$(CH_3)_2O$ and boron halides yield the methyl halide at 76°.[23] The greater rate of reaction of the silicon ether may be explained by the formation of a halogen–silicon coördinate bond involving vacant silicon 3d orbitals[2] in the rate-controlling step.

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[23] (a) M. Ramser and E. Wiberg, *Ber.*, **63**, 1136 (1930); (b) E. Wiberg and W. Sutterlin, *Z. anorg. Chem.*, **202**, 22 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Reaction of Hydroxylamine and its N-Methyl Derivatives with Diborane

BY D. H. CAMPBELL, T. C. BISSOT AND R. W. PARRY

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Hydroxylamine–borane and N-methylhydroxylamine–borane have been prepared in impure form as solids at −112°. These lose H_2 on warming to room temperature. Pure N,N-dimethylhydroxylamine–borane has been prepared as a volatile liquid, which is relatively stable at room temperature. The decomposition of the borane complex is catalyzed by B_2H_6 and by the decomposition residues. The role of B_2H_6 in the decomposition is interpreted in terms of a proposed reaction scheme.

The reactions of the N-methylhydroxylamines and diborane differ in several important ways from the previously discussed[1] reactions of diborane with the O- and O,N-methylhydroxylamines. In the case of the O-methyl derivatives the stoichiometry of the reaction with B_2H_6 was very good to excellent; experimental ratios of CH_3ONR_2/B_2H_6 were always very close to 2.00. In the case of the N-methylhydroxylamines these ratios were in the range 1.8 to 1.92 (values which deviate from 2.00 by an amount significantly greater than the errors in experimental measurements). Reasons for these observations have been found in the properties of the hydroxylamine–borane complexes. The pure compound $HON(CH_3)_2BH_3$ was unusually stable for a compound containing hydridic and protonic hydrogens in the same molecule, but it displayed extreme sensitivity toward various catalysts which promote its decomposition. The possible role of such catalysts is considered herein.

The Reaction of Diborane and Hydroxylamine.—Diborane and solid anhydrous hydroxylamine either gave no reaction over the temperature range −186 to −96° or gave unpredictable explosive interaction. In the presence of diethyl ether as a reaction medium diborane and an ether suspension of anhydrous hydroxylamine reacted in approximate agreement with the equation

$$nB_2H_6 + 2nNH_2OH \xrightarrow[Et_2O]{-112°} 2(H_3BNH_2OH)_n$$

Hydrogen evolution was trivial under these conditions but stoichiometric reaction ratios, $HONH_2/B_2H_6$, invariably were relatively poor even in ether[2] as can be seen in Table I.

If the temperature of the ether-insoluble hydroxylamine adduct of diborane was allowed to rise slowly above −112°, hydrogen was liberated. The total number of moles of H_2 per mole of hydroxylamine used approached 1 at 25°. The product remaining after loss of one mole of hydrogen was a white solid which dissolved in water, methanol and ethanol with the evolution of small amounts of hydrogen. The material was insoluble in liquid ammonia, ether, benzene, toluene and 1,4-dioxane. The product remaining after the loss of two moles of hydrogen dissolved only with difficulty in water but readily in dilute acid or base. A polymer of the type $[-H_2BNH_2O-]_n$ would be reasonable for the 25° decomposition product. Additional B–N cross-linking would be expected for the 125° material. Above 70° the borane group itself begins to undergo direct pyrolysis.[3] A very marked decrease in the rate of hydrogen evolution was observed after two-thirds of a mole of H_2 per mole of hydroxylamine had been evolved.[4] As in the previously discussed case of methoxyamine–borane,[1] the observation correlated with an increase in the viscosity of the reacting mass. It is assumed that increasing rigidity of the polymer prevented free interaction of the acidic and hydridic hydrogen in the addition complex. A more detailed correlation with compound structure or reaction mechanism is not now available.

TABLE I

SUMMARY OF THE PROPERTIES OF THE BORANE ADDITION COMPOUNDS OF HYDROXYLAMINE AND ITS N-METHYL DERIVATIVES

Compound	M.p., °C.	Volatility	Ratio amine/ B_2H_6 in prep.[b]	Approx. temp. at which 50% dec. in 24 hr., °C.
$HONH_2BH_3$	Solid at **−78°**	None (dec.)	1.8–2.1	−75 (impure)
$HONHCH_3BH_3$	Liquid[a] at **−78°**	None	1.92	15 (impure)
$HON(CH_3)_2BH_3$	2–4°	6 mm. at 25°	1.92	25 (impure) 55 (pure)

[a] Sample impure; low melting point may be due to impurities. [b] Each value is a result of several runs. The theoretical value is 2.

