using the equation

$$d = \frac{|\mu_a| \pm |\mu_u|}{\epsilon \Delta z}$$

Both signs must be included as only the absolute magnitude of the dipole moment can be measured. Since the maximum change in dipole moment observed was either 110 or 1020 D, the value of d is found to be $\leqslant$ 2.5 Å. or $\leqslant$ 25 Å. The result thus indicates that activation takes place near the center of the fibrinogen molecule.

A potential source of doubt regarding the interpretation of the low $\Delta\mu$ is the possibility that the charge pattern may readjust, through proton migration, to minimize $\Delta\mu$ regardless of the site of loss of the negative charges.[35] However, it seems unlikely that the result would be so closely similar at pH 7, where the migrating protons will be exchanging on histidine residue, and at pH 9–10 where they will be exchanging on tyrosine and lysine residues.

The two peptides have nearly equal charges; therefore it could also be possible that the peptides are released equidistant from the center of symmetry of fibrinogen so that the net effect, assuming proper positions for the α-amino groups, would be the change of only one charge. Using this hypothesis one cannot exclude the possibility that activation takes place at each end of the fibrinogen molecule.[36]

While the unknown effects of the ionic atmosphere[28] leave the magnitudes of the calculated dipole moments somewhat in doubt, it would take a very large error to invalidate the conclusion that if activation occurs at only one site, this site is near the center of the molecule.

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MADISON, WISCONSIN

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[35] C. Tanford, private communication.

[36] We are indebted to Dr. F. R. Bettelheim for his comments and suggestions on the preceding interpretation.

NOTES

Thermodynamic Properties of the Ammonium Ion

BY AUBREY P. ALTSHULLER

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Structural and spectroscopic data on the ammonium ion recently have been available which make possible the statistical thermodynamic calculation of the thermodynamic functions C_p°, $(H^\circ - H_0^\circ)/T$, $-(F^\circ - H_0^\circ)/T$ and S° for $NH_4^+(g)$. The N–H internuclear distance in NH_4^+ has been obtained from both neutron diffraction[1–3] and nuclear magnetic resonance measurements.[4,5] The most accurate determination of the N–H distance[5] gives a value of 1.032 ± 0.005 Å. Thus the moment of inertia, I, has the value $(4.75 \pm 0.05) \times 10^{-40}$ g. cm.^{2}. The vibrational frequencies of the spherical top NH_4^+ (T_d symmetry is assumed for NH_4^+ in the gaseous state) have been found to be $\nu_1(1) = 3041$ cm.$^{-1}$; $\nu_2(2) = 1682$ cm.$^{-1}$; $\nu_3(3) = 3090$ cm.$^{-1}$ and $\nu_4(3) = 1403$ cm.$^{-1}$ from infrared measurements on films of NH_4Cl.[6]

The values of the thermodynamic functions C_p°, $(H^\circ - H_0^\circ)/T$, $-(F^\circ - H_0^\circ)$ and S° for NH_4^+ (g) from 200 to 1000°K. as calculated by the rigid rotator-harmonic oscillator approximation are listed in Table I for the ideal gas state at one atmosphere pressure.

TABLE I

THERMODYNAMIC FUNCTIONS FOR THE AMMONIUM ION IN THE IDEAL GAS STATE IN CAL./DEG./MOLE

T, °K.	C_p°	$(H^\circ - H_0^\circ)/T$	$-(F^\circ - H_0^\circ)/T$	S°
200	7.98	7.98	33.25	41.23
298.16	8.34	8.04	36.43	44.47
400	9.30	8.23	38.81	47.04
500	10.56	8.58	40.67	49.25
600	11.91	9.03	42.27	51.29
700	13.23	9.54	43.69	53.23
800	14.47	10.08	45.00	55.08
900	15.61	10.64	46.21	56.85
1000	16.65	11.19	47.36	58.55

The values of the thermodynamic functions probably are accurate to ±0.1 cal./deg./mole. However, at the temperatures near 1000°K. neglect of anharmonicity and other effects may increase the uncertainties in the thermodynamic functions.

