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AUTHOR: Thomas Charles Bissot, Ph. D., 1956
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A STUDY OF THE REACTIONS OF DIBORANE WITH METHYL SUBSTITUTED HYDROXYLAMINES AND WITH PHOSPHORUS TRIFLUORIDE

by
Thomas C. Bissot

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Committee in charge:

Associate Professor Robert W. Parry, Chairman
Professor Ernest F. Barker
Assistant Professor Richard B. Bernstein
Doctor James D. O'Rourke
Associate Professor Peter A. S. Smith

Abstract

A STUDY OF THE REACTIONS OF DIBORANE WITH METHYL SUBSTITUTED HYDROXYLAMINES AND WITH PHOSPHORUS TRUFLUORIDE

by Thomas C. Bissot

Evidence now available suggests that many of the reactions of diborane proceed through the formation of a BH_3 addition compound, which may undergo secondary decomposition to give a variety of products. Borane adducts of hydroxylamine derivatives are subject to many secondary reactions and, hence, are of particular interest in outlining the chemistry of diborane.

In this investigation, diborane was allowed to react with methyl substituted hydroxylamines and the properties, stability, and mode of decomposition of the resulting adducts determined. In addition, the reaction of the very weak "Lewis" base, PF_3, with diborane was studied in an attempt to prepare a compound PF_3BH_3. A typical high vacuum apparatus was employed in manipulating these materials.

The melting points, vapor pressure curves, and Trouton constants were measured for all of the methyl substituted hydroxylamines. The values observed are what one would expect from the hydrogen bonding in these molecules. The base strengths of these compounds were measured in aqueous solution.

These methyl substituted hydroxylamines react with diborane in a 2/1 ratio to form a borane addition compound. The stoichiometry of the reaction was very good for the OCH_3 hydroxylamines but small deviations were observed for the OH hydroxylamines. These addition compounds undergo secondary reactions before there is any observable dissociation back into the amine and diborane. It was found that the hydroxylamines could be displaced from their borane addition compounds by trimethylamine, the displacement being quantitative for the trimethyl derivative.

$CH_3ONH_2BH_3$ and $CH_3ONHCH_3BH_3$ explode upon rapid heating to 100°, but decompose slowly at lower temperatures to liberate hydrogen gas. The hydrogen evolution is accompanied by a shift of the methoxy group from the nitrogen to the boron and a shift of a hydride unit from the boron to the nitrogen. Following disproportionation, trimethoxyborane can be isolated from the decomposition products. The trimethylhydroxylamine-borane also undergoes this shift and disproportionation but does not explode upon rapid heating. A different decomposition mechanism is proposed for this compound.

When $CH_3ONH_2BH_3$ and $CH_3ONHCH_3BH_3$ are hydrolyzed by 50% KOH, a hydridic hydrogen is lost from the boron and reduction of the amine occurs. The behavior appears to parallel the thermal decomposition of these compounds. On the other hand, when $CH_3ON(CH_3)_2BH_3$ is hydrolyzed by a basic

solution, three hydridic hydrogens per boron are found and the original O,N,N-trimethylhydroxylamine is recovered unchanged. The difference is ascribed to the partial ionization of these ammonium type compounds in strongly alkaline solutions.

$HONHCH_3BH_3$ and $HON(CH_3)_2BH_3$ lose hydrogen at low temperatures when they are prepared using an excess of diborane. The dimethyl derivative is found to be surprisingly atable at 25° when it is pure, but when heated up to 55°, it loses one mole of hydrogen to leave an $(ON(CH_3)_2BH_2)$ polymer. Diborane catalyzes the decomposition at room temperature. The stability of pure $HON(CH_3)_2BH_3$ is attributed to deactivation of the hydridic hydrogens through coordination of the borane group.

The compound PF_3BH_3 has been prepared by the reaction between phosphorus trifluoride and diborane. The properties of this compound are very similar to those reported for $OCBH_3$.

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INTRODUCTION

The development of the chemistry of boron was much slower than that of its neighbor carbon in the periodic table. Whereas many of the type reactions of carbon compounds were known prior to the turn of the century, boric acid and the borates were almost the only known boron compounds. The brilliant researches of Stock (1) opened the field of the boron hydrides, a field which has been greatly expanded by Schlesinger, Burg, and their students during the past twenty-five years. Since about 1948 an increasingly large number of workers have been attracted to the field. Some materials with important industrial applications, such as lithium tetrahydridoborate (III)* (lithium borohydride) and sodium tetrahydridoborate (III) (sodium borohydride), have evolved from these studies.

This investigation represents a portion of a broad program covering the reactions of boron hydrides. It is hoped that information concerning the reactions of these intriguing compounds will permit the ultimate systematization of this broad area of inorganic chemistry.

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*The nomenclature used throughout this work is based on the scheme for nomenclature in boron compounds presented by G. W. Schaeffer and T. Wartik at the 125th meeting of the American Chemical Society, Kansas City, Missouri, 1954. This set of nomenclature rules has been approved by most of the outstanding workers in the field.

BACKGROUND

All of the known boron hydrides may be represented by two type formulas. Those of the formula B_nH_{n+4} are B_2H_6, B_5H_9, B_6H_{10}, and $B_{10}H_{14}$ while those of the formula B_nH_{n+6} are B_4H_{10}, B_5H_{11}, and B_6H_{12}. The hydrides of the latter type are less stable in general and tend to decompose, forming hydrogen and boron hydrides of the first type. In general, the stability toward hydrolysis increases with the molecular weight.

Diborane, B_2H_6, the lowest member of the series has been studied more extensively than the higher hydrides because its reactions are simpler and it is easier to prepare. Campbell (2) has divided the reactions of diborane into three classifications: (1) reaction as a typical Lewis acid, (2) those involving the hydridic character of the hydrogens, and (3) the disproportionation of substituted diboranes and rearrangements of addition products.

The chemical reactions of diborane as a Lewis acid occur through a splitting into borane (BH_3) groups. The electron acceptor strength of common boron acids is generally considered to lie in the order, $BF_3 > BH_3 > B(CH_3)_3 > B(OCH_3)_3$ (3). This order may be modified depending upon the reference base used. For example, the order for BF_3 and BH_3 appears to be reversed with carbon monoxide since $OCBH_3$ (4) is a well-characterized compound, but no one has been able to prepare a compound between BF_3 and CO (5). Some examples of borane

complexes which do not react further by reaction of the second or third type are arranged in the order of increasing stability as follows: $(CH_3)_2OBH_3$ (6), $OCBH_3$ (4), $(CH_3)_2SBH_3$ (7), $(CH_3)_3AsBH_3$ (8), $(CH_3)_3PBH_3$ (9), $C_5H_5NBH_3$ (10,11), $(CH_3)_3NBH_3$ (4), $LiH{\cdot}BH_3$ (12). One of the characteristic reactions of these addition compounds is the displacement of a weaker base by a stronger one. Trimethylamine is often used as a test for borane and will displace a weaker base from its complex with BH_3.

