$$S^\circ_{298}[N_2H_4 \cdot H_2O(g)] = 57.4 + 45.1 - 39.1 = 63.4 \text{ cal./°/mole} \quad (9)$$

The heat of formation of hydrazine hydrate can be obtained from the heats of formation of $N_2H_4(g)$,[7] and from the heat of dissociation. The value obtained is

$$\Delta H_f^{298}[N_2H_4 \cdot H_2O(g)] = 22.75 - 57.80 - 13.97 = -49.02 \text{ kcal./mole} \quad (10)$$

V. Discussion

An analysis of the pressure–temperature relation of a hydrazine and water gas mixture shows that a hydration reaction occurs in which the hydrate is in equilibrium with its constituents. The facts that the slope of the pressure curve is a uniform and monotonic function of the temperature and that the log K is linear with the reciprocal temperature are offered as evidence for the existence of only one hydrate, the monohydrate, in the temperature and pressure range $5 < t < 90°$ and $2 < p < 10$ mm. This conclusion is in agreement with that drawn by Semishin[2] for hydrazine hydrate in the liquid phase as a result of his melting-point measurements.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

A New Boron Base, $Na_2HB(CH_3)_2$

BY ANTON B. BURG AND GEORGE W. CAMPBELL, JR.[1]

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Upon contact with sodium in liquid ammonia at −78°, $(CH_3)_4B_2H_2$ is split equally into $(CH_3)_2BH \cdot NH_3$ (recognized by its later conversion to volatile $(CH_3)_2BNH_2 + H_2$) and the new salt $Na_2HB(CH_3)_2$. This reaction can be made quantitative because the ammoniation of $(CH_3)_4B_2H_2$, to form a solute which reacts with sodium in liquid ammonia to liberate one equivalent of H_2, is so much slower than the corresponding reaction of B_2H_6 that it does not compete. The salt $Na_2HB(CH_3)_2$ is stable as a white solid *in vacuo* even at 90°. It hydrolyzes rapidly and quantitatively to $(CH_3)_2BOH$, $2H_2$ and 2NaOH. Dissolved in liquid ammonia, it is yellow, diamagnetic, well ionized, and unstable relative to disproportionation—a reaction promoted by $(CH_3)_4B_2H_2$. In liquid methyl ether it passes a filter but is highly aggregated—possibly colloidal. The $HB(CH_3)_2^=$ ion has high base-strength, expected because of a pair of unshared electrons on B, and demonstrated by the addition of $B(CH_3)_3$ in liquid ammonia to form a yellow solution of $Na_2HB(CH_3)_2 \cdot B(CH_3)_3$. This is stable *in vacuo* at 100° and probably is B–B bonded. Addition in the same ratio occurs also in liquid methyl ether, but the product loses the $B(CH_3)_3$ *in vacuo* at 25°. Here it is probable that $NaHB(CH_3)_3$ is formed (but easily converted to trimethylboron and sodium hydride), in view of other evidence that the reactions of $Na_2HB(CH_3)_2$ in methyl ether are hydridic—thus SiH_3Cl is converted to SiH_4. The fate of the $B(CH_3)_2^-$ residue of such reactions is uncertain.

Tetramethyldiborane[2] reacts with ammonia at −78°, presumably forming $NH_4(CH_3)_2BH(NH_2)BH(CH_3)_2$, but the process is far slower than the analogous reaction of diborane,[3–5] for the $(CH_3)_4B_2H_2$–NH_3 mixture must remain for at least 90 minutes at −78° before one can demonstrate, by introducing sodium and measuring the resulting hydrogen, the availability of one ammonium ion per mole. If very little time for ammoniation is allowed, as when tetramethyldiborane is brought immediately into contact with a melting solution of sodium in liquid ammonia, the solution turns green (or yellow if the sodium is not in excess) and no hydrogen is obtained even after many hours at −78°. The B-content of the tetramethyldiborane now can be recovered as equimolar proportions of two products, one of which decomposes at room temperature to form one mole each of hydrogen and the volatile $(CH_3)_2BNH_2$[6] (ammonolysis of a dimethylborine group) and the other of which is easily hydrolyzed to yield only hydrogen, $(CH_3)_2BOH$,[2] and NaOH in proportions indicating the formula $Na_2HB(CH_3)_2$.

