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 $\bar{S}°$ values from K. K. Kelley, "Entropies of Inorganic Substances," Revision, Bureau of Mines Bulletin 477, 1948.

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

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## 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.

has been reported by Burg and his co-workers,[4] for the trimeric P-dimethylphosphinoborane and the trimeric As-dimethylarsinoborane it is very stable for a boron–nitrogen compound containing two active hydrogens per boron. It is unaffected after weeks in contact with moist air and is hydrolyzed only very slowly by cold water.

The pyrolysis of methylamine-borane has been studied by a number of previous investigators[5] but this initial pyrolysis product never has been characterized.

## Experimental

**A. Preparation of Trimeric N-Methylaminoborane.**—In a typical preparation, 3 mmoles of diborane was condensed with liquid nitrogen, together with a small excess of anhydrous methylamine (7 millimoles). The mixture was then allowed to warm up to room temperature over a period of about three hours. A small amount of hydrogen was produced in this preparation of methylamine borine. Air was then admitted to the system and the tube was removed from the vacuum line, stoppered with a calcium sulfate drying tube, and heated on a steam-bath for two hours. The liquid in the tube changed into a crystalline mass after the first hour of heating. This white solid was then placed in a clean tube, which was replaced on the vacuum line. A beaker of boiling water was placed around the bottom of the tube and the trimeric N-methylamino-borane sublimed under high vacuum. The product collected as a ring of fine needles on the walls of the tube just above the surface of the bath. The tube was removed from the line and broken on each side of the ring. The long white needles were then scraped from the walls; yield about 0.22 g. or 85%.

The analysis of the product is summarized in Table I.

TABLE I

| Anal. for $(CH_3NHBH_2)_3$, % | Obsd. | Calcd. |
|---|---|---|
| Carbon | 28.00 | 28.00 |
| Hydrogen | 14.02 | 14.10 |
| "Active" hydrogen | 4.35 | 4.70 |
| Boron | 25.0 | 25.23 |
| Nitrogen | 32.78 | 32.66 |

**B. Molecular Weight Determinations.**—The molecular weight of the solid was estimated from the freezing point depressions of benzene and nitrobenzene solutions using a standard Beckmann apparatus. The results indicated molecular weights of 121 and 141 for two trials in benzene and 134 for nitrobenzene.

The molecular weight was also determined by the vapor pressure lowering of liquid ammonia solutions. The apparatus designed by D. R. Schultz[6] was modified by using a large slush bath of ethylene chloride as the constant temperature medium. A molecular weight of 127 was obtained.

A trimer of $CH_3NHBH_2$ has a calculated molecular weight of 128.7.

**C. Decomposition into 1,3,5-Trimethylborazene.**—A quantity, 0.2364 g., of $(CH_3NHBH_2)_3$ was placed in an evacuated sealed tube and heated at 200° for four hours. Upon opening the tube, 5.96 mmoles of hydrogen, identified by a molecular weight of 2.1, was found. This gives a ratio of hydrogen per mole of starting material of 3.24. The 1,3,5-trimethylborazene was purified by vacuum condensation, the portion collecting in a trap at −45° being retained. A 74% yield was obtained based on the equation

$$(CH_3NHBH_2)_3 \xrightarrow{200°} 3H_2 + (CH_3NBH)_3 \quad (2)$$

The 1,3,5-trimethylborazene produced was characterized by vapor pressure measurements over the temperature range 50 to 75°, and by vapor phase molecular weight measurements based on vapor density (obsd. = 126; theor. = 122.5). The melting point of the solid was 0 to −1° as compared to −9° reported by Wiberg, Bolz and Buckheit[2] and −7 to −8° reported by Schaeffer and Anderson.[5] It is believed that the higher value of 0 to −1° indicates greater purity of the sample studied and does not negate the characterization of the borazene.

**D. Properties of Trimeric N-Methylaminoborane.** The compound may be recrystallized from methyl or ethyl alcohol as long white fibrous needles. An analysis for boron and "active" hydrogen on this recrystallized material demonstrated that the composition was unchanged. In addition to the above solvents, the compound is very soluble in acetone and liquid ammonia. It is moderately soluble in benzene, ether and chloroform and is insoluble in carbon tetrachloride, petroleum ether and water. The insolubility in water may be primarily a wetting problem.

The density of the compound is 0.90 g./ml. as determined by centrifuging a few crystals in a series of mixtures of carbon tetrachloride and kerosene. The crystals would remain suspended in the mixture with a density of 0.90 g./ml.

A sample of the solid was allowed to stand exposed to the moist air of the laboratory for three weeks, during which time no noticeable hydrolysis occurred. A portion placed in cold water will float for hours but will disappear after about a day. A 20% solution of hydrochloric acid must be heated to boiling to bring about rapid hydrolysis.

**E. X-Ray Power Diffraction Data for Trimeric N-Methylaminoborane.**—In Table II are listed the interplanar spacings (*d* values) and the relative line intensities found to be characteristic of the compound. The powder patterns were taken with copper K$\alpha$ radiation in a cylindrical camera of 57.3 mm. diameter. The low absorbing glass capillaries used to hold the sample had a diameter of 0.2 mm. and a wall thickness of 0.01 mm.

TABLE II

| *d* | I | *d* | I | *d* | I |
|---|---|---|---|---|---|
| 7.1 | VS | 2.68 | VW | 1.20 | VW |
| 4.26 | VS | 2.29 | W | 1.88 | VW |
| 4.00 | MS | 2.27 | W | 1.77 | VW |
| 3.45 | M | 2.19 | W | 1.70 | VW |
| 3.06 | VW | | | | |

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## The System $Ba(NO_3)_2$–$KNO_3$; Characterization of the Double Salt $Ba(NO_3)_2 \cdot 2KNO_3$[1]

BY MEYER M. MARKOWITZ, JOHN E. RICCI AND PAUL F. WINTERNITZ

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The literature referring to the phase relationships in the system $Ba(NO_3)_2$–$KNO_3$ is contradictory. Harkins and Clark[2] characterized the system as being of a simple eutectic type on the basis of an investigation at liquidus temperatures. Ricci[3] in replotting their data demonstrated indications for the presence of the binary compounds $2Ba(NO_3)_2\cdot$

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