Diborane, although classed as a volatile hydride, behaves more like the typical salt-like hydrides (LiH, CaH_2, etc.) in its reactions with proton donor substances to evolve hydrogen gas. Typical examples are the reactions of diborane with water and methyl alcohol. In the first, boric acid and hydrogen are the products, while the second produces dimethoxyborane and hydrogen (13). The first step in these reactions may be the transitory existence of a borane complex H_2OBH_3 or CH_3HOBH_3 (14).

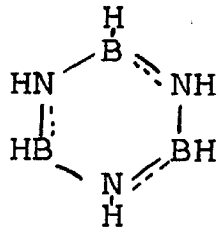
$$B_2H_6 \rightleftharpoons 2\,BH_3$$

$$BH_3 + H_2O \longrightarrow (H_2OBH_3) \longrightarrow BH_2OH + H_2$$

$$BH_2OH + H_2O \longrightarrow (H_2OBH_2OH) \longrightarrow BH(OH)_2 + H_2 \quad \text{etc.}$$

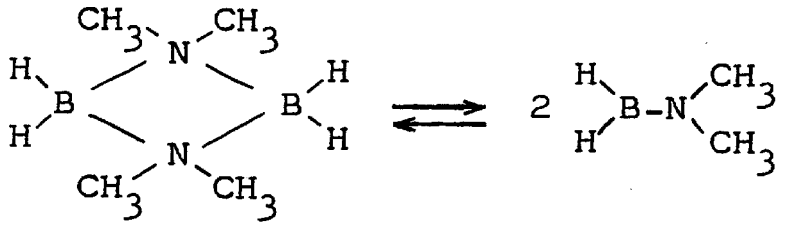
These must be recognized as being only reaction mechanism intermediates. With less protonic substances, such as the primary and secondary amines, phosphines, and arsines, the borane adduct can be isolated before the second type of reaction between the adjacent protonic and hydridic

hydrogens occurs. Methylamine-borane, for example, is a liquid which is quite stable at room temperature (15). When heated to 100° it yields one mole of hydrogen to form the compound $(CH_3NHBH_2)_x$. A substance of this empirical formula was first mentioned by Burg and Randolph (16). Molecular weight measurements in this laboratory have shown it to be a trimer in liquid ammonia, benzene, and nitrobenzene. When this trimeric N-methylamino-borane is heated up to 200°, the second mole of hydrogen is liberated and the 1,3,5-trimethylborazene is formed (15,17,18). The borazenes contain a six-membered ring composed of alternating boron and nitrogen atoms, which make them isosteric with substituted benzenes. The parent compound, $B_3N_3H_6$,

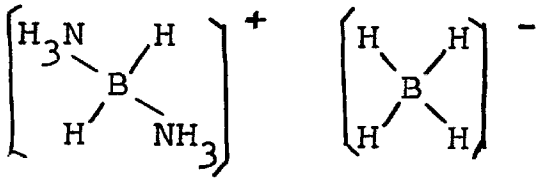


can be prepared by heating the "diammoniate of diborane," $(B_2H_6 \cdot 2NH_3)$, at 200° for several hours. The preparation of a number of B- and N-methyl substituted borazenes has been reported (15).

Dimethylamine-borane loses one equivalent of hydrogen at 80° to form N-dimethylaminoborane. The compound is a dimer at room temperature, but exists in a monomer-dimer equilibrium at higher temperatures (19,20).



The addition compound of ammonia with diborane is different from those which have been discussed previously. The material is a salt-like nonvolatile solid which has been shown by molecular weight determinations to be a dimer in liquid ammonia. Recent chemical and physical evidence, obtained in this laboratory (21), has shown that the structure is:



The splitting out of H_2 from certain borane complexes leads to some very interesting compounds. $(CH_3)_2PHBH_3$ (9) and $(CH_3)_2AsHBH_3$ (8) upon heating yield hydrogen together with some unusually stable and unreactive low polymers. The reasons for the stabilization of $[(CH_3)_2PBH_2]_3$ and $[(CH_3)_2AsBH_2]_3$ pose a challenging problem in the theory of chemical bonding.

The third type of reaction which diborane may undergo is first, the disproportionation of substituted diboranes, and second, the rearrangements of addition compounds. As an example of the former, a monohalo diborane such as B_2H_5Cl disproportionates to form B_2H_6 and BCl_3 (22). The N-dimethylaminoborane, in addition to the monomer-dimer equilibrium, disproportionates according to the equation (20):

$$3\ (CH_3)_2NBH_2 \rightleftharpoons [(CH_3)_2N]_2BH + (CH_3)_2NB_2H_5$$

μ-monoaminodiborane decomposes slowly at room temperature (23).

$$2\ H_2NB_2H_5 \rightleftharpoons B_2H_6 + 2\ [H_2NBH_2]_x$$

As a final example of this type, dimethoxyborane disproportionates as follows (13):

$$6\ (CH_3O)_2BH \rightleftharpoons B_2H_6 + 4\ B(OCH_3)_3$$

Another type of self reaction of borane complexes is the rearrangement of the addition compounds. The borane complex of methyl cyanide undergoes an internal shift of two hydride units giving polymers of the (C_2H_5NBH) unit (24). Brown (25) has reported similar shifts of an H^- in the borane addition compounds of aldehydes, ketones, and esters. For example, acetaldehyde reacts with diborane as follows:

$$4\ CH_3CHO + B_2H_6 \longrightarrow 2\ (C_2H_5O)_2BH$$

Since hydroxylamine has the possibility of undergoing a combination of all these three types of reaction with diborane, Campbell (2) undertook an investigation of the system hydroxylamine - diborane. In the absence of a solvent he found that hydroxylamine does not appear to react with diborane at temperatures up to -100°, but reacts explosively at higher temperatures. In the presence of ether approximately two moles of hydroxylamine combined with one of diborane at temperatures as low as -112°. The resulting addition compound began to lose hydrogen at significant rate at -78°. The amount of hydrogen lost was approximately one mole at room temperature and two at about

125°, leaving a white solid as a residue.

Campbell also found that methoxyamine formed a two to one adduct with diborane. The temperature at which loss of hydrogen began at a significant rate was not reproducible in his series of experiments. In addition to the hydrogen, two volatile materials were isolated from the decomposition of methoxyamine-borane. One was a liquid which slowly decomposed at room temperature to give a solid and diborane. The second was a volatile solid which did not give off hydrogen upon hydrolysis. Since only small amounts were obtained, these materials were not completely identified.

