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The Reactions between Tetramethyldiborane and Ammonia. The Dimethyldiammineboron(III) Cation, the Dihydridodimethylborate Anion, and Ammonia Dimethylborane

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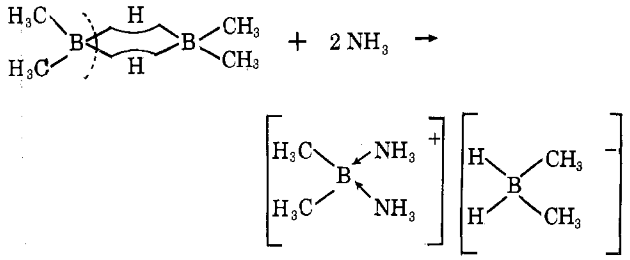
Chemical and physical evidence supports the structure $[(CH_3)_2B(NH_3)_2^+][H_2B(CH_3)_2^-]$ for the unstable product of the direct reaction of ammonia and tetramethyldiborane. The stable compounds $[(CH_3)_2B(NH_3)_2]X$ (where X = Cl or Br) have been prepared by the reaction of $[(CH_3)_2B(NH_3)_2][H_2B(CH_3)_2]$ with HX. Ammonia in the cation $[(CH_3)_2B(NH_3)_2^+]$ can be replaced by ethylenediamine to give corresponding salts of the stable chelate cation $[(CH_3)_2B(en)^+]$. Salts of the anion $[H_2B(CH_3)_2^-]$ are also reported. The reaction of ammonia with ethereal solutions of $(CH_3)_2BH_2(CH_3)_2$ gives the nonelectrolyte $(CH_3)_2BHNH_3$. Factors governing stability and bridge cleavage are considered.

In their pioneer investigations of the reactions between the methylboranes and ammonia, Schlesinger, Horvitz, and Burg[1] found that tetramethyldiborane reacts with ammonia at −78° to give a white solid of empirical composition $[(CH_3)_2HB(NH_3)]_n$ which decomposes rapidly above 10°. Neither the true molecular formula nor the structure of this product has ever been established.

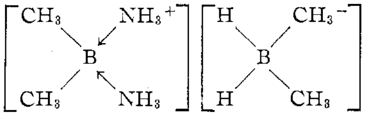
If one extrapolates the chemistry of diborane and ammonia to tetramethyldiborane and ammonia, a nonsymmetrical cleavage of the double bridge bonds would be anticipated.



On the other hand, the expected cation with two methyl groups and two ammonia molecules around a single boron atom might exhibit such serious crowding of groups that a symmetrical cleavage product, $(CH_3)_2HBNH_3$, could well be formed preferentially. In the study described herein, the system tetramethyldiborane–ammonia has been examined under a variety of conditions. A close parallel to the corresponding diborane–ammonia system has been found, indicating that steric factors are not definitive in determining the nature of the product.

The existence of stable dihydridoboron(III) cations, $[H_2B(NR_3)_2^+]$, containing large bases such as tertiary amines, phosphines, arsines, and dialkyl sulfides was described by Miller and Muetterties,[2] indicating relatively high stability for these ions despite crowding around the boron. Further, the ions $[(C_6H_5)_2B(bipy)^+]$, $[C_6H_5BH(C_5H_5)_2^+]$, and $[I_2B(py)_2^+]$ have been reported.[3–5] Cations of the form $[R_2B(NH_3)_2^+]$ were mentioned by Nöth[6a] and by Mikhailov[6b] and coworkers, but no definitive evidence for, or characterization of, the methylammonia ions was given in the earlier publications. The early study of Burg and Campbell[7] on the reaction of tetramethyldiborane with sodium in liquid ammonia at −78° provides no real basis for deciding on the form of the cleavage process in reactions of $(CH_3)_4B_2H_2$ with ammonia. Salts of the anion $[H_2B(CH_3)_2^-]$ have not been characterized previously.

The Compound $[(CH_3)_2B(NH_3)_2][H_2B(CH_3)_2]$.—The direct reaction of tetramethyldiborane and ammonia at −78° is analogous to the comparable diborane reaction in that the product is the nonsymmetrical cleavage product



The saltlike nature of the product was confirmed by conductivity measurements in liquid ammonia. The conductance value obtained (99 mhos) is comparable to that expected for a two-ion salt such as KCl under similar conditions.[8] Solid $[(CH_3)_2B(NH_3)_2^+][H_2B(CH_3)_2^-]$ melts with decomposition at room temperature to give H_2 and $(CH_3)_2BNH_2$ (see also ref 1). Since it is well known that the stability of boron compounds is strongly dependent upon purity, a special effort was made to prepare high-purity $(CH_3)_4B_2H_2 \cdot 2NH_3$. Despite all such efforts, no sample stable at 25° was ever prepared.