The conditions for such a result are very specific. The sodium must be used in excess and the removal of the solvent ammonia (first by vacuum sublimation at −78° or lower) must be completed by successive treatments with pure trimethylamine until no more emerges at −50°. Then after the removal of hydrogen and $(CH_3)_2BNH_2$ *in vacuo* at room temperature, the non-volatile product is extracted from the excess sodium by liquid methyl ether at −40°. Attempts to simplify the process by using just two gram atoms of sodium per mole of tetramethyldiborane, or by omitting the use of trimethylamine to eliminate all but one mole of ammonia, lead to solid products containing more than half of the boron, part of which comes off as $B(CH_3)_3$ upon hydrolysis.

The Constitution of $Na_2HB(CH_3)_2$ in Terms of Its Chemical Behavior.—Cryoscopic and conductance measurements on the liquid ammonia solution of the product empirically designated as $Na_2HB(CH_3)_2$ clearly indicate the monomeric but fairly well ionized salt implied by the formula as written. However, in liquid methyl ether this salt is highly aggregated, for it does not appreciably lower the vapor tension of the solvent. In this possibly colloidal solution it behaves as a source of hydride, reacting mole-for-mole with SiH_3Cl to yield an amount of SiH_4 corresponding to all of the non-C–H hydrogen. The high availability of hydride from $Na_2HB(CH_3)_2$ (however it may be

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(1) Abstracted from a dissertation presented by George W. Campbell, Jr., to the Faculty of the Department of Chemistry, University of Southern California, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, February, 1951. Presented in substance at the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951.

(2) First prepared by H. I. Schlesinger and A. O. Walker, THIS JOURNAL, **57**, 621 (1935).

(3) A. Stock and E. Pohland, *Ber.*, **59B**, 2213 (1926).

(4) H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **60**, 290 (1938).

(5) A. B. Burg, *ibid.*, **69**, 747 (1947).

(6) H. I. Schlesinger, L. Horvitz and A. B. Burg, *ibid.*, **58**, 409 (1936).

aggregated) can be understood by a comparison with borohydride. Since the replacement of H on B by CH_3 groups decreases the ability of the boron to hold bases,[7] a hydride ion should be more available from the $(CH_3)_2BH_2^-$ ion than from BH_4^-. Now if by some means a proton could be removed from the B in $(CH_3)_2BH_2^-$, the remaining unshared electron pair should tend more to repel the other B-linked hydrogen as hydride. This would be the situation in the $HB(CH_3)_2^{=}$ ion.

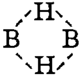
One may consider next the properties more directly attributable to the unshared electrons on the B atom of $HB(CH_3)_2^{=}$. By extrapolation from the isoelectronic series OH_3^+, NH_3, CH_3^-, it is evident that the hypothetical $BH_3^{=}$ ion should have a very high base strength, or ability to share electrons to form covalent bonds. Replacement of two H atoms by the base-enhancing CH_3 groups, to form $HB(CH_3)_2^{=}$, should mean extraordinary electron-donor powers.

Relevant to these ideas is the mole-for-mole reaction of $B(CH_3)_3$ with $Na_2HB(CH_3)_2$ in liquid ammonia (yellow in this solvent, and not rapidly changed at −78°) to form $Na_2HB(CH_3)_2{\cdot}B(CH_3)_3$ (also yellow in solution); after evaporation of the solvent this addition product proves to be completely stable *in vacuo* at 100°. It dissolves in methyl ether without residue, showing that NaH was not formed in the reaction. On the other hand, the colorless methyl ether solution of $Na_2HB(CH_3)_2$ receives $B(CH_3)_3$ at −78° to form a precipitate, also of the composition $Na_2HB(CH_3)_2{\cdot}B(CH_3)_3$; from this the $B(CH_3)_3$ escapes completely at 0 to 20° *in vacuo*. After the loss of the $B(CH_3)_3$ the residue is neither soluble in methyl ether nor capable of coloring liquid ammonia; hence although the composition still corresponds to $Na_2HB(CH_3)_2$, the original salt has been irreversibly disrupted.

The different products, having the same empirical formula $Na_2HB(CH_3)_2{\cdot}B(CH_3)_3$, are accountable in terms of two possible reactions. One would be the addition of $B(CH_3)_3$ to the electron-donor B atom of the $HB(CH_3)_2^{=}$ ion to form $Na_2HB_2(CH_3)_5$—disodium pentamethyldiborohydride—which could well be the first genuine case of a salt of the diborohydride type in which at least one B–H bond exists.[8] The other would be the removal of hydride from the $Na_2HB(CH_3)_2$ to form $NaHB(CH_3)_3$ and material empirically formulated as $NaB(CH_3)_2$.