The Reaction of Diborane and N-Methylhydroxylamine.—This reaction, conducted only in

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[1] T. C. Bissot, D. H. Campbell, R. W. Parry, THIS JOURNAL, **80**, April (1958).

[2] The advantages of diethyl ether as a solvent in some boron hydride reactions have been demonstrated previously. Emeleus and Stone (*J. Chem. Soc.*, 840 (1951)) observed poor stoichiometry for the reaction between diborane and non-solvated hydrazine, but Steindler and Schlesinger (THIS JOURNAL, **75**, 756 (1953)) obtained the compound $H_3BNH_2NH_2BH_3$ with excellent stoichiometry in the presence of diethyl ether.

[3] This statement is based on fact that H_2 loss from the analogous compound $CH_3ON(CH_3)_2BH_3$, which contains no protonic hydrogens, begins near 70°.

[4] More detailed information on this phenomenon is available in "The Chemistry of Boron Hydrides and Related Hydrides." W.A.D.C. Technical Report 56-318, 1956.

ether, resembled the reaction of diborane and hydroxylamine except for minor points. The addition product of the N-methylhydroxylamine was a clear ether-soluble liquid at −78°. Above −78° hydrogen was lost, and the liquid increased in viscosity until the mass solidified near room temperature. The ratio of H_2 lost per formula weight of complex was about 0.45 at room temperature. No volatile products other than hydrogen were observed until the temperature was raised to 100° and above. At this temperature methylamine contaminated with traces of ammonia was obtained and the ratio of $H_2/HONR_2BH_3$ approached 1.4. About 19% of the total nitrogen in the complex was recovered as methylamine. The polymerization upon loss of hydrogen parallels closely the process described previously for the hydroxylamine–borane.

The residue remaining in the tube after pyrolysis at 220° was a yellow solid. Upon hydrolysis with dilute HCl enough additional hydrogen was obtained from the residue to bring the total "hydridic" hydrogen per molecule of complex up to *two* instead of the expected *three*. The recovery of methylamine at high temperatures and the loss of a hydridic hydrogen from the boron indicate an internal oxidation–reduction reaction somewhat comparable to that described previously for the methoxyamine boranes.[1] The process can be represented in simplified form by the equation

$$[\text{-}H_2B\text{-}O\text{-}NHCH_3\text{-}]_n \longrightarrow [\text{-}BOH\text{-}]_n + nH_2NCH_3$$

The absence of methyl group on the oxygen permits easy formation of the O–B bond through loss of hydrogen; this constitutes a major difference between the present rearrangement and the potentially explosive shift described earlier.[1]

The Reaction of N,N-Dimethylhydroxylamine and Diborane.—This addition reaction was conducted with and without ether as a solvent. In contrast to the observations with hydroxylamine, the reaction without a solvent was not explosive and gave stoichiometry comparable to that observed in the presence of ether. As in the two preceding cases, the ratio of $NOH(CH_3)_2$ to B_2H_6 deviated from the expected value of two; fortunately, however, the isolation of the pure N,N-dimethylhydroxylamine–borane and a study of its properties gave a reasonable explanation for the observed deviations in the entire series.

In the decomposition of the two previous compounds no volatile product other than hydrogen separated at temperatures below 100°. In contrast, the pure N,N-dimethylhydroxylamine–borane could be distilled from the reaction mixture at 25° as a liquid which has a vapor pressure of 6 mm. at 25°, freezing point of 2 to 4° and a molecular weight by vapor density at room temperature of 70 ± 6. (Theoretical for $HON(CH_3)_2BH_3$ is 74.9.) The small weight of the sample, resulting from its low vapor pressure at 25°, accounted for the large experimental uncertainty in vapor density. Analysis of the pure $HON(CH_3)_2BH_3$ gave B = 14.4%; N = 18.6%; hydridic H = 3.92%; theoretical for $HON(CH_3)_2BH_3$ is: B = 14.44; = 18.69; hydridic H = 4.04.

When the pure complex was distilled from the rapidly decomposing system at room temperature, it turned out to be surprisingly stable. A pure sample standing at 25° for five days was less than 5% decomposed. If, however, the pure liquid was returned to the tube containing the initial decomposition products, rapid evolution of hydrogen began immediately at room temperature. The yield of pure $HON(CH_3)_2BH_3$ obtained from the early preparations, in which excess diborane was used, was found to correlate with the amount of undecomposed compound calculated from the observed hydrogen evolution. The results are shown in Table II.