Salts Containing the Cations $[(CH_3)_2B(NH_3)_2^+]$ and $[(CH_3)_2B(en^+)]$.—Reaction of an excess of the diam-

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[1] H. J. Schlesinger, L. Horvitz, and A. A. Burg, *J. Am. Chem. Soc.*, **58**, 409 (1936).

[2] N. E. Miller and E. L. Muetterties, *ibid.*, **86**, 1033 (1964).

[3] J. M. Davidson and C. M. French, *Chem. Ind.* (London), 350 (1959).

[4] J. E. Douglass, *J. Am. Chem. Soc.*, **84**, 212 (1962); **86**, 5431 (1964).

[5] E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **15**, 182 (1960).

[6] (a) H. Nöth, *Angew. Chem.*, **72**, 638 (1960); H. Nöth and H. Beyer, *ibid.*, **71**, 383 (1959); (b) B. M. Mikhailov and T. K. Kosminskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk.*, 1703 (1963).

[7] A. B. Burg and G. W. Campbell, *J. Am. Chem. Soc.*, **74**, 3744 (1952).

[8] V. F. Hnizda and C. A. Kraus, *ibid.*, **71**, 1565 (1949); see Experimental Section.

moniate of tetramethyldiborane with HCl or HBr in diethyl ether at −78° can be represented by

$$[(CH_3)_2B(NH_3)_2{}^+][H_2B(CH_3)_2{}^-] + HX \xrightarrow{(C_2H_5)_2O} H_2 + [(CH_3)_2B(NH_3)_2{}^+]X^- + (C_2H_5)_2OHB(CH_3)_2$$

The salts formed, $[(CH_3)_2B(NH_3)_2]X$ where X = Cl or Br, were stable at room temperature despite expected crowding around the boron.

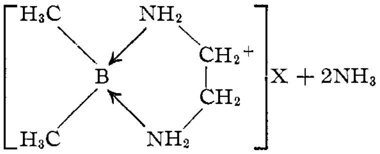
A sample of $[(CH_3)_2B(NH_3)_2]Br$ hydrolyzes completely in water solution (in less than 2 hr) to give NH_4Br as the only recoverable solid product. The presumed reaction is

$$[(CH_3)_2B(NH_3)_2]Br + H_2O \longrightarrow (CH_3)_2BOH + NH_4Br + NH_3$$

Similarly, treatment of $[(CH_3)_2B(NH_3)_2]Br$ with hydrogen at 120° for 6 hr at a pressure of 3200 psi gave NH_4Br as the only solid product rather than the desired $[H_2B(NH_3)_2]Br$.

In an earlier communication[9] from this laboratory the reaction between $[(CH_3)_2Ga(NH_3)_2]X$ and ethylenediamine to give $[(CH_3)_2Ga(en)]X$ was reported. In an exactly analogous reaction the compound $[(CH_3)_2B(en)]X$ has been prepared

$$[(CH_3)_2B(NH_3)_2]X + H_2NCH_2CH_2NH_2 \longrightarrow$$



The chloride and bromide salts showed no decomposition over a 24-hr period at a temperature slightly above 50°.

A comparable displacement reaction involving ethylenediamine and the dihydridodiammineboron(III) cation, $[H_2B(NH_3)_2{}^+]$, instead of the dimethyldiammineboron(III) cation, $[(CH_3)_2B(NH_3)_2{}^+]$, was also tried. When an excess of ethylenediamine was used with $[H_2B(NH_3)_2{}^+][BH_4{}^-]$, the expected amount of ammonia was displaced, but difficulty in removal of excess ethylenediamine prevented complete characterization of the product. Addition of ethylenediamine to a liquid ammonia solution of $[H_2B(NH_3)_2]X$ gave a mixture of $[H_2B(NH_3)_2]X$ and $[H_2B(en)]X$.