Most of the borane addition compounds which have been discussed up to this point have been formed with relatively strong donor molecules. The compound $OCBH_3$ is an example of the other extreme in which the BH_3 group is coordinated to a very weak Lewis base. This adduct is stable at low temperatures but decomposes to diborane and carbon monoxide at room temperature. It is the most volatile borane addition compound known (m.p. -137.0°; extrapolated b.p. -64°).

The coordinating ability of PF_3 bears a remarkable resemblance to that of CO in a number of cases. $PtCl_2 \cdot 2PF_3$ and $Ni(PF_3)_4$ (26) are very similar to $PtCl_2 \cdot 2CO$ and $Ni(CO)_4$ in terms of both physical properties and stability. It would appear reasonable that the analogy could be extended and that a compound similar to carbon monoxide-borane might

exist with PF_3. The attempted preparation of such a compound has never been reported, but it has recently been predicted that PF_3 would not coordinate to boron.

Chatt (27) proposed the theory that there are two types of coordination involved in the stable complexes formed between weak donor molecules such as carbon monoxide, ethylene, and phosphorus trifluoride with platinous salts and metals which display zero valency such as nickel. The first is the classical covalent link such as is used in complex formation by compounds of boron, aluminum, magnesium, etc., and the second is by a mechanism, essentially covalent, by which the filled d orbitals of an acceptor atom contribute to the bonding. The addition compounds formed by the alkyl phosphines with acceptor molecules such as boron and aluminum compounds, which do not contain filled d orbitals, are attributed to the first or classical type of coordination. In the case of phosphorus trifluoride, the tendency to donate the lone pair of electrons is greatly reduced by the inductive effect of the fluorines. Chatt, therefore, predicted that PF_3 would not coordinate with Lewis acids which did not contain filled d orbitals. As experimental proof of this prediction, the failure to obtain complex formation of PF_3 with $AlCl_3$ and with $AlBr_3$ were cited. In addition boron trifluoride, one of the strongest acceptor molecules known, has been reported not to react with PF_3 (28).

STATEMENT OF THE PROBLEM

A reinvestigation of the volatile materials produced in the decomposition of methoxyamine-borane led to the identification of one of these as trimethoxyborane (methyl borate). Since a shift of groups between the nitrogen and the boron would be necessary to form this product, it appeared desirable to investigate the course of this shift in greater detail. The study was extended to include the diborane addition compounds formed with all the possible methyl substituted derivatives of hydroxylamine. Some physical and chemical properties of these amines, such as their vapor pressures and base strengths, were desirable in order to help elucidate the stability and mode of decomposition of the diborane adducts.

The similarity of the coordinating abilities of carbon monoxide and phosphorus trifluoride in a number of cases suggested that a compound PF_3BH_3 might exist which would be analogous to $OCBH_3$. The isolation of such a compound would constitute additional evidence (29) against the theory of contributing d orbitals. The system B_2H_6 - PF_3 was, therefore, investigated.

EXPERIMENTAL RESULTS--METHYL SUBSTITUTED HYDROXYLAMINES

The reactive nature and high volatility of diborane required that it be stored and used in a high vacuum apparatus. A typical vacuum line, described previously by Campbell (2), was used in this investigation. Some of the principal components, in addition to the pumping system, were a fractionation train, gas storage bulbs, liquid storage tubes, a reaction system, and a Toepler pump for moving noncondensable gases.

The diborane was prepared by the reaction of lithium aluminum hydride on boron trifluoride etherate in ether solution (30). After purification by low temperature fractionation, the vapor pressure at -111.8° was 225 mm.

Although all of the methyl derivatives of hydroxylamine have been described in the early literature, the physical and chemical properties of these materials are for the most part either inaccurately described or unknown. Since these properties were important in delineating the conditions for their reaction with diborane, the necessary data have been obtained.

Preparation and Properties of Methyl Substituted Hydroxylamines

Preparation

Methoxyamine.--Methoxyamine hydrochloride (Eastman Organic Chemicals) was treated with an excess of 50% KOH in

a small one-piece distillation apparatus. The fraction boiling at 45-50° was distilled onto KOH pellets contained in a receiver which was immersed in an ice-water bath. The free base was then decanted into a tube containing BaO and equipped with a Standard-Taper joint. The tube was attached to the line and the methoxyamine was allowed to stand in contact with the BaO for several days. The CH_3ONH_2 prepared in this manner was contaminated with small amounts of other amines, chiefly ammonia. These were removed by fractional condensation: effected by holding the first trap at -63°, the second at -79°, and the third at -196°. The desired component was retained in the second trap.

O,N-Dimethylhydroxylamine.--This methyl substituted hydroxylamine was prepared by the following reactions:

$$C_2H_5OC(O)Cl + HONH_2 \cdot HCl \xrightarrow{K_2CO_3} C_2H_5OC(O)NHOH$$

$$C_2H_5OC(O)NHOH + (CH_3O)_2SO_2 \longrightarrow C_2H_5OC(O)N(CH_3)OCH_3$$

$$C_2H_5OC(O)N(CH_3)OCH_3 \xrightarrow{\text{alc. KOH}} C_2H_5OC(O)OK + CH_3ONHCH_3$$

$$CH_3ONHCH_3 + HCl \longrightarrow CH_3ONHCH_3 \cdot HCl$$

The literature directions (31,32) were followed without modification. The hydrochloride salt was recrystallized from absolute alcohol by the addition of dry ether. The melting point was 115-116° (literature 115-116°). The free base was prepared in the following manner. A few milliliters of 50% KOH were frozen in the bottom of a tube which was equipped with a Standard-Taper joint. The amine hydrochloride was placed on top of the frozen solution and the

tube attached to the vacuum line. After evacuating the tube, it was allowed to warm up to room temperature. The contents were mixed by agitating a small iron-cored stirring bar with a magnet. The free O,N-dimethylhydroxylamine was then distilled into another tube containing BaO and was dried for several days before using. No further purification was required since all fractions had identical vapor pressures. As an extra check on the identity and purity of the material, the molecular weight was checked by vapor density. The value observed, 61.7 (theory 61.10), is within the experimental error of the measurement.