Pertinent to the question of which solvent led to which product would be evidence indicating that one solvent exclusively favors boron–base reactions while the other permits only hydride reactivity. The differences of color and state of aggregation alone would hint at a sharp difference of chemical character, and the SiH_3Cl reaction certainly suggests that hydride reactions are characteristic of the methyl ether solution. One may argue further that such a salt as $NaHB(CH_3)_3$ should be very unstable, as the product of adding $B(CH_3)_3$ to $Na_2HB(CH_3)_2$ in methyl ether proved to be; actually a highly valid attempt to make $NaHB(CH_3)_3$, from sodium hydride and $B(CH_3)_3$ in methyl ether, was quite unsuccessful. Finally, it is noted that diborane adds to $Na_2HB(CH_3)_2$ in methyl ether, yielding products which are stable *in vacuo* at room temperature, and containing 1.4 BH_3 groups per mole of $Na_2HB(CH_3)_2$. If the BH_3 group were attached directly to B in the $HB(CH_3)_2^{=}$ ion, there would be no explanation of the absorption of 0.4 BH_3 beyond the 1:1 ratio. However, if hydride were removed to form $NaBH_4$, the remaining $B(CH_3)_2^-$ ions could hold BH_3 by means of their unshared electrons, or they could form ionic polymers, or both, amply accounting for the absorption of the extra diborane.

Thus it appears that in liquid ammonia the unshared electrons on boron are readily accessible for donor-bonding, whereas the manner of aggregation in methyl ether may well be such as to deny access to those electrons, while allowing hydride to be removed by various reagents.

Facts and Ideas Relevant to the Process of Formation of $Na_2HB(CH_3)_2$.—The addition of ammonia–sodium to tetramethyldiborane occurs most probably as an immediate cleavage of the  $B\overset{H}{\underset{H}{}}B$ bridge system by the combined action of electrons and ammonia. The initial presence of the $HB(CH_3)_2^{=}$ ion is indicated by the result of the addition of $(CH_3)_4B_2H_2$ and $B(CH_3)_3$ simultaneously to sodium in liquid ammonia: the previously mentioned stable salt $Na_2HB_2(CH_3)_5$ is formed quantitatively according to the equation

$$(CH_3)_4B_2H_2 + 2Na + NH_3 + B(CH_3)_3 \longrightarrow Na_2HB_2(CH_3)_5 + (CH_3)_2BH{\cdot}NH_3$$

This clean result is possible only because $B(CH_3)_3$ does not absorb electrons from sodium–ammonia, forming neither $B(CH_3)_3^{=}$ nor $B_2(CH_3)_6^{=}$ ions—a fact which in itself suggests that the addition of sodium–ammonia to $(CH_3)_4B_2H_2$ requires a mechanism available only to diborane-like compounds and not possible for ammoniated borine derivatives such as $(CH_3)_3B{\cdot}NH_3$, $(CH_3)_2BH{\cdot}NH_3$, or $NH_4(CH_3)_2BH(NH_2)BH(CH_3)_2$.

The alternative hypothesis that tetramethyldiborane first takes on two electrons to form the $(CH_3)_4B_2H_2^{=}$ ion, which later would be split by ammonia unsymmetrically to form $HB(CH_3)_2^{=}$ and $(CH_3)_2BH{\cdot}NH_3$, loses favor in view of the relatively high NH_3-solution-stability of the structurally similar $HB_2(CH_3)_5^{=}$ ion; furthermore, attempts to form the $(CH_3)_4B_2H_2^{=}$ ion, either by adding $(CH_3)_2BH$ groups (as tetramethyldiborane) to a known solution of $Na_2HB(CH_3)_2$ or by adding more than a half-molar proportion of $(CH_3)_4B_2H_2$ to sodium in liquid ammonia—methods parallel to the successful formation of $Na_2HB_2(CH_3)_5$—led to a quick fading of the yellow color, and the final product of a procedure similar to the isolation of $Na_2HB(CH_3)_2$ was a mixture which yielded a fair proportion of $B(CH_3)_3$ upon hydrolysis. Thus it appears that the $(CH_3)_4B_2H_2^{=}$ ion may well be unstable relative to disproportionation, and accordingly could not have played any important

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[7] H. I. Schlesinger, N. W. Flodin and A. B. Burg, THIS JOURNAL, 61, 1078 (1939).