Salts Containing the Anion $[H_2B(CH_3)_2{}^-]$.—Burg and Campbell[7] reported the synthesis of $Na_2[(CH_3)_2BH]$ by the reaction of tetramethyldiborane with excess sodium in liquid ammonia, but the conditions of their study were clearly designed to promote a direct reaction between sodium and tetramethyldiborane and to prevent the initial formation of $[(CH_3)_2B(NH_3)_2{}^+]$ prior to the reaction. In the study described herein the dimethylammineboron(III) cation was prepared, *then* allowed to react with sodium in liquid ammonia. The reaction was

$$[(CH_3)_2B(NH_3)_2{}^+][H_2B(CH_3)_2{}^-] + Na \xrightarrow[-78°]{NH_3(l)} {}^1/_2H_2 + Na^+[H_2B(CH_3)_2{}^-] + [(CH_3)_2BNH_2] + NH_3$$

The products isolated were H_2, $(CH_3)_2BNH_2$, NH_3, and $Na[H_2B(CH_3)_2]\cdot x$(solvent). Some tendency for the latter salt to decompose to give NaH and $[HB(CH_3)_2]_n$ was noted. As expected, the decomposition is promoted by conditions which remove $[HB(CH_3)_2]_2$.

In order to determine whether or not the anion was unstable in the absence of a proton donor, an attempt was made to synthesize it in ammonia, then displace the solvate ammonia with *dimethyl* ether at −45° (Figure 1B). The solid resulting after solvent removal at 25° had a composition corresponding to $Na[H_2B(CH_3)_2]\cdot 0.5(CH_3)_2O$ and appeared to be stable against spontaneous decomposition at room temperature. On the other hand, an attempt to synthesize $Na[H_2B(CH_3)_2]$ directly in *diethyl* ether gave evidence for the complex anion in solution, but it decomposed when the solvent was removed. The reaction is summarized by

$$NaH + {}^1/_2H_2B_2(CH_3)_4 \xrightarrow[25°]{(C_2H_5)_2O} Na[H_2B(CH_3)_2](soln)$$

Evidence for formation of the expected dimethylborohydride ion was provided by the dissolving of NaH in ether solution containing the tetramethyldiborane. NaH is normally insoluble in ether. On the other hand, when an attempt was made to remove the ether and isolate the solid, amorphous and reactive NaH was produced. The other product was probably $(CH_3)_2HBO(C_2H_5)_2$. It is significant that the decomposition of the anion gives no hydrogen in the absence of a proton door, suggesting that decomposition of the diammoniate of tetramethyldiborane is a result of the interaction of protonic hydrogens on the cation with the readily freed hydridic hydrogen on the $[H_2B(CH_3)_2{}^-]$ anion. These facts suggest that a compound of the form $\{H_2B[N(CH_3)_3]_2\}[H_2B(CH_3)_2]$ might well be stable enough to handle in normal fashion.

The Reaction of Tetramethyldiborane with Ammonia in Ethers. The Synthesis of $(CH_3)_2HBNH_3$. If highly purified $(CH_3)_4H_2B_2$ is dissolved in pure dimethyl ether at −78° and the system is then treated with ammonia, the resulting process can be represented by

$$(CH_3)_2BH_2B(CH_3)_2 + 2(CH_3)_2O \xrightarrow[-78°]{(CH_3)_2O} 2(CH_3)_2OBH(CH_3)_2$$

$$(CH_3)_2OBH(CH_3)_2 + NH_3 \xrightarrow[-78°]{(CH_3)_2O} H_3NBH(CH_3)_2 + (CH_3)_2O$$

Similar reactions occur when either diethyl ether or tetrahydrofuran is used. The compound $H_3NBH(CH_3)_2$ is a white solid which can be sublimed under vacuum at about 20° but which melts with decomposition near 25°. It is essentially a nonelectrolyte in liquid ammonia (4 mhos cm^{-1}).

Experimental Section

Materials. (1) **Tetramethyldiborane.**—This compound was prepared by a high-pressure variation of the method of Schlesinger and Walker.[10] A 45-g sample of $B(CH_3)_3$ and a 5.5-g sample of B_2H_6 were placed in a 500-cc stainless steel tank and kept at 25° for 1 week. Fractionation of the mixture in the vacuum system gave 40 g of $(CH_3)_2BH_2B(CH_3)_2$ (80% yield based on B_2H_6). The vapor pressure was 48 mm at 0°.

(2) **Other Reagents.**—NH_3 was dried over sodium and dis-

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(9) D. F. Shriver and R. W. Parry, *Inorg. Chem.*, **1**, 835 (1962).

(10) H. J. Schlesinger and A. O. Walker, Jr., *J. Am. Chem. Soc.*, **57**, 621 (1935).

tilled in the vacuum line. Reagent grade dimethyl ether, diethyl ether, and tetrahydrofuran were distilled from CaH_2 in the vacuum line. Commercial NaH (Metal Hydrides) was purified by leaching with liquid ammonia in the vacuum system. Ethylenediamine purified as described elsewhere[9] was used. All other reagents were reagent grade of highest available purity.