O,N,N-Trimethylhydroxylamine.--The trimethyl derivative was prepared as described by Jones and Major (33), using the reaction of methyl iodide with the O,N-dimethylhydroxylamine.

$$CH_3I + 2\ CH_3ONHCH_3 \xrightarrow{\text{ether}} CH_3ONHCH_3 \cdot HI + CH_3ON(CH_3)_2$$

The ether solution was filtered and phenyl isocyanate was added to remove any unreacted CH_3ONHCH_3 as the N-phenyl-N'-methyl-N'-methoxy urea derivative. The ether and the free O,N,N-trimethylhydroxylamine were distilled out and dry HCl passed into the ether solution. The recrystallized hydrochloride salt had a melting point of 122.5-123.5°. The literature value is 123°. The free base was prepared and dried using the method described for the previous amine. No further purification was required. The molecular weight was measured by vapor density as 76.2 (theory 75.11).

N-Methylhydroxylamine.--The N-methylhydroxylamine was prepared by the following series of reactions using literature directions:

$$(\phi)_2CO + HONH_2 \cdot HCl \xrightarrow{NaOH} (\phi)_2CNOH + 2\ H_2O + NaCl \quad (34)$$

$$(\phi)_2CNOH + (CH_3O)_2SO_2 \xrightarrow{NaOH} (\phi)_2CN(O)CH_3 + (\phi)_2CNOCH_3{}^*$$

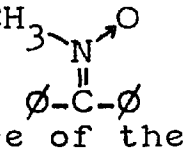
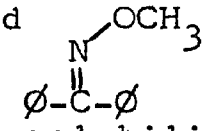
$$(\phi)_2CN(O)CH_3 + H_2O + HCl \xrightarrow{100^\circ} HONHCH_3 \cdot HCl + (\phi)_2CO \quad (35)$$

$$HONHCH_3 \cdot HCl + CH_3ONa \longrightarrow CH_3OH + NaCl + HONHCH_3 \quad (36)$$

The N-methylhydroxylamine is a solid of rather low volatility at room temperature. The material required a large number of fractional condensations before a portion was obtained whose vapor pressure did not change upon further fractionation. Because of the low vapor pressure, the purity was checked by a nitrogen analysis rather than by molecular weight (observed, 29.69% N; theory 29.77% N).

N,N-Dimethylhydroxylamine.--This hydroxylamine was prepared by the action of a methyl Grignard reagent upon ethyl nitrate in ether solution (37). After hydrolysis, the amine was removed by steam distillation and collected in dilute HCl. The resulting solution was evaporated to dryness and the crude hydrochloride was purified by two to four crystallizations from an ether-alcohol mixture. The salt was

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*The structural isomers  and  are readily separated by the difference of their solubilities in petroleum ether (30-50°). The N-methyl compound is slightly soluble, whereas the other is insoluble.

thoroughly dried under high vacuum on the vacuum line. The melting point observed was 103-106°. Hepworth (37) listed a m.p. of 102°, while Cope (38) reported 106.5-109°.

The free anhydrous $HON(CH_3)_2$ could not be prepared using the method described by Hepworth. His procedure involved distilling the amine, together with some water from a flask containing the crude hydrochloride and concentrated KOH. The distillate was extracted with ether and the ethereal solution dried with BaO. After several distillations he obtained a fraction boiling at 94.5 to 95.5°, which he thought was the anhydrous free base, and for which he reported nitrogen analysis of 22.78 and 22.82% (theory 22.94%). In the current investigation this procedure was modified somewhat by utilizing vacuum techniques for the initial separation of the amine after adding an excess of KOH to the recrystallized hydrochloride salt. When a large amount of BaO was used to dehydrate the mixture of water and amine obtained in the distillation, it was found that all of the material was absorbed. When a somewhat smaller amount of BaO was used, some of the liquid could be recovered. The melting point was about 0° and the vapor pressures, measured over the range of 0 to 88°, extrapolated to a boiling point of 93.5°. However, a molecular weight determination and a titration of a weighed amount indicated that a significant amount of water was still present in the amine.

The weak base strength of the N,N-dimethylhydroxylamine suggested that it might be displaced from its

hydrochloride salt by ammonia. This procedure was found to work very satisfactorily. A quantity of the recrystallized $HON(CH_3)_2 \cdot HCl$ was dried at room temperature for several hours under high vacuum. An excess of anhydrous ammonia, dried over sodium, was distilled into the tube and stirred until the solution was clear. The mixture of ammonia and the hydroxylamine was then distilled away from the ammonium chloride and separated by fractional condensation. The $HON(CH_3)_2$ was retained in a trap maintained at -80° with a Dry Ice-isopropyl alcohol bath. The displacement was quantitative since the remaining hydrochloride salt would not reduce silver nitrate.

The melting point and boiling point of the anhydrous material were raised considerably, m.p. 17.7°, b.p. 100.7°. Nitrogen analysis, 22.56 and 22.70% N, are in agreement with the theoretical value of 22.94%. The molecular weight values of this amine, determined over a range of temperature, show that there is considerable association in the vapor phase.

Temperature ° C.	Apparent Molecular Weight
59.0	73.0
64.8	70.5
69.4	69.2
98.3	64.6

The values approach the theoretical molecular weight of 61.09 at the higher temperatures. This anhydrous base was found to be quantitatively absorbed by alkaline drying

agents such as BaO and KOH pellets. The hydroxyl group on this amine is responsible for the similarity of its physical and chemical properties with those of water. Since the amine and water also apparently form a low boiling azeotrope, they cannot be completely separated by ordinary means.

Physical Properties

Melting points.--The melting points of these hydroxylamines divide the group into two categories. The ones with a methyl group on the oxygen are very low melting materials, whereas those with a hydrogen on the oxygen have melting points near room temperature. The data for the O,N-dimethyl- and the O,N,N-trimethylhydroxylamines were determined using the magnetic plunger method first described by Stock (39,40). A sample of the amine was condensed with liquid nitrogen in a ring which supported the glass plunger. A cooling bath of mixed methyl pentanes was cooled well below the melting point of the amine and placed around the melting point apparatus. A carbon dioxide vapor pressure thermometer was used to measure the temperature of the bath. The cooling bath was then allowed to warm up slowly, with constant stirring to keep the temperature uniform. When the pointer dropped, the vapor pressure of the carbon dioxide gave the temperature at which the material melted. For the above two amines the melting points on three separately purified samples were reproducible to within less than a tenth of a degree.

The melting points of the N-methyl- and the N,N-dimethylhydroxylamines were determined visually in the same apparatus that was used to determine vapor pressures. A National Bureau of Standards calibrated mercury thermometer was used to measure the temperature.

The results of this investigation and the values recorded by previous workers are collected in the following table.