[8] The supposed $Na_2B_2H_6$ of A. Stock and E. Pohland (ref. 3) was shown by J. S. Kaspar, L. V. McCarty and A. E. Newkirk, *ibid.*, 71, 2583 (1949), to contain sodium borohydride as a major component.

part in a reaction through which nearly pure $Na_2HB(CH_3)_2$ could be isolated. In any case special assumptions would be required to explain the formation of $HB_2(CH_3)_5^{=}$ ions by the simultaneous addition of $B(CH_3)_3$ and $(CH_3)_4B_2H_2$ to Na–NH_3 if $B(CH_3)_3$ were required to displace the stronger electron-acceptor $(CH_3)_2BH$ from an initially formed $(CH_3)_4B_2H_2^{=}$ ion.

The idea that the yellow color resulting from the Na–NH_3–$(CH_3)_4B_2H_2$ reaction might be due to odd electrons, as in a $(CH_3)_2BH^-$ radical-ion, was disposed of by measurements (done with the necessary aid of Dr. S. S. Dharmatti) showing the solution to be diamagnetic.

If the $HB(CH_3)_2^{=}$ ion and $(CH_3)_2BH{\cdot}NH_3$ really are present in a liquid ammonia solution with excess sodium at −78°, it becomes important to consider two questions: why the $(CH_3)_2BH{\cdot}NH_3$ does not react with sodium to form hydrogen as BH_3NH_3 apparently does,[4] and why $HB(CH_3)_2^{=}$ is not found to react with ammonia to form $H_2B(CH_3)_2^-$ and NH_2^- ions, in the manner of the carbon bases which are formed from certain substituted olefins with sodium in liquid ammonia.[9] The latter question no doubt is a matter of temperature and the availability of an adequate reaction mechanism, while the former may be answered in terms of the known reaction of $(CH_3)_3B{\cdot}NH_3$ with sodium in liquid ammonia. This reaction probably yields $NaNH_2{\cdot}B(CH_3)_3$, but it forms hydrogen so slowly at −33°[10] (as compared with the faster reaction of BH_3NH_3 at −78°)[4] as to indicate that the decrease of Lewis-acid strength by methylation of borine[7] leads to diminished proton availability from the complex-bonded ammonia. The ability of $(CH_3)_2BH{\cdot}NH_3$ to endure in ammonia–sodium at −78° thus would not be surprising. However, it is to be emphasized that the solution of $Na_2HB(CH_3)_2$ and $(CH_3)_2BH{\cdot}NH_3$, with excess sodium in liquid ammonia, changes character rapidly at temperatures much above −78°, so that a most careful procedure is necessary for the isolation of pure $Na_2HB(CH_3)_2$.

One may consider also the question why $(CH_3)_2BH{\cdot}NH_3$ and the $HB(CH_3)_2^{=}$ ion can be formed and continue to exist in equimolar proportions in the Na–NH_3 solution, without conversion of one into the other. If ammonia is too weakly basic to displace electrons from $HB(CH_3)_2^{=}$ to form $(CH_3)_2BH{\cdot}NH_3$ and solvated electrons, one might expect the reverse process—displacement of NH_3 from $(CH_3)_2BH{\cdot}NH_3$ by the available electrons, to form more $HB(CH_3)_2^{=}$ ions. Evidently one situation of the $(CH_3)_2BH$ group must be metastable relative to the other; and the equal formation of $HB(CH_3)_2^{=}$ and $(CH_3)_2BH{\cdot}NH_3$ must be due to a special mechanism permitted by the peculiar structure of diborane-like substances.

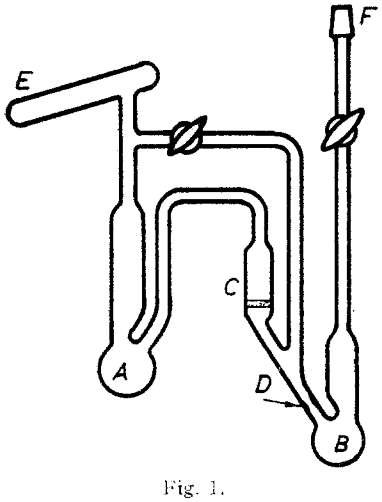

Fig. 1.

The prospect of such a reaction to form $BH_3^{=}$ ions and BH_3NH_3 from diborane itself is not very favorable, for the ammoniation of diborane is far more rapid than that of tetramethyldiborane. However, in an experiment performed by the senior author some fifteen years ago at the University of Chicago, it was observed that a Na–NH_3 solution at −78°, into which diborane was carried on a stream of ethane, yielded only 0.5 equivalent of H_2 per B_2H_6 during two hours at −78°. The reaction of BH_3NH_3 with Na–NH_3[4] is slow enough to permit the interpretation that much of the diborane added to ammonia–sodium to form $BH_3^{=}$ and BH_3NH_3, but the isolation of a salt such as Na_2BH_3 probably would prove unusually difficult.