General Procedures. (1) **Conventional Procedures.**—Standard vacuum line apparatus and techniques were employed. Infrared absorption spectra were obtained with a Perkin-Elmer Model 21 spectrometer. X-Ray powder patterns were taken with a North American Phillips Corp. X-ray diffraction unit equipped with an 11.46-cm diameter camera; nickel-filtered copper Kα radiation was employed.

(2) **Low-Temperature Conductivity Studies.**—The conductivity cell was made and calibrated by D. H. Campbell in this laboratory. It was a simplified version of the unit described by Hnizda and Kraus.[8] The tubular cell body was made from 22-mm glass tubing and was 154 mm long. The upper end was a 19/38 ₸ joint which permitted attachment of the cell to the vacuum line. Lightly platinized platinum electrodes, each about 1 cm^2 in area, were mounted rigidly about 3 mm apart. Glass bead spacers were used. The electrodes were spot welded to 22-gauge platinum wire which protruded about 5 mm from the end of the 6-mm glass tubes; the end of each 6-mm tube contained a metal-to-glass seal similar to those described by Hnizda and Kraus.[8] Each 6-mm tube, about 75 mm long, was bent and ring sealed through the side of the cell body at a point about 100 mm from the bottom of the tube. These 6-mm tubes provided a path for the 22-gauge platinum wire leads. The cell could be cooled repeatedly in liquid nitrogen without leakage. The cell constant (0.1840 cm^{-1}) was determined by comparison with a cell having a known constant. Stirring of the solution was carried out with a small Teflon-coated magnetic stirring bar. Slush baths were used for temperature control. The volume of the liquid ammonia was measured in a graduated tube connected to the vacuum system. A direct reading ac bridge, equipped with a Wagner earthing device to reduce errors caused by capacitance coupling, was used for resistance measurements. A comparison of conductivity measurements made in this cell on potassium chloride–liquid ammonia solutions with the precision literature values[8] indicated that our equivalent conductance values were in error by *less than* 5%.

The Synthesis and Characterization of $[(CH_3)_2B(NH_3)_2][H_2B(CH_3)_2]$. The Reaction of Tetramethyldiborane and Ammonia in the Absence of Solvent.—A 1.93-mmole sample of pure $(CH_3)_2BH_2(CH_3)_2$ was condensed into a reaction tube (25-mm diameter), then the tube was thermostated at −78°. Since some decomposition of $(CH_3)_2BH_2(CH_3)_2$ can occur on distillation, 0.40 mmole of $(CH_3)_2BH_2(CH_3)_2$ was pumped out leaving 1.53 mmoles of *very pure* tetramethyldiborane in the apparatus. [Any decomposition products are more volatile at −78° than the pure $(CH_3)_2BH_2B(CH_3)_2$.] A 25-mmole sample of ammonia was added and allowed to melt, and the reaction tube was held at −78° for 2 hr. Excess ammonia was then removed by continuous pumping at −78° for 38 hr (most of the excess NH_3 was removed after 16 hr) followed by pumping at −45° for 2 hr. The white solid product remaining, $[(CH_3)_2B(NH_3)_2][H_2B(CH_3)_2]$, began to lose H_2 at 0° and melted slightly below 25°. It decomposed completely in 1 hr at 25° to give H_2 (identified by vapor density) and $(CH_3)_2BNH_2$ (identified by vapor density, vapor pressure,[10,11] and its infrared spectrum[12]). Even though the initial ratio of moles of NH_3 to moles of $(CH_3)_2BH_2B(CH_3)_2$ was varied from 0.80 to 300 and the reaction time at −78° varied from 2 to 6 hr, the solid product always had a composition of $(CH_3)_2BH_2B(CH_3)_2 \cdot 2NH_3$. It always decomposed completely at 25° to give $(CH_3)_2BNH_2$ and H_2. If all of the excess ammonia were not removed by pumping at temperatures of −45° and below, the excess NH_3 would be recovered unchanged in the products of decomposition.

Conductivity measurements were made using the previously described apparatus. In a typical run, a sample of ammonia (11.5 ml of liquid measured at −35° and with a measured conductivity of less than 10^{-6} mho) was distilled directly onto a purified sample of $(CH_3)_4B_2H_2$ (0.53 mmole). The cell was allowed to stand for 4 hr at −78° and was then warmed to −35° where conductivity measurements were made. This solution containing 0.046 mole of $[(CH_3)_2B(NH_3)_2][H_2B(CH_3)_2]$/l. of ammonia had an equivalent conductance of 95 mhos cm^{-1}. In a second run, excess ammonia was removed at −78° and at −45° producing a solid product which was then redissolved in fresh, purified ammonia. The equivalent conductance of this solution measured at −35° was 99 mhos cm^{-1} for a solution containing 0.037 mole/l. of ammonia. KCl at a concentration of 0.01307 mole/l. has a reported value of 109 mhos cm^{-1} while KCl at a concentration of 0.01651 mole/l. has a value of 103 mhos cm^{-1}.[8] KI at a concentration of 0.0158 mole/l. has an equivalent conductance of 186 mhos cm^{-1}.[8] Reactions of the type described below completed the characterization of the product.