The entropy of the reaction

$$NH_3(g) + H^+(g) \longrightarrow NH_4^+(g)$$

at 298.16°K. may now be calculated. The entropy of NH_3(g) is 46.01 e.u.[7] The entropy of H^+(g) is 26.01 e.u. from the Sackur–Tetrode equation and from Table I the entropy of NH_4^+(g) at 298.16°K. is 44.47 e.u. Thus the entropy of the protonation reaction is −27.55 e.u.

Combining the entropy of the gaseous ammonium ion with its partial molal entropy in water,[8] 26.8 ±

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[1] G. H. Goldschmid and D. G. Hurst, *Phys. Rev.*, **83**, 88 (1951); **86**, 797 (1951).

[2] H. A. Levy and S. W. Peterson, *ibid.*, **86**, 766 (1952).

[3] H. A. Levy and S. W. Peterson, THIS JOURNAL, **75**, 1536 (1953).

[4] H. S. Gutowsky, G. B. Kistiakowsky, G. E. Pake and E. M. Purcell, *J. Chem. Phys.*, **17**, 972 (1949).

[5] R. Bersohn and H. S. Gutowsky, *ibid.*, **22**, 643, 651 (1954).

[6] E. L. Wagner and D. F. Hornig, *ibid.*, **18**, 296 (1950).

[7] F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," NBS Circular 500, 1952.

[8] C. C. Stephenson, *J. Chem. Phys.*, **12**, 318 (1944).

0.3 e.u., the entropy of hydration may be calculated. An entropy change of -6.35 e.u. must be included in the calculation to correct for the volume change in transferring the ion from the gas phase to the solvent.[9] Consequently, the entropy of hydration, $-\Delta S_{\text{hyd.}}$, at 298.16°K. is 11 e.u. This entropy value falls between the $-\Delta S_{\text{hyd.}}$ value for Na^+ of 14.6 e.u. and that for K^+ of 6.1 e.u.[10] The NH_4^+ ion has a crystallographic radius of about 1.45 Å. which is quite close to the radius of Rb^+ of 1.48 Å. If NH_4^+ were to fall on the same line as the alkali metal ions in a plot of $\Delta S_{\text{hyd.}}$ *versus* effective radius,[11] then its entropy of hydration would be about 4 e.u.[10,11]

It is of interest to consider why the entropy of hydration of NH_4^+ is 7 e.u. more negative than that of a monatomic ion of the same size with a spherically symmetrical charge distribution of the same magnitude. Two effects are probably responsible. First, the charge distribution of the ammonium ion is concentrated at the four hydrogen atoms; consequently, a fixed NH_4^+ ion would lower the entropy of the surrounding water molecules through ion–dipole interactions more than would a uniformly charged ion. Since the NH_4^+ should be able to rotate appreciably in the solvent, this effect would be somewhat nullified. Secondly, even if the NH_4^+ were discharged so as to form a hypothetical NH_4 molecule in water, hydrogen bonding of the type N–H · · · O would occur. Hydrogen bonding is usually due to a partial charge separation $\overset{-}{X}\text{–}\overset{+}{H}\cdots\overset{-}{Y}$ resulting in dipole–dipole interactions (resonance contributions to hydrogen bonding may make a small contribution).[12] Consequently, the two effects are not readily separable, since they are both due to electrostatic interactions leading to a weak N–H · · · O bond. In summary, it may be concluded that electrostatic interactions resulting from hydrogen bonding and from the non-uniform charge distribution of NH_4^+ are both responsible for the more negative entropy of hydration of NH_4^+ compared to a monatomic ion of uniform charge distribution (plus one charge) and of the same radius.