Experimental Part

The Reaction of Ammoniated $(CH_3)_4B_2H_2$ with Sodium in Liquid Ammonia.—The reaction of ammoniated tetramethyldiborane with sodium in liquid ammonia was first studied by means of an apparatus and procedure as described by Schlesinger and Burg for ammoniated diborane.[4] Approximately 0.2 molar solutions of $(CH_3)_4B_2H_2$ in liquid ammonia, after standing 10 minutes at −78°, upon treatment with well over one equivalent of sodium, reacted to give only 0.17 to 0.20 equivalent of hydrogen per mole; another, having stood 15 minutes before the sodium treatment, gave 0.56 equiv.; others after 90–120 minutes, gave 0.95 to 0.99 equiv. In no case was hydrogen produced without sodium treatment; with it, the evolution was rapid but stopped suddenly at the point indicated.

The Reaction of $(CH_3)_4B_2H_2$ with Na in NH_3; Isolation of $Na_2HB(CH_3)_2$.—The study of the direct reaction of tetramethyldiborane with sodium in liquid ammonia (and the products derived from this reaction) utilized the apparatus of Fig. 1. In using this apparatus, the system was vacuum-flamed and filled with dry hydrogen from the vacuum line through F. Tube-end E was then broken off and, in a stream of dry hydrogen, an accurately weighed sample of pure sodium was introduced into A, and the tube E was sealed. The system was then evacuated again, and dry ammonia was condensed in A to form a sodium solution. The solution was frozen by liquid nitrogen and a measured quantity of tetramethyldiborane was condensed above it. On warming to −77°, the solution melted, and with shaking the reaction occurred without the evolution of hydrogen. All free ammonia was then evaporated away, and that which was loosely bound was liberated by treatment with trimethylamine at −77° and re-evaporating. This process was repeated with fresh portions of trimethylamine at successively higher temperatures, finally reaching −50° with the fourth portion. The process was then repeated at this temperature until a vapor tension measurement showed the recovered amine to be free of ammonia. The residue was then warmed slowly *in vacuo* to room temperature, the hydrogen and other volatile products being removed. The non-volatile residue was then dissolved in liquid methyl ether, condensed in A from the vacuum line, and the solution was poured through the sintered glass filter C, removing it from the excess sodium and pieces of glass. Finally the ether solution in tube B was removed from the filter system by sealing off at D. Tube B was then attached to the vacuum line for further investigation of the product.

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(9) W. C. Fernelius and G. W. Watt, *Chem. Revs.*, **20**, 221 (1937).

(10) J. R. Smith and C. A. Kraus, THIS JOURNAL, **73**, 2753 (1951).

Using the apparatus and procedure described above, it was observed that although the trimethylamine protects the reaction product against ammonolysis up to −50° (as against −70° without the displacement), one mole of ammonia was retained. On warming the residue from the displacement process to room temperature, one mole of hydrogen and one mole of aminodimethylborine, $(CH_3)_2BNH_2$, evolved per mole of tetramethyldiborane. The non-volatile solid product remained in the reaction tube. The detailed results of four experiments are given in Table I.

TABLE I

AMMONOLYSIS OF THE REACTION PRODUCT OF $(CH_3)_4B_2H_2$ AND SODIUM

Experiment	1	2	3	4
Mmoles of sodium added	1.08	1.62	1.83	2.96
Mmole of $(CH_3)_4B_2H_2$	0.290	0.383	0.364	0.629
H_2 evolved from NH_3 solution at −77°	None	None	None	None
After $(CH_3)_3N$-displacement process:				
Mmole of H_2 evolved at 25°	0.290	0.359	0.338	0.563
Mmole of $(CH_3)_2BNH_2$ evolved at 25°	0.278	*a*	*a*	*a*

[a] Identified but not determined.

Formula and Analysis of the Non-volatile Reaction Product.—The solid product obtained from the reaction of tetramethyldiborane and sodium, followed by the displacement process, the ammonolysis at room temperature and the filtration process, is stable up to 90° *in vacuo*. The formula was determined by hydrolytic analysis, producing hydrogen and dimethylboric acid, which were measured as gases. The sodium was determined gravimetrically as sodium sulfate. The acid hydrolysis follows the equation

$$Na_2HB(CH_3)_2 + H_2O + 2HCl \longrightarrow 2NaCl + (CH_3)_2BOH + 2H_2$$

The results of the best three of eight such experiments were

Na 0.71, R_2BOH_2 0.34 (calcd. 0.36), H_2 0.72 (calcd. 0.71)
Na 0.87, R_2BOH 0.44 (calcd. 0.43), H_2 0.94 (calcd. 0.87)
Na 0.75, R_2BOH 0.39 (calcd. 0.37), H_2 0.81 (calcd. 0.75)

all in millimoles. The somewhat wider scattering of the other results was due to experimental difficulties which could be minimized by sufficient practice. The average of all eight experiments was equivalent to 2.00 Na, 0.98 R_2BOH and 2.17 H_2.