The Preparation and Characterization of $[(CH_3)_2B(NH_3)_2]Br$ and $[(CH_3)_2B(NH_3)_2]Cl$.—In a typical experiment a 1.15-mmole sample of highly purified $(CH_3)_2BH_2B(CH_3)_2$ contained in the reaction tube of a vacuum filtration apparatus[13] was converted to $[(CH_3)_2B(NH_3)_2][H_2B(CH_3)_2]$ by methods described above. A 10-ml sample of dry diethyl ether and a 1.00-mmole sample of dry HBr were then added to the reaction tube. The system was held at −78° for 6 hr during which time a 1.01-mmole sample of H_2 was evolved and a white precipitate formed. The precipitate was filtered off in the vacuum filtration system and washed several times with ether. The yield, based on HBr, was 75%. Additional product contained in the solvent was not recovered.

Anal. Calcd for $[(CH_3)_2B(NH_3)_2]Br$: B, 6.98; N, 18.1; Br, 51.7; C, 15.5; H, 7.75; mol wt, 154. Found: B, 7.05, 7.08; N, 17.9, 18.1; Br, 51.4; C, 15.4, 15.3; H, 7.18, 7.22. The molecular weight by vapor pressure depression of liquid ammonia solution[14] was 164 ± 10. Values were measured over a concentration range of 0.5–4.0 *m* and were then extrapolated to infinite dilution. The X-ray powder pattern gave *d* values as follows: 7.25 (w), 6.19 (vs, br), 5.12 (s), 4.38 (s), 4.24 (vvs), 4.07 (m), 3.94 (s), 3.72 (w), 3.53 (s), 3.38 (s), 3.03 (s), 2.95 (m), 2.88 (s), 2.71 (m), 2.56 (m), 2.50 (w), 2.45 (w), 2.41 (w), 2.36 (w), 2.17 (w, br), 2.12 (w, br), 1.97 (w), 1.92 (w), 1.88 (w), 1.81 (m) [w = weak, m = medium, s = strong, v = very, br = broad]. The infrared spectrum taken in KBr pellets using NaCl optics showed a broad, strong band containing the C–H and N–H stretching modes with a peak at 2940 cm^{-1} and extending over the range 2800–3300 cm^{-1}. It showed no B–H stretching frequencies but showed additional principal peaks (cm^{-1}) as follows: 1600 (w), 1480 (w, sh), 1410 (vs), 1305 (m), 1190 (m, w), 1080 (m), 1065 (m), 1010 (w, sh). A more detailed assignment of the infrared spectrum is being carried out by R. C. Taylor and his associates.

The chloride salt, $[(CH_3)_2B(NH_3)_2]Cl$, was prepared by a method identical with that used for the preparation of the bromide salt except that HCl was substituted for HBr.

Anal. Calcd for $[(CH_3)_2B(NH_3)_2]Cl$: B, 9.80; N, 25.4; Cl, 32.1; C, 21.8; H, 11.0. Found: B, 9.20; N, 25.4; Cl, 32.1; C, 21.0; H, 11.2. The X-ray powder pattern gave the following interplanar spacings: 6.91 (w), 6.23 (vvs), 5.67 (m), 5.21 (s), 4.74 (w), 4.02 (vw), 3.86 (vw), 3.76 (vw), 3.71 (s), 3.63 (vvs), 3.37 (m), 3.26 (vvw), 3.11 (vw), 3.03 (vw), 2.95 (s), 2.81 (vw), 2.74 (vvs), 2.60 (m), 2.44 (w), 2.37 (w), 2.34 (vw), 2.26 (vw), 2.22 (m), 2.20 (w), 2.17 (w). The infrared spectrum was essentially the same as that of the bromide salt, as would be expected.

The Preparation of the Salts $[(CH_3)_2BNH_2CH_2CH_2NH_2^+]X^-$.—A 340-mg sample of $[(CH_3)_2B(NH_3)_2]Cl$ was placed in a tube attached to a vacuum filtration device. A 5-ml sample of dry

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(11) E. Wiberg, K. Hertwig, and A. Boltz, *Z. Anorg. Allgem. Chem.*, **256**, 177 (1948).