The lattice energies of NH_4Cl, NH_4Br and NH_4I in the CsCl type lattice have been calculated by the Born–Mayer method to be 161.6, 154.0 and 145.5 kcal./mole, respectively.[13] A more detailed calculation[14] results in a lattice energy of 171.4 kcal./mole for NH_4Cl. Combining this higher lattice energy for NH_4Cl, 171 kcal./mole, with the heat of formation of NH_4Cl in the CsCl type lattice[7] and the heat of formation of $Cl^-(g)$,[7] the heat of formation of $NH_4^+(g)$ resulting is 154 kcal./mole. If this heat of formation of the ammonium ion of 154 kcal./mole is used, along with the heats of formation of $NH_3(g)$[7] and $H^+(g)$,[7] then the heat of the protonation reaction, $NH_3(g) + H^+(g) \rightarrow NH_4^+(g)$ at 298.16°K. is -202 kcal./mole. From the heat and entropy of the protonation reaction, the free energy of the protonation reaction is -194 kcal./mole. Consequently, the protonation reaction is a highly spontaneous process.

Since the heats of formation of the gaseous and aqueous ammonium ion are 154 and -31.7 kcal./mole,[7] the heat of hydration of the ammonium ion is 79 kcal./mole. This value of the heat of hydration for NH_4^+ is about the same as for the K^+ ion.[11] The augmented electrostatic energy within the hydration sphere, which is due to the same causes as discussed above for the entropy of hydration, is probably responsible for this high heat of hydration of NH_4^+.

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[9] W. H. Latimer and C. M. Slansky, This Journal, **62**, 2019 (1940).

[10] $\Delta S_{\text{hyd.}}$ values for the alkali metal ions were calculated using $S°$ values from K. K. Kelley, "Entropies of Inorganic Substances," Revision, Bureau of Mines Bulletin 477, 1948.

[11] W. M. Latimer, K. S. Pitzer and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).

[12] C. A. Coulson, "Valence," Oxford University Press, London, 1952, pp. 287–307.

[13] W. E. Bleick, *J. Chem. Phys.*, **2**, 160 (1934).

[14] A. May, *Phys. Rev.*, **52**, 339 (1937).

Preparation and Properties of Trimeric N-Methylaminoborane[1]

By T. C. Bissot and R. W. Parry

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Among the more interesting of the boron–nitrogen compounds are the borazenes. The structure and properties of these compounds have been well characterized and have been compared with those of benzene and its alkyl derivatives.

Hitherto there has been no report of a "saturated borazene" of the formula $[R_2NBR_2]_3$ in which R is either hydrogen or a methyl radical, which would be structurally similar to cyclohexane or its methyl derivatives. The compound $(CH_3)_2NBH_2$ is known to exist as a dimer at room temperature and as a monomer at higher temperatures, while H_2NBH_2 is reported as a high polymer.[2] However, recent observations in this Laboratory indicate that HCH_3NBH_2 is trimeric and is in all probability a six-membered ring composed of alternating boron and nitrogen atoms.

The new compound, trimeric N-methylaminoborane, was first isolated in low yield from the decomposition products obtained in the pyrolysis of O,N-dimethylhydroxylamine-borane.[3] It can be prepared more conveniently and in yields of 80 to 90% by heating methylamine-borane at 100°

$$3CH_3NH_2BH_3 \xrightarrow{100°} 3H_2 + (CH_3NHBH_2)_3 \quad (1)$$

The identity of the compound was proved by chemical analysis, molecular weight determinations and its decomposition at 200° into hydrogen and 1,3,5-trimethylborazene.

Although this compound does not display the extreme stability toward heat and hydrolysis which

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[1] Contribution from the Department of Chemistry of the University of Michigan.

[2] A. B. Burg and C. L. Randolph, Jr., This Journal, **73**, 953 (1951); E. Wiberg, A. Bolz and P. Buckheit, *Z. anorg. Chem.*, **256**, 285 (1948); H. I. Schlesinger, *et al.*, Univ. of Chicago, Signal Corps Contract W3434-SC-174 Final Report (1948–1949).

[3] A study of the reaction of hydroxylamine and the five possible methyl substituted hydroxylamines with diborane is being conducted in this Laboratory and will be published in the near future.