TABLE II

REACTION BETWEEN N,N-DIMETHYLHYDROXYLAMINE AND EXCESS DIBORANE

	Run number		
	1	2	3
Solvent	Ether	None	Ether
Ratio $HON(CH_3)_2/B_2H_6$	1.94	1.91	1.91
$H_2/HON(CH_3)_2$	0.43	0.72	0.32
% Complex not decomposed[a]	57	28	68
% Pure complex recovered	50 ± 3	30 ± 3	65 ± 3

[a] Based on hydrogen evolution.

When extra diborane was added to the pure compound, vigorous hydrogen evolution began. Data are summarized in Table III. Although small amounts of diborane were used up in the reaction, most of it was recovered and at least 12 moles of hydrogen was liberated for every mole of diborane consumed. The high ratio indicates that the effect of the diborane was definitely catalytic and no primary stoichiometric process including diborane was involved. On the other hand, the fact that small amounts of diborane were used up in a secondary process justifies the poor stoichiometry in the reactions of diborane with $HONH_2$, $HONHCH_3$ and $HON(CH_3)_2$. The observation that excess B_2H_6 catalyzes the decomposition suggested that better results would be obtained if an excess of amine were used rather than an excess of diborane. The prediction was verified by experiment. When the amine was in excess, hydrogen evolution, prior to separation of the pure complex, corresponded to only 2.3% decomposition; when diborane was in excess, hydrogen evolution under comparable conditions corresponded to from 50 to 70% decomposition. Unfortunately, the N,N-dimethylhydroxylamine and its borane adduct have vapor pressures which are too close together to

TABLE III

CATALYTIC DECOMPOSITION OF PURE N,N-DIMETHYLHYDROXYLAMINE–BORANE BY DIBORANE AT 25°

	Trial 1	Trial 2
Mmoles B_2H_6 added per mole of pure $HON(CH_3)_2BH_3$	0.78	0.14
Moles H_2 liberated per mole of pure $HON(CH_3)_2BH_3$	0.82 (0.5 hr.)	1.07 (28 hr.)
% added B_2H_6 which was recovered unchanged	91	35
Mmoles B_2H_6 *consumed* for each mmole of pure $HON(CH_3)_2BH_3$ decomposed	0.07	0.09
Mmoles H_2 released for each mmole B_2H_6 consumed	15	12

permit easy vacuum-line fractionation. Due to mechanical purification losses, only a 70% yield of the pure N,N-dimethylhydroxylamine–borane was recovered, although better separation procedures would undoubtedly have given higher yields. These observations suggest that pure hydroxylamine–borane and N-methylhydroxylamine–borane might be prepared as stable compounds if a way could be found to minimize contact between the complex and the excess diborane.

The thermal decomposition of the N,N-dimethylhydroxylamine–borane was studied by holding a sample in a sealed tube at 55°. The liquid changed directly into a white solid without going through various stages of increasing viscosity. Upon opening the tube exactly one mole of hydrogen per mole of complex was found. The formula suggested for the white solid which remained is

$$[-ON(CH_3)_2BH_2-]_x$$

Since no suitable solvent was found, the value of x was not determined. The $[ON(CH_3)_2BH_2]$ polymer underwent further decomposition upon heating to high temperatures. A sample of $HON(CH_3)_2BH_3$ upon prolonged pyrolysis at 100° yielded hydrogen equivalent to 1.25 moles H_2 per mole $HON(CH_3)_2BH_3$ plus small amounts of a high-boiling liquid.

No direct evidence for an internal oxidation–reduction reaction such as was found for N-methylhydroxylamine–borane could be obtained. Dimethylamine did not distil from the solid residues under the conditions used. A sample of the N,N-dimethylhydroxylamine–borane was allowed to react with a small excess of trimethylamine. An 80% yield of $(CH_3)_3NBH_3$ was obtained, and the amine displaced was identified as N,N-dimethylhydroxylamine.