(12) H. J. Becher, *Spectrochim. Acta*, **19**, 575 (1963).

(13) R. W. Parry, D. R. Schultz, and P. R. Girardot, *J. Am. Chem. Soc.*, **80**, 2 (1958).

(14) R. W. Parry, G. Kodama, and D. R. Schultz, *ibid.*, **80**, 24 (1958).

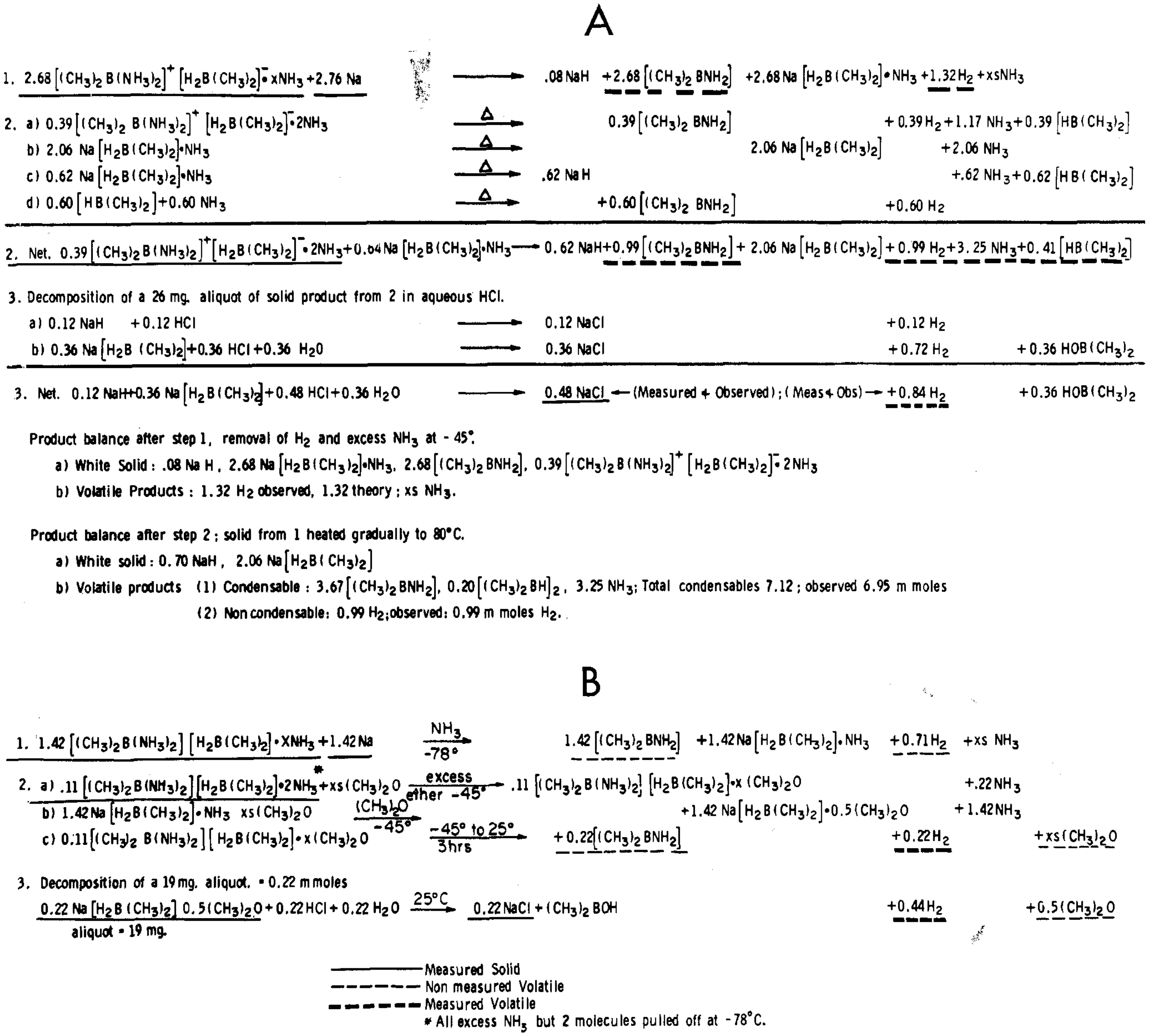
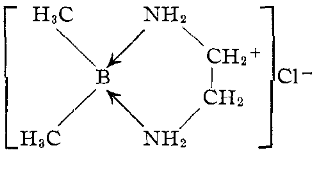


Figure 1.

purified ethylenediamine was distilled into the reaction tube and the system held for 1 hr at room temperature. Ammonia equal to 97% of that expected from its complete displacement was separated and identified by vapor pressure and gas density. Excess ethylenediamine was difficult to remove from the reaction residue. Most of the excess was removed by pumping on the reaction system for 24 hr while the residue was heated up to 50°. The residue was then transferred to the glass frit and washed with several portions of dry diethyl ether. The yield of



was quantitative. The bromide salt was prepared in an identical manner using the bromide–ammonia salt as the starting material.