If the displacement by trimethylamine is omitted in the preparation process, the analysis of the final product may be in fair agreement with that of $Na_2HB(CH_3)_2$ except that a small amount of trimethylboron is always obtained in the hydrolysis. Hence the displacement appears to be a necessary step if the preparation of pure $Na_2HB(CH_3)_2$ is to be attempted.

The Na–NH_3 Addition Reaction with Tetramethyldiborane in Excess.—The sodium–ammonia reaction, when tetramethyldiborane is in excess, proceeds in much the same manner as when sodium is in excess, but less cleanly. The mixture of $(CH_3)_4B_2H_2$ and Na–NH_3 becomes yellow very shortly after melting, indicating that all of the sodium has been used in the reaction. The excess of tetramethyldiborane, however, appears to catalyze further reaction of the first product, for the color of the solution fades at a rate roughly in proportion to the excess reagent, and only a small excess is necessary for complete decolorization. In one such experiment, employing 1.06 mmoles of Na and 0.64 mmole of $(CH_3)_4B_2H_2$ (20% excess) in the usual process, the room-temperature ammonolysis yielded 0.93 mmole of H_2 (45% excess). The residue after evaporation of the methyl ether extract, upon hydrolysis yielded 83% of the Na, 0.353 mmole of $(CH_3)_2BOH$ (20% low, in terms of recovered Na), 1.22 mmoles of H_2 (38% high for Na_2HBR_2), and 0.147 mmole of $B(CH_3)_3$. Qualitatively similar results were obtained in two other experiments, with the general conclusion that some of the excess $(CH_3)_4B_2H_2$ is held in the form of disproportionation products in the final residue, which yields $B(CH_3)_3$ and excess hydrogen on hydrolysis.

Very similar results are obtained if $Na_2HB(CH_3)_2$ is prepared in solid form, dissolved in liquid ammonia, and then treated with tetramethyldiborane. In one such experiment, 0.379 mmole of $Na_2HB(CH_3)_2$, intensely yellow in liquid ammonia, lost color soon after treatment with 0.402 mmole of $(CH_3)_4B_2H_2$; then after removal of all volatile material, the residue was hydrolyzed to yield 0.60 mmole of $(CH_3)_2BOH$, 1.34 mmoles of H_2, and 0.152 mmole of $B(CH_3)_3$. In a second experiment, 0.094 mmole of $(CH_3)_4B_2H_2$ similarly destroyed the color of 0.281 mmole of $Na_2HB(CH_3)_2$, and the hydrolysis of the non-volatile residue gave only 0.201 mmole of $(CH_3)_2BOH$ but 0.143 mmole of $B(CH_3)_3$. Here it appeared that the effect of a trace of $(CH_3)_4B_2H_2$ went far beyond its own disproportionation.

The Magnetic Properties of the Na–NH_3 Addition Products.—A sample of sodium in liquid ammonia was treated with a slight excess of tetramethyldiborane in a tube appropriate for magnetic measurement and the products were determined to be diamagnetic. The measurements were made at three different temperatures from −138 to −79° without indication of any temperature dependency. Since the tetramethyldiborane was in excess, the intense yellow color of the products faded slowly to colorless but without effect upon the diamagnetism. Hence it appears that there are no odd-electron compounds in the initial products of the reaction of tetramethyldiborane with sodium in ammonia.

The Reaction of $Na_2HB(CH_3)_2$ with Trimethylboron in Methyl Ether.—In the more precise of two experiments, 0.487 mmole of $Na_2HB(CH_3)_2$ and 0.632 mmole of $B(CH_3)_3$ were allowed to stand for 24 hours in 2 ml. of liquid methyl ether at −78°. A flocculent precipitate developed very slowly. After removal of the methyl ether and the excess $B(CH_3)_3$, by distillation at −78°, the residue was warmed to room temperature and then 0.495 mmole of $B(CH_3)_3$ evolved *in vacuo*. Since all of the original $B(CH_3)_3$ was recovered, it appears that a 1:1 addition product of $B(CH_3)_3$ precipitated at −78° and decomposed at room temperature.