Discussion

The thermal decomposition of the N,N-dimethylhydroxylamine–borane was different in several respects from that of $HONH_2BH_3$ and $HONHCH_3BH_3$. In the decomposition of the latter two compounds there was a range of about 100° between the temperature at which a significant amount of hydrogen was first produced and the temperature at which one mole was collected. Furthermore, a change in rate of H_2 evolution was noticed after loss of $^2/_3$ of a mole of hydrogen but not after loss of one mole. On the other hand, pure $HON(CH_3)_2BH_3$ was relatively stable at 25° but decomposed rapidly when the temperature was raised just 30°. In addition, the rate of hydrogen evolution decreased almost to zero at 55° after the expected *one mole* of hydrogen had been liberated. The foregoing differences in loss of hydrogen from $HONH_2BH_3$, $HONHCH_3BH_3$ and $HON(CH_3)_2BH_3$ can be attributed to the volatility of the N,N-dimethylhydroxylamine–borane and to the fact that the pure liquid product and the decomposition product do not appear to be mutually soluble. Since they separated as distinct phases, the polymerization which accompanied the loss of hydrogen did not impede the decomposition of the unreacted material. Furthermore, the decomposition of the dimethyl compound was not complicated by the loss of the hydrogen attached directly to nitrogen, as was the case with the other two complexes.

When carefully purified, $HON(CH_3)_2BH_3$ was amazingly stable for a compound containing a rather strongly protonic and a hydridic hydrogen in the same molecule. The role of B_2H_6 in promoting H_2 evolution suggests a reasonable explanation for the stability of this pure material. In general, the coördination of the BH_3 group to a base reduces the "hydridic character"[5] of the attached hydrogens, the degree of reduction being almost proportional to the strength of the coördinate link which is formed. For example a weakly complexed addition compound such as F_3PBH_3 or $OCBH_3$ inflames spontaneously in moist air. In contrast strongly complexed compounds such as $(CH_3)_3NBH_3$ and H_3NBH_3 are reasonably stable and are attacked only slowly by water or air. In $HON(CH_3)_2BH_3$ it is logical to assume that the hydridic hydrogens of the borane group are deactivated since the BH_3 is tightly bound. The hydrogens are then unavailable for interaction with the weakly acidic hydrogen of the –OH group. On the other hand the hydrogens on diborane are available for ready reaction since BH_3 groups are readily available for coördination. After formation of the BON bond, the BH_3 which was attached originally to the amine could be released to another molecule, or B_2H_6 could be reformed.

$$\begin{tikzcd} \begin{matrix} BH_3 \text{ or} \\ B_2H_6 \end{matrix} + HON(CH_3)_2BH_3 \arrow[r] & H_2 + H_2BON(CH_3)_2BH_3 \arrow[d] \\ & [H_2BON(CH_3)_2] + BH_3 \end{tikzcd}$$

It would be logical to assume that the first step in the above process is the coördination of the BH_3 to the OH group of the amine, though this is not proved. The fact that a slight excess of diborane was always consumed in the reactions of the hydroxylamines ($HONR_2$, $R = H$ or CH_3) with diborane can be explained by utilization of the above mechanism. It is almost certain that BH_3 attack on the complex occurs to some extent during complex formation; if then the second step of the interaction, involving release of the BH_3 group, is not always quantitative, a slight excess of B_2H_6 will be consumed in the reaction. Excellent stoichiometry was obtained in the reaction of diborane and the O-methylhydroxylamines where the reaction of the complex with B_2H_6 was blocked.[1] It was also noticed that loss of hydrogen from the pure methoxyamine boranes was not catalyzed by diborane, an observation which is consistent with the above mechanism.

The hydroxylamine boranes do not have to shift any groups to form a boron–oxygen bond. As indicated above, the B–O bond arises directly from the interaction of the protonic hydrogen of the hydroxyl group and the hydridic hydrogen of the borane. This reaction appears to take place smoothly as the temperature is raised and no true explosions ever were encountered in heating a hydroxylamine-borane after the addition com-

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[5] The term "hydridic character" as used here is an operational one which refers to the ease with which interaction with a proton donor may be effected. Obviously it is strongly dependent upon mechanistic arguments as the discussion shows.

pound was once formed. A sample of the N,N-dimethyl derivative was heated directly up to 100°. Such behavior contrasts sharply with explosive decomposition of methoxyamine boranes[1] in which smooth B–O bond formation was restricted by the methyl group.

The explosion of the diborane–hydroxylamine mixture at low temperatures can be attributed to sudden vigorous interaction of previously unreacted condensed phases or perhaps to impurities. Hydroxylamine itself will detonate if subjected to sudden intense heating, but the free base is much less subject to the detonation if coördinated.[1]

In Table I are summarized the approximate temperatures at which 50% of the hydroxylamine–borane adducts are decomposed through loss of hydrogen from the original reaction mixtures. The data suggest that the OH hydrogen in hydroxylamine is the most acidic, that in the N-methyl is next and that in the N,N-dimethyl derivative is least acidic. This interpretation would be consistent with the assumed inductive effect of the methyl groups.