TABLE 1

MELTING POINTS OF HYDROXYLAMINE AND ITS METHYL SUBSTITUTED DERIVATIVES

Compound	Melting Point °C.	Investigator
$HONH_2$	33.05	Lobry de Bruyn (41)
	32-33	Bruhl (42)
$HONHCH_3$	42	Kjellin (36)*
	38.2, 38.7	This investigation
$HON(CH_3)_2$	17.5-17.8	This investigation
CH_3ONH_2	-86.4	Campbell (2)
CH_3ONHCH_3	-97.0	This investigation
$CH_3ON(CH_3)_2$	-97.2	This investigation

*The observations of Kjellin were apparently rather crude. The boiling point which he reported for $HONHCH_3$ was in error by a large factor (Table 7). Extensive purification in this investigation failed to raise the melting point above the reported value.

Vapor pressures and related constants of hydroxylamine and its methyl substituted derivatives.--When handling volatile compounds in a high vacuum apparatus, a knowledge of their vapor pressures at various temperatures is essential. Not only are the values necessary in order to design a separation procedure, but they provide a rapid check on the identity and purity of the separated material. Except for Campbell's (2) observations of methoxyamine below room temperature, no vapor pressure data were available in the published literature for the methyl substituted hydroxylamines. In view of these facts, a portion of this investigation was directed toward obtaining these data.

The details of the measurement varied with the temperature range which was involved.

1. -80 to 0°.--Four different two phase systems were used as constant temperature baths in this region. These were slush baths of chloroform (-63.5°), chlorobenzene (-45.3°), carbon tetrachloride (-22.8°), and ice-water (0°). A Dry Ice-isopropyl alcohol bath was used at -78°. For intermediate temperatures a large bath of isopropyl alcohol was cooled to the desired temperature. This bath was well-stirred, and the temperature measured with an alcohol thermometer. Since alcohol thermometers are often unreliable, the one used in these measurements was calibrated each time it was used against two phase slush baths of CCl_4, C_6H_5Cl, and H_2O.

A mercury manometer was used to measure the pressures, which were read to the nearest 0.1 mm. with a cathetometer.

2. 0° to room temperature.--The desired temperature was achieved by using a large well-stirred water bath cooled to the desired temperature. A mercury thermometer with 0.01° graduations, which had been calibrated and certified by the National Bureau of Standards, was used to measure the temperature of the bath.

3. Above room temperature.--An immersible tensimeter designed after the one described by Burg and Schlesinger (4) was used to determine vapor pressures above room temperature. The tensimeter was immersed in a constant temperature bath controlled to $\pm$ 0.05°. Two National Bureau of Standards calibrated thermometers, -5 to 50° and 50 to 110°, were used with stem corrections applied where they were significant.

The vapor pressure data were then fitted to an equation of the form,

$$(1) \quad \mathrm{Log}_{10} P = -A/T + B - CT^2 ,$$

by the method of averages. The boiling point of the amine was checked with the literature value by substituting 760 mm. for P in the resulting equation.

The heat of vaporization was derived from the

empirical equation rather than by a graphical method. Rearranging the form of the Clausius equation,

(2) $dP/dT = P\Delta H/RT^2$, one obtains (3) $\Delta H = RT^2/P \times dP/dT$.

Differentiating equation (1) yields

(4) $dP/dT = 2.303\ P\ (A/T^2 - 2CT)$,

or (5) $\Delta H = 2.303\ R\ (A - CT^3)$.

The entropy of vaporization $\Delta H/T$ proved to be of assistance in correlating the reactions of these methyl substituted hydroxylamines with diborane.

Chemical Properties

The base strength of hydroxylamine and its methyl substituted derivatives.--The base strength of this series of compounds in water solution was determined potentiometrically. A dilute solution of the hydrochloride salts was titrated with 0.05 N NaOH and a typical titration curve was obtained.

The hydrochloride salts of these amines were carefully purified and dried. A quantity was weighed out and diluted to obtain a solution which was approximately 0.0025 molar. A one hundred milliliter aliquot was transferred to a four-necked flask. The central neck contained a stirrer; two necks were used for the electrodes, while the fourth was used for the burette. A Beckman model G pH meter with a combination glass-calomel electrode system was carefully standardized against a potassium acid phthalate buffer.

TABLE 2

THE VAPOR PRESSURE OF METHOXYAMINE

Empirical equation $\text{Log}_{10}P = -2018.0/T + 9.7025 - 5.255 \times 10^{-6}T^2$

Temp. °C.	Observed Pressure mm.	Calculated Pressure mm.	ΔP Cal.-Obs.
-63.5	0.75	0.70	-0.05
-45.3	3.55	3.74	+0.19
-22.8	20.5	20.6	+0.1
-20.4	24.2	24.2	0
-17.6	29.0	29.0	0
-13.3	38.2	38.2	0
-10.4	45.6	45.8	+0.2
-6.8	56.4	56.8	+0.4
0.0	83.9	83.7	-0.2
9.4	138.8	138.5	-0.3
10.1	143.5	143.6	+0.1
12.6	162.9	162.4	-0.5
14.4	177.3	177.6	+0.3
16.0	192.1	192.7	+0.6
17.7	208.4	209.0	+0.6
19.1	222.8	222.9	+0.1
20.1	233.6	233.2	-0.3
21.1	243.9	245.7	+1.8
24.8	291.1	290.7	-0.4
29.8	362.9	363.7	+0.8
34.9	451	450	-1
40.3	561	561	0
44.8	670	668	-2
48.2	761	760	-1

TABLE 3

THE VAPOR PRESSURE OF O,N-DIMETHYLHYDROXYLAMINE

Empirical equation $\text{Log}_{10}P = -1908.9/T + 9.4000 - 4.714 \times 10^{-6}T^2$

Temp. °C.	Observed Pressure mm.	Calculated Pressure mm.	ΔP Cal.-Obs.
-45.2	6.1	6.35	+0.25
-42.0	8.0	8.03	+0.03
-36.5	11.8	11.7	-0.1
-31.4	16.8	17.0	+0.2
-27.0	23.1	22.9	-0.2
-22.6	30.6	30.7	+0.1
-18.0	40.8	41.1	+0.3
-13.3	54.9	54.5	-0.4
-7.3	77.8	77.2	-0.6
-4.2	91.5	91.9	+0.4
0.0	114.4	115.2	+0.8
4.0	141.1	141.4	+0.3
8.0	173.2	173.5	+0.3
12.0	210.9	210.9	0
16.0	253.8	253.9	+0.1
19.7	301.4	301.0	-0.4
23.9	361.5	361.8	+0.3
28.0	430.4	431.3	+0.9
32.9	526.6	527.1	+0.5
37.5	630.2	631.2	+1.0
42.4	765.0	760.7	-4.3