The Reaction of $Na_2HB(CH_3)_2$ with Trimethylboron in Liquid Ammonia.—An ammonia solution of 0.32 mmole of $Na_2HB(CH_3)_2$ was treated with 0.83 mmole of $B(CH_3)_3$. After 24 hours at −78° the ammonia was sublimed from the system and the residue was slowly warmed to 50° *in vacuo*. In this process the excess $B(CH_3)_3$ was sublimed from the system as the ammonia complex $(CH_3)_3BNH_3$, from which the $B(CH_3)_3$ was liberated by treatment with aqueous HCl (a previously tested procedure) and determined as 0.56 mmole. Hence the product retained 0.84 mole of $B(CH_3)_3$ per mole of the $Na_2HB(CH_3)_2$ initially present. The product formed a solution in methyl ether (whether simple or colloidal was not determined), unlike the unstable precipitate of similar composition.

The Reaction with Trimethylboron during the Preparation Process.—It has been observed that when disproportionation of the dimethylborine group occurs, during the preparation of $Na_2HB(CH_3)_2$, the resulting $B(CH_3)_3$ is retained very firmly by the product, even at elevated temperatures. To study this effect more thoroughly, tetramethyldiborane was allowed to react with sodium (in excess) in liquid ammonia, as in the preparation of $Na_2HB(CH_3)_2$, except that more than a molar ratio of $B(CH_3)_3$ was also added to the original mixture. There was no visible difference at any point in this preparation from the similar process without $B(CH_3)_3$. The products, prior to the methyl ether extraction, were warmed to 100° *in vacuo* for a short period of time. The solid product was then extracted with methyl ether, and the extract was then analyzed by hydrolysis; the sodium was determined gravimetrically. The analysis agreed with that of $Na_2HB(CH_3)_2$, except that an equivalent amount of $B(CH_3)_3$ was obtained (in addition to the usual hydrolysis products), indicating the formation of a substance having the formula $Na_2HB(CH_3)_2 \cdot B(CH_3)_3$. The detailed analytical results are Na, 0.388 mmole; $(CH_3)_2BOH$, 0.188 mmole (calcd. 0.194); H_2, 0.464 mmole (calcd. 0.388); $B(CH_3)_3$, 0.210 mmole (calcd. 0.194).

These results indicate that the reaction product obtained by this process corresponds to that obtained by treating an ammonia solution of $Na_2HB(CH_3)_2$ with $B(CH_3)_3$, since the composition of the products, the solubility in methyl ether, and the observations of stability apparently are similar.

The Reaction of $Na_2HB(CH_3)_2$ with Chlorosilane.—A methyl ether solution of $Na_2HB(CH_3)_2$ was treated with more than a molar quantity of chlorosilane at −78° for 48 hours. The reaction produced an equivalent amount of silane. The excess chlorosilane was recovered unchanged. In one

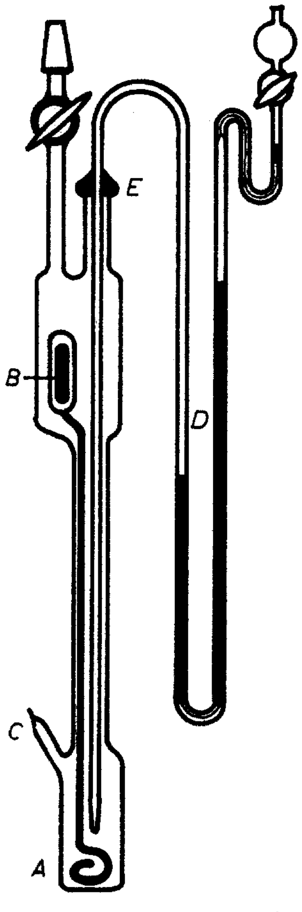

Fig. 2.—Apparatus for cryoscopic molecular weight determinations in liquid ammonia.

case 0.598 mmole of SiH_3Cl, upon reaction with 0.456 mmole of $Na_2HB(CH_3)_2$, yielded 0.464 mmole of SiH_4; in another case, 0.800 mmole of SiH_3Cl gave 0.518 mmole of SiH_4 by reaction with 0.531 mmole of the salt.

The solid residue from the reaction was expected to contain the hypothetical substance $NaB(CH_3)_2$, but it has not been possible to demonstrate this, probably because of the small scale of the experiment.