Anal. Calcd for $[(CH_3)_2BNH_2CH_2CH_2NH_3]Cl$: B, 7.93; N, 20.51; Cl, 36.0; C, 35.2; H, 10.3. Found: B, 7.66; N, 20.4; Cl, 34.8; N, 20.4; C, 34.8; H, 10.0. Interplanar spacings from X-ray powder data are: 6.86 (vs), 6.44 (vs), 5.44 (s), 5.25 (m), 5.08 (vs), 4.77 (w), 4.30 (w), 4.10 (w), 3.93 (vs), 3.86 (m), 3.81 (m), 3.58 (m), 3.45 (m), 3.36 (s), 3.21 (w), 3.13 (w), 3.06 (w), 2.81 (s), 2.74 (s), 2.64 (s), 2.57 (m), 2.53 (w), 2.47 (w) 2.41 (m), 2.35 (w). The infrared spectrum was quite complex· all of the expected absorptions were present; the stronge- peaks (cm^{-1}) follow: 3200 (s), 2940 (vs), 1600 (m), 1480 (m) 1410 (s), 1320 (vs), 1305 (vs), 1255 (m), 1190 (s), 1080 (vs) 1065 (vs), 1010 (vs), 820 (m), 685 (w).

Anal. Calcd for $[(CH_3)_2BNH_2CH_2CH_2NH_4]Br$: Br, 44.2. Found: Br, 43.9. Interplanar spacings from X-ray powder data are: 6.89 (vs), 6.49 (vvs), 5.72 (m), 5.11 (vs), 4.82 (m), 4.40 (m), 4.21 (w, br), 4.07 (vvs), 3.89 (vs), 3.79 (w), 3.66 (s), 3.57 (w), 3.47 (w), 3.39 (s), 3.26 (m), 3.18 (m), 3.06 (m), 2.85 (s), 2.72 (s), 2.56 (s), 2.49 (w, br), 2.42 (m), 2.32 (w, br), 2.23 (w), 2.18 (w, br). The infrared spectrum was very close to that of the chloride salt.

The Synthesis of Salts Containing the Anion $[H_2B(CH_3)_2^-]$. The Reaction of $[(CH_3)_2B(NH_3)_2][H_2B(CH_3)_2]$ with Sodium in Liquid Ammonia.—In a typical run a 3.07-mmole sample of $[(CH_3)_2B(NH_3)_2][H_2B(CH_3)_2]$ was prepared in a reaction tube containing a glass ampoule of sodium (2.76 mg-atoms). Liquid NH_3 (10 ml) was added, the sodium ampoule was broken, and the tube was allowed to stand at −45° for 2 hr. A clear solution resulted and a volume of hydrogen equivalent to 1.32 mmoles was evolved. Excess NH_3 was removed by pumping first at −78° for 16 hr, then at −45° for 3 hr. A white solid remained in the reaction tube. When allowed to warm to room temperature, the solid began to evolve H_2; on heating to 80° it evolved 6.95 mmoles of condensable gas and 0.99 mmole of H_2. A white, extremely reactive solid remained in the tube. A 26-mg sample of this solid was treated with 6 M HCl; 0.83 mmole of H_2 and 0.48 mmole of NaCl were identified.

The foregoing data which are representative of several runs can be interpreted in quantitative detail as shown in Figure 1A.

In a second run evidence for $Na[H_2B(CH_3)_2]\cdot$solvent as a stable solid at room temperature was obtained. A 1.54-mmole sample of $[(CH_3)_2B(NH_3)_2^+][H_2B(CH_3)_2^-]$ was allowed to react with 1.57 mg-atoms of Na in liquid ammonia at −45°. After removing the H_2 (0.71 mmole) and excess NH_3 as before, the solid which remained was dissolved in 5 ml of dry dimethyl ether, then the dimethyl ether was pumped off at −45°. The solid was then treated with another portion of dimethyl ether and the ether was removed as before. On warming to room temperature the solid evolved 0.21 mmole of H_2 over a period of 3 hr. After volatiles were removed, a 19-mg sample of the solid was treated with 6 M aqueous HCl. A 0.44-mmole sample of H_2 was evolved and 0.22 mmole of NaCl remained. The foregoing data may be interpreted in quantitative detail as shown in Figure 1B.