TABLE 4

THE VAPOR PRESSURE OF O,N,N-TRIMETHYLHYDROXYLAMINE

Empirical equation $\log_{10}P = -1805.1/T + 9.5424 - 7.738 \times 10^{-6}T^2$

Temp. °C.	Observed Pressure mm.	Calculated Pressure mm.	ΔP Cal.-Obs.
-78.5	0.9	0.95	+0.05
-63.5	3.6	3.9	+0.3
-45.2	17.3	16.7	-0.6
-39.0	26.5	25.7	-0.8
-35.0	35.5	33.5	-2.0
-29.8	47.5	46.7	-0.8
-25.2	61.7	61.4	-0.3
-20.0	81.5	82.8	+1.3
-14.1	113.6	113.6	0
-9.3	144.4	145.8	+1.4
-4.8	186.0	181.6	-4.4
0.0	226.9	228.1	+1.2
3.9	270.1	271.3	+0.4
8.3	328.0	329.1	+1.1
11.8	379.1	380.0	+0.9
15.9	448.0	448.4	+0.4
20.0	525.4	524.7	-0.7
23.3	597.5	593.5	-4.0

TABLE 5

THE VAPOR PRESSURE OF N-METHYLHYDROXYLAMINE

Solid Phase

Empirical equation $\text{Log}_{10}P = 13.7/T - 4.261 + 5.63 \times 10^{-5}T^2$

Temp. °C.	Observed Pressure mm.	Calculated Pressure mm.	ΔP Cal.-Obs.
0.0	0.9	1.0	+0.1
5.0	1.5	1.4	-0.1
10.0	2.0	2.0	0
15.0	2.9	2.9	0
20.0	4.2	4.2	0
25.0	6.1	6.1	0
30.0	9.0	9.0	0
35.0	13.5	13.4	-0.1

Liquid Phase

Empirical equation $\text{Log}_{10}P = -2597/T + 9.570$

20.0*	5.2	5.2	0
25.0*	7.3	7.3	0
30.0*	10.0	10.1	+0.1
35.0*	13.9	13.9	0
40.0	19.1	19.0	-0.1
45.0	25.8	25.4	-0.4
50.2	34.6	34.7	+0.1
55.0	45.4	45.4	0
60.0	59.8	59.7	-0.1
65.0	76.8	77.8	+1.0

*Supercooled liquid.

TABLE 6

THE VAPOR PRESSURE OF N,N-DIMETHYLHYDROXYLAMINE

Empirical equation $Log_{10}P = -2796.5/T + 11.3033 - 6.750 \times 10^{-6}T^2$

Temp. °C.	Observed Pressure mm.	Calculated Pressure mm.	ΔP Cal.-Obs.
17.6	13.0	13.1	+0.1
19.1	14.5	14.5	0
25.2	21.4	21.4	0
29.8	28.5	28.5	0
34.7	38.0	38.1	+0.1
40.3	52.4	52.4	0
44.9	67.3	67.3	0
50.3	90.1	89.7	-0.4
55.1	114.6	114.2	-0.4
60.2	146.0	146.7	+0.7
65.1	183.3	183.8	+0.5
70.2	229.7	231.2	+1.5
75.1	284.4	285.5	+1.1
80.2	351.7	351.7	0
85.0	427.0	426.0	-1.0
90.0	521	517	-4

TABLE 7

BOILING POINTS OF HYDROXYLAMINE AND ITS METHYL SUBSTITUTED DERIVATIVES

Compound	Boiling Point °C.	Investigator
$HONH_2$	56-57/22 mm.	Bruhl (42)
	58/22 mm.	Lobry de Bruyn (41)
$HONHCH_3$	62.5/15 mm.	Kjellin (36)
	62.5/68.7 mm.	This investigation
	115.0/760 mm.	This investigation
$HON(CH_3)_2$	94.5-95.5	Hepworth (37)
	100.7	This investigation
CH_3ONH_2	49-50	Troube, Ohlendorf, and Zander (43)
	48.4	This investigation
CH_3ONHCH_3	42.2-42.6	Jones (31)
	42-43	Major and Fleck (32)
	42.4	This investigation
$CH_3ON(CH_3)_2$	30	Jones and Major (33)
	30.2	This investigation

TABLE 8

HEATS OF VAPORIZATION AND TROUTON CONSTANTS OF HYDROXYLAMINE AND ITS METHYL SUBSTITUTED DERIVATIVES

Compound	Boiling Point °K., 760 mm.	ΔH Vap. cal./mol.	ΔH/T eu.
$HONH_2$*	383.2	16,600	43.4
$HONHCH_3$	388.2	11,880	30.6
$HON(CH_3)_2$	373.9	9,560	25.6
CH_3ONH_2	321.4	7,630	23.8
CH_3ONHCH_3	315.6	7.370	23.4
$CH_3ON(CH_3)_2$	303.4	6,300	20.8

*The data for hydroxylamine, taken from the tables of Stull (44), were compiled from very early and crude measurements. The entropy of vaporization is undoubtedly too high.

Both the four-necked titration flask and the buffer solution were thermostated at 25 ± 0.1°.

The dilute solution of the amine hydrochloride was then titrated with 0.05 N NaOH from a 5 ml. micro burette. The pH of the solution was recorded after the addition of each 0.2 ml. of base; near the endpoint much smaller increments were taken.

The pKa of the amine was then calculated over the middle third of the titration curve by the formula:

$$pKa = pH + \text{Log} \frac{\text{total ml. NaOH} - \text{ml. NaOH}}{\text{ml. NaOH}} .$$

The values calculated over the central portion of the curve rarely deviated by more than 0.005 pK unit from their average. The titrations were repeated using 100 ml. aliquots of the same hydrochloride solution and adding weighed amounts of KCl to vary the ionic strength of the solution. The averages from these titrations were then plotted as a function of the square root of the ionic strength and the extrapolated value of pKa at infinite dilution was obtained.

The glass electrode was used in this study because of its simplicity and because of errors arising from the reducing action of hydroxylamine on the noble metal salts of the usual reference electrode (45). In order to estimate the magnitude of the errors in the procedure, the constant for NH_4OH was determined using the identical procedure. The value obtained, pKb 4.73, is in reasonably good agreement

with the precision value of Bates and Pinching (46), who reported a value of 4.751. In view of the inherent errors in the glass electrode, such as the asymmetry potential, and the uncertainties in standardizing the pH meter, the error which has been assigned to the pKb values of these hydroxylamines is ± 0.02 pK unit.

