symmetry number changes. Assuming that the first H_2O molecule goes to the one charged site forming the stable three methyl hydrogens complex and the second H_2O does the same at the other charged site, a $\Delta\Delta S^\circ_{0,2}$ of $R \ln 4 = 2.75$ cal/(deg mol) is predicted. This agrees well with the experimentally determined value, supporting the notion that the two waters add on different ends of the ion. For $p = 3$, the situation is very different with $\Delta\Delta S^\circ_{0,2} = 0.5$ cal/(deg mol). The lower value for $p = 3$ compared with $p = 2$ may be due to experimental error, partly because the van't Hoff plots, as already mentioned, were obtained over a narrow temperature range. However, it is also possible that the small $\Delta\Delta S^\circ_{0,2}$ is a consequence of the second H_2O preferentially binding to the first H_2O.[13b] If this occurs then the $\Delta\Delta S^\circ_{0,2}$ is no longer expected to be equal to 2.75 cal/(deg mol). The actual value will reflect true differences in entropy associated with the addition of the first and second H_2O molecules. Clearly, better data are required to prove that the difference in $\Delta\Delta S^\circ_{0,2}$ for $p = 2$ and 3 reflects differences in bonding of the two H_2O's. Such accuracy is within the capability of the method and we hope to demonstrate this in future work. The present results provide an illustration of how thermochemical data can lead to useful insights into the structures of the hydrates of multiply charged ions.