An Attempt to Synthesize $Na[H_2B(CH_3)_2]$ Directly. The Reaction of NaH and $[HB(CH_3)_2]_2$ in Ether.—In a typical experiment a 10.8-mg sample of NaH (0.45 mmole) was placed in a reaction tube on the vacuum line, a 1.50-mmole sample of $(CH_3)_4B_2H_2$ and a 2.0-mmole quantity of diethyl ether were distilled into the tube, and it was allowed to warm to room temperature. After 1 hr all but a trace of the normally insoluble NaH was dissolved in the ether, indicating complex formation. When the volatile materials were pumped off, a 3.50-mmole sample of volatile material was recovered (1.50 mmoles of $(CH_3)_4B_2H_2$ and 2.0 mmoles of $(C_2H_5)_2O$). The solid remaining showed only diffuse lines of NaH. The formation process is clearly reversible under the conditions used.

The Synthesis of $(CH_3)_2BHNH_3$. The Reaction of Tetramethyldiborane and Ammonia in Ethereal Solvents.—A 1.66-mmole sample of pure $(CH_3)_2BH_2B(CH_3)_2$ was treated in a reaction tube on the vacuum line with 13.5 mmoles of dry $(CH_3)_2O$ for 1 hr, then a 13.5 mmole sample of NH_3 was added and the system was allowed to stand for 2 hr more at −78°. Excess ammonia and solvent were removed by pumping at −78° for 12 hr, at −45° for 3 hr, and finally at 0° for 1 hr. The product decomposed completely in 1 hr forming 3.24 mmoles of H_2 and 3.21 mmoles of $(CH_3)_2BNH_2$. Similar results were obtained using diethyl ether and tetrahydrofuran as solvents. In no case was a material obtained which was stable at room temperature.

Conductivity measurements were carried out by preparing the solute as above in the conductivity cell, removing ether and excess ammonia at −45°, then adding fresh, pure ammonia and measuring the conductivity at −35°. The equivalent conductance was 4 mhos in a concentration of 0.050 mole of $(CH_3)_2BH_2NH_3$/l. of NH_3. The solid is almost a nonelectrolyte, supporting the molecular formula.

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Reactions of the Metallic Sodium Surface with Atmospheric Gases[1]

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Sodium metal surfaces, prepared by condensation of the metal under vacuum, have been exposed to water vapor, dried oxygen, moist CO_2, and dried and moist laboratory air at room temperature and at pressures between 10^{-3} torr and 1 atm. The surfaces were examined using the electron diffraction technique and Na_2O, NaOH, and Na_2CO_3 identified as the only initial reaction products. Oxygen was found to react with the metal surface to form Na_2O directly, and higher oxides of sodium did not appear under any of the reaction conditions.

I. Introduction

The reactions of metallic sodium with atmospheric gases have been observed since the discovery of the metal, and the literature concerned with these reactions is so extensive that only a few of the relevant papers are mentioned here.[3] However, the initial reaction products have not been established, and the identification of the initial reaction products on the metal surface exposed to reactive gas may help to indicate the mechanism by which the final products are formed.

The reaction of sodium with dry oxygen was discussed by Cathcart, Hall, and Smith,[4] who postulated that the initial reaction product of the reaction is Na_2O but could not exclude the possibility that Na_2O_2 is formed at the oxide–oxygen interface. Their experiments, using carefully dried oxygen, showed that the reaction of the surface almost stopped after the formation of a layer of surface oxide calculated to be 1500 A thick. Trace amounts of nitrogen are said to affect the reaction.[5] Reactions of the surface with other atmospheric gases have not been studied under controlled conditions.

Electron diffraction investigations have been made of the reaction products of sodium by Yamaguchi.[6]

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(1) This work is taken from a thesis presented by L. McKnight to the Graduate School of the University of Michigan in partial fulfillment of the requirements of the Ph.D. degree, March 1961.

(2) Bell Telephone Laboratories, Inc., Murray Hill, N. J.

(3) A complete review of the properties and reactions of the metal has been published by M. Sittig, "Sodium, Its Manufacture, Properties and Uses," Reinhold Publishing Corp., New York, N. Y., 1956.

(4) J. V. Cathcart, L. L. Hall, and G. P. Smith, *Acta Met.*, **5**, 245 (1957).

(5) J. W. Moyer and W. A. Ruggles, *J. Opt. Soc. Am.*, **44**, 86 (1954).

(6) S. Yamaguchi, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **37**, 424 (1940); **38**, 106 (1940).