The base strengths of hydroxylamine and methoxyamine have been reported previously in the literature. The basic ionization constant usually reported for hydroxylamine (47, 48) is the early value of Winkelbleck (49), 6.6×10^{-9}, corresponding to a pKb of 8.18. The pKb value, 7.40, given by Ishikawa and Aoki (50) appears to be erroneous. The value closest to that found in this investigation (8.03) is that of Kolthoff and Stenger (51) who listed the pKb of hydroxylamine as 7.97. The ionization constant for methoxyamine of 2.4×10^{-5} recently reported by Vodrazka (52) corresponds to a pKa of 4.62. This is within the assigned error of the value obtained, pKa 4.60.

Brown (53) has found that the series of methylamines display the same order of base strengths when trimethylborane is used as the reference acid, as they do when one uses the proton. If the inductive effect of the methyl group was the only factor in determining the strength of the base, the order expected would be $NH_3 < NH_2CH_3 < NH(CH_3)_2 < N(CH_3)_3$. The order actually observed with a proton and with trimethylborane as reference acids is $NH_3 < N(CH_3)_3 < NH_2CH_3 < NH(CH_3)_2$.

TABLE 9

pKa VALUES FOR AMMONIA, HYDROXYLAMINE, AND METHYL SUBSTITUTED HYDROXYLAMINES

Compound	Ionic Strength	$\sqrt{\mu}$	Average Apparent pKa	Value of pKb at Infinite Dilution
NH_3	0.058	0.241	9.310	
	0.0213	0.146	9.298	
	0.0025	0.050	9.277	
	0.00	0.00	9.27	4.73 ± 0.02
$HONH_2$	0.0226	0.150	6.012	
	0.0075	0.087	5.997	
	0.0023	0.048	5.985	
	0.00	0.00	5.97	8.03 ± 0.02
$HONHCH_3$	0.0226	0.150	6.002	
	0.0100	0.100	5.968	
	0.0034	0.058	5.969	
	0.0026	0.051	5.983	
	0.00	0.00	5.96	8.04 ± 0.02
$HON(CH_3)_2$	0.0626	0.252	5.276	
	0.0212	0.145	5.246	
	0.0026	0.051	5.218	
	0.00	0.00	5.20	8.80 ± 0.02
CH_3ONH_2	0.100	0.316	4.674	
	0.044	0.210	4.652	
	0.022	0.148	4.639	
	0.0091	0.095	4.601	
	0.00216	0.047	4.611	
	0.00	0.00	4.60	9.40 ± 0.02
CH_3ONHCH_3	0.0615	0.248	4.780	
	0.205	0.143	4.768	
	0.00223	0.048	4.752	
	0.00	0.00	4.75	9.25 ± 0.02
$CH_3ON(CH_3)_2$	0.0672	0.259	3.746	
	0.0206	0.144	3.704	
	0.00223	0.047	3.671	
	0.00	0.00	3.65	10.35 ± 0.02

A number of theories have been proposed to explain this order of base strengths of alkyl amines (53-56). The opinion is divided as to whether the inductive effect of the alkyl group is opposed by a steric factor or by solvent interaction. Brown (53) has argued that the decrease in the basicity of $(CH_3)_3N$ is due to a steric strain, operating at the back of the molecule, by the three bulky methyl groups on the small central atom (B strain). Trotman-Dickenson (54) has noted that the replacement of hydrogens on the amine by alkyl groups reduces the hydration energy for the ammonium ion form, since the bonding between the amine ion and solvent is through the hydrogens of the former.

The base strengths of hydroxylamine and its methyl derivatives, which have been measured in this investigation, display the same order as ammonia and its methyl derivatives. In Figure 1 the pKa values of the methylamine series and the experimental values for the hydroxylamines are plotted as a function of the number of substituents replacing hydrogen on the nitrogen atom. The oxygen atom is somewhat smaller than a methyl group but it is much larger than the hydrogen atom. Therefore, hydroxylamine is placed in the vertical row with methylamine rather than with ammonia, since the steric relationships would be more nearly comparable.

The similarity between the two series of hydroxylamines and the methylamine series is immediately apparent. The inductive effect of the methyl group in going from one