The displacement of N,N-dimethylhydroxylamine by trimethylamine is consistent with the fact that the latter is the stronger base.[6]

Experimental

a. **Materials. 1. Hydroxylamine.**—Free anhydrous hydroxylamine was prepared and handled as described elsewhere.[6] In order to estimate the accuracy in the weighing and handling of hydroxylamine by the previously described techniques, weighed samples of the free base were titrated with standard acid. Results of several experiments indicated that the weight of the sample was reproducibly about 8% above the theoretical weight obtained from the titration. The discrepancy undoubtedly is due to ether adhering to the crystals. An 8% correction was applied to the weights of all samples handled in the above manner.

2. **N-Methyl- and N,N-Dimethylhydroxylamines.**—The preparation and properties of these free bases are described elsewhere.[6]

3. **Diborane.**—Prepared from $LiAlH_4$ and BF_3 etherate.

4. **Diethyl Ether.**—See reference 1.

b. **Procedure. 1. Of Diborane.**—A procedure analogous to that previously described[1] was employed except for a few essential modifications. All reactions were conducted at −112°. The free hydroxylamine, which was insoluble in ether, required approximately 20 hr. for nearly complete reaction. The more ether soluble methyl and dimethyl derivatives gave complete reaction in 2 hr. or less at −112°.

The rate of absorption of B_2H_6 by an ether suspension of hydroxylamine was studied at −112°. At definite time intervals unreacted B_2H_6 was distilled from the system, purified, measured and returned to the reactor. The rate of complex formation was slow, but the ratio of B_2H_6 to NH_2OH approached the theoretical value of 0.5 as a limit. More detailed data are available elsewhere.[4]

2. **N,N-Dimethylhydroxylamine in Excess.**—In a typical run a 5-mmole sample of $HON(CH_3)_2$ was weighed out and dissolved in 3 ml. of diethyl ether. After adding 2.39 mmoles of B_2H_6, the system was warmed to −112° and stirred for 45 minutes. The mixture was separated by distillation through a trap at −63° which retained the compound and the excess amine. In this preparation only 0.11 of a mmole of H_2 was obtained. The excess amine and the borane complex were separated by fractionation in the vacuum system.

c. **Thermal Decomposition of the Borane Adducts.**—After the excess B_2H_6 and solvent separated at −78°, the temperature of the complex was raised to −64°; after the rate of hydrogen evolution dropped almost to zero, the gas was removed, purified and measured. This procedure was repeated at regular temperature intervals up to 220°. At some of the higher temperatures volatile products such as methylamine or pure N,N-dimethylhydroxylamine–borane separated. These were trapped and purified in the vacuum system and identified by physical and chemical properties.

d. **Analytical Methods.**—These are described elsewhere.[1]

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(6) T. C. Bissot, R. W. Parry and D. H. Campbell, THIS JOURNAL, **79**, 796 (1957).

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

The Reaction of Lewis Acids of Boron with Sodium Hydride and Borohydride[1]

BY HERBERT C. BROWN AND PAUL A. TIERNEY[3]

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In the presence of diglyme, sodium hydride absorbs diborane to form sodium borohydride. In the presence of excess diborane, additional diborane is absorbed to yield $NaBH_4 \cdot BH_3$. In diglyme solution boron trifluoride readily reacts with sodium hydride to form diborane. Diglyme solutions of sodium borohydride react readily with boron trifluoride in either stoichiometric or excess amounts to liberate diborane quantitatively. Boron trichloride also can be used in stoichiometric amount; however, excess boron trichloride reacts with diborane to form chloroborane etherates, resulting in reduced yields of diborane. Dimethoxyboron chloride reacts with sodium borohydride in diglyme to give diborane and methyl borate. Methyl chloride is reduced to methane by sodium borohydride in diglyme.

The discovery that lithium hydride reacts readily with diborane in ethyl ether solution to form lithium borohydride provided a greatly improved synthetic route to lithium borohydride and other metal borohydrides (through metathesis).[4,5] Similarly, the discovery that both lithium hydride and lithium borohydride reacted readily with boron trifluoride in ether solution to form diborane pro-

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(1) Addition Compounds of the Alkali Metal Hydrides. IX.

(2) Based upon a thesis submitted by Paul A. Tierney in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Standard Oil Research Foundation Fellow, 1955–1956; Parke, Davis and Co. Fellow, 1956–1957.

(4) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, THIS JOURNAL, **75**, 199 (1953).

(5) H. I. Schlesinger, H. C. Brown and E. K. Hyde, *ibid.*, **75**, 209 (1953).