The Reaction of $Na_2HB(CH_3)_2$ with Diborane in Methyl Ether.—Methyl ether solutions of $Na_2HB(CH_3)_2$ were treated with diborane at −78°. During a 72-hour period a white precipitate formed. Upon removal of the excess diborane it was found that an addition reaction had occurred, although the mole ratio of borine (BH_3) to $Na_2HB(CH_3)_2$ in the products was considerably greater than one-to-one. The addition product did not release any diborane at 25° *in vacuo* over a period of 72 hours. In one case 0.415 mmole of $Na_2HB(CH_3)_2$ upon treatment with 0.348 mmole of B_2H_6, absorbed 0.295 mmole of it, or 1.42 BH_3 per $Na_2HB(CH_3)_2$. A second experiment gave the ratio as 1.43, but the agreement was fortuitous, since the size of the second salt-sample was far less accurately known. This reaction might be chiefly an example of the hydride reactivity of $Na_2HB(CH_3)_2$, but attempts to show the existence of sodium borohydride in the very small-scale reaction products have so far been unsuccessful.

Tensiometric Determinations of the Molecular Weight of $Na_2HB(CH_3)_2$ in Solution.—Samples of $Na_2HB(CH_3)_2$ were prepared in a suitable bulb which could be attached to a differential manometer for the comparison of the vapor tension of the pure solvent with that of the solution. The two bulbs, one containing the solution and the other the pure solvent, were then immersed in melting chlorobenzene, thus establishing a constant uniform temperature of approximately −46°. In liquid ammonia, the results indicated a molecular weight of 98 ± 10% (formula weight 87.8); although it was found afterward that some 30% of the solute had disproportionated, the reaction products probably were similar enough to $Na_2HB(CH_3)_2$ that the average molecular weight was not greatly affected—a belief supported by the cryoscopic and conductance results for the undamaged salt at −78°.

When liquid methyl ether was the solvent, however, no such disproportionation was observed. In this case the vapor tension of the methyl ether (277 mm.) was not measurably changed (0.01 mm. accuracy) by the presence of 1.5 mole per cent. $Na_2HB(CH_3)_2$. Hence it appears that in methyl ether at this concentration $Na_2HB(CH_3)_2$ was highly aggregated—or possibly colloidal.

Cryoscopic Determination of the Molecular Weight of $Na_2HB(CH_3)_2$ in NH_3.—The apparatus shown in Fig. 2 was used for the cryoscopic studies in liquid ammonia. The sample of pure $Na_2HB(CH_3)_2$ was prepared in the usual manner, with the filter system attached at C, as in Fig. 1, and the point E closed temporarily by a glass plug, to permit easy manipulation of the whole apparatus during filtration. Then the HCl-vapor-tension thermometer D was inserted at E (against a stream of dry nitrogen) and sealed in by means of Apiezon wax. Slow cooling was managed by surrounding the system A by an empty Dewar cylinder which was immersed in liquid nitrogen. This system permitted a satisfactory rate of cooling, with minimal heat capacity in the immediate surroundings. Temperature-uniformity during cooling was maintained by the magnetically operated stirrer B. In no experiment was the observed supercooling greater than 0.2°. By comparison with pure ammonia, it was observed that 0.0463 g. of $Na_2HB(CH_3)_2$ in 2.73 g. of ammonia lowered the freezing point 0.204 ± 0.008°, indicating a molecular weight value of 80.8 ± 3 (calcd. value, 87.8). This result would imply a degree of dissociation between 6 and 14%.

The Conductance of $Na_2HB(CH_3)_2$ in Solution.—The conductance of $Na_2HB(CH_3)_2$ in liquid ammonia at −77° was measured by conventional methods. A solution 0.017 molar in $Na_2HB(CH_3)_2$ had a specific conductance of 1.43×10^{-3} ohm^{-1}, and a molar conductance of 84. Since electrolytes in liquid ammonia at −33° have molar conductances around 300 at infinite dilution,[11] it would appear that the $Na_2HB(CH_3)_2$ was about 20% ionized in this solution—comparable to fairly strong electrolytes at similar concentrations.

The specific conductance of a methyl ether–$Na_2HB(CH_3)_2$ system, approximately 0.02 formal in $Na_2HB(CH_3)_2$, was less than 1.5×10^{-5} ohm^{-1}. This result might well have been anticipated, since methyl ether is not a good ionizing solvent, and the tensiometric study showed high aggregation.

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(11) E. C. Franklin, "Nitrogen System of Compounds," Reinhold Publishing Corp., New York, N. Y., 1935, pp. 17–18.