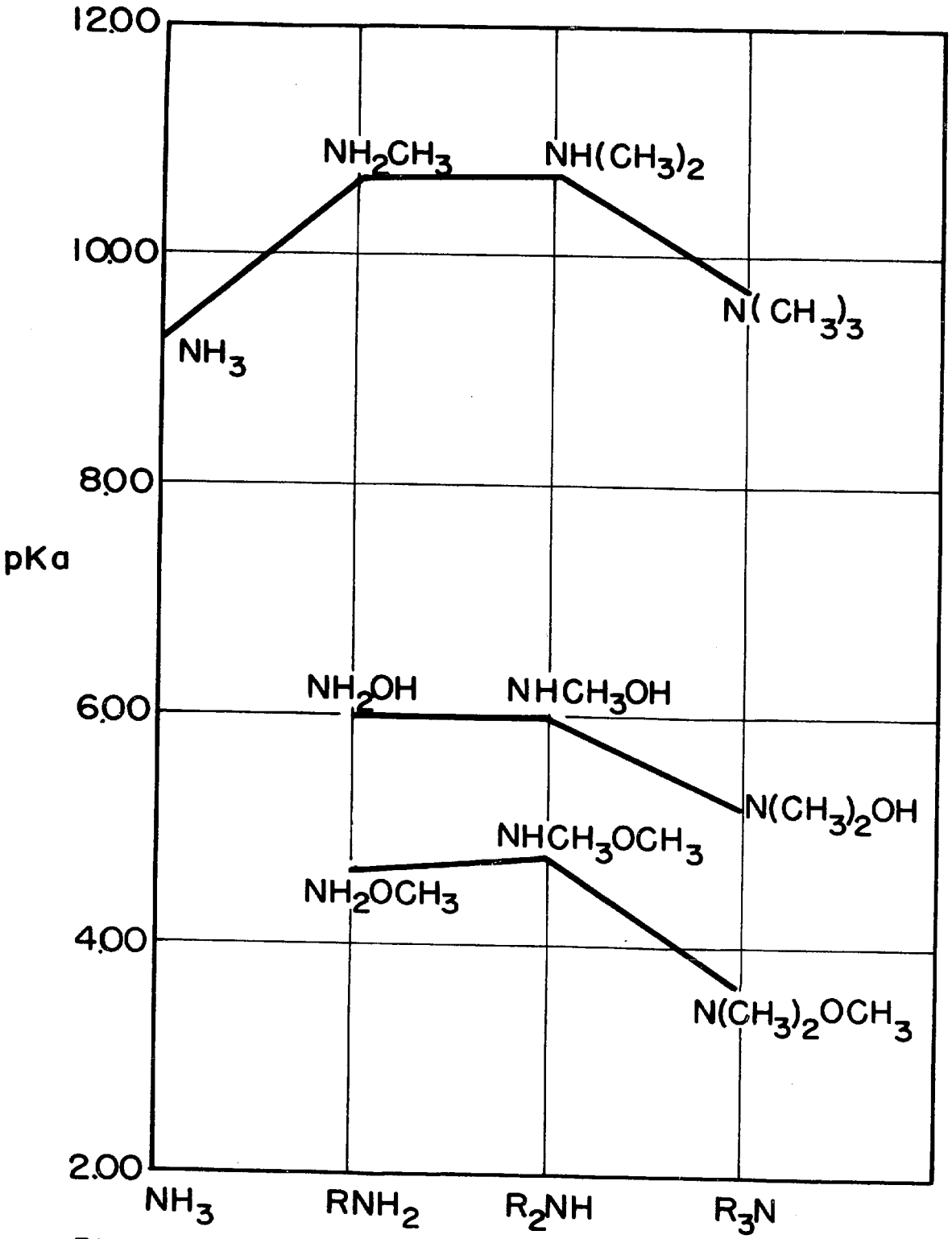


Figure 1. pKa Values for CH_3, OH, and OCH_3 Substituted Amines

to two substitutents is small and is zero in the hydroxylamines containing the OH group. In going from two to three substituents there is a large decrease in the base strength for all three series.

The electron-withdrawing power of the hydroxyl group is seen to reduce the electron-donating power of the nitrogen by a large amount. The difference between the hydroxyl and the methoxy series is much smaller. On the basis of an inductive effect alone it would be expected that methoxyamine would be slightly stronger than hydroxylamine, but the converse is seen to be true. This anomalous effect of the methoxy group is known in other instances. An example is methoxyacetic acid, CH_3OCH_2COOH (pKa 3.48), which is a stronger acid than glycolic acid, $HOCH_2COOH$ (pKa 3.82).

The values obtained for these hydroxylamines can be correlated best in terms of the steric strain model proposed by Brown. If solvation was the important factor one would expect a different order with the amines containing an OH group, since this hydrogen would contribute to the bonding with the solvent. This does not appear to be the case.

Reaction of Methyl Substituted Hydroxylamines with Diborane

Reaction of Methoxyamine with Diborane

The details of the reaction of methoxyamine with diborane were essentially the same as those described by Campbell (2). The free base was prepared and purified as

described previously. It was shown that small amounts of impurities, particularly ammonia and other methoxyamine decomposition products, had a very large influence on the course of the reaction. These effects will be described later.

In a typical run, approximately 0.3 gram of the amine was weighed out in a micro weighing tube and transferred into the reaction tube. The reaction tube was equipped with a manometer and an electromagnetic stirrer. One to five milliliters of anhydrous diethyl ether, which had been dried for several days over CaH_2, were distilled into the reaction tube and the mixture stirred until solution was complete. This solution was then frozen with liquid nitrogen and a small excess of diborane added. (Based on two moles of the amine reacting with one of diborane.) The diborane was measured as the vapor in a calibrated trap. The reaction tube and its contents were then warmed up to the temperature of a carbon disulfide slush bath (-112°). The contents were stirred with the electromagnetic stirrer. Within 15 to 20 minutes a decrease in the pressure of the diborane and the appearance of a white precipitate indicated that the reaction had occurred at -112°. The system was then warmed to -80°, stirred for another half hour, and the excess diborane and ether removed from the addition compound.

The quantitative separation of the ether and diborane required careful fractionation. A bath at -80° was placed on the tube containing the mixture. The vapors were then

passed through a trap at -112° to retain the ether, and the diborane was collected in a third trap at liquid nitrogen temperature. This process was repeated again with the ether collected in the second trap and a very small amount of additional diborane was isolated. The diborane fractions were distilled from a trap maintained at -155° by a mixed pentane bath. Vapor pressures of the ether at 0° and of the diborane at -112° showed that both fractions were pure.

The stoichiometry of the reaction indicated that two moles of methoxyamine react with one mole of diborane. The data from a number of runs are listed in Table 10.

TABLE 10

STOICHIOMETRY OF THE REACTION BETWEEN METHOXYAMINE AND DIBORANE

Run No.	mmoles CH_3ONH_2	mmoles B_2H_6	ratio CH_3ONH_2/B_2H_6
8	6.78	3.42	1.98
9	5.64	2.80	2.01
10	7.15	3.57	2.00
11	7.69	3.88	1.98
14	6.24	3.12	2.00

The methoxyamine-borane is a white solid which melts with decomposition at 55°. The vapor pressure of the addition compound is negligible at room temperature but is detectable at 40° since in one run part of a sample, which was

heated at 40° for several hours, sublimed into the cooler portions of the tube. It is very soluble in ether at temperatures above 0° but precipitates out when cooled much below that temperature. At 25° it decomposes very slowly. A 4.82 mmole sample, after standing 24 hours at room temperature, lost only 0.4 mmole of hydrogen, indicating that less than 10% of the compound had decomposed.

A quantity of the addition compound was hydrolyzed with dilute hydrochloric acid and analyzed for "active" hydrogen and boron. The results were 4.63% "active" hydrogen (theory 4.96%) and 17.8% boron (theory 17.77%). The amount of methoxyamine hydrochloride in the hydrolysis products was estimated from a titration curve on an aliquot. This indicated that at least 93% of the nitrogen was still present as CH_3ONH_2.

The thermal decomposition of methoxyamine-borane was studied rather extensively. This decomposition can occur in two ways. If it is heated up to approximately 90° the material detonates violently, destroying all of the glassware in the vicinity. Due to the violence of this explosion, the decomposition products were never isolated and identified.

This decomposition can also be brought about slowly. As the temperature is gradually raised, the solid gives off hydrogen at a slow rate until a temperature of 55.0-55.5° is reached. The solid then melts down to a clear liquid and the rate of H_2 evolution is accelerated. Within ten minutes

or less at this temperature, two thirds of one mole of hydrogen is given off and the liquid becomes increasingly viscous. An additional four days are required at this temperature for another third of a mole of hydrogen to be liberated. A volatile solid, similar to that reported by Campbell, is released from the viscous mass during this heating period. The evolution of hydrogen did not stop at one mole but continued at a very slow rate. It was found experimentally that after the loss of one mole of hydrogen, the residue could be safely heated above 90°. Hydrogen evolution continued and the residue changed into a white solid. The heating was continued up to 300° and the residue was analyzed. The results were:

Boron	31.7%
Nitrogen	45.8%
Carbon	3.53%
Hydrogen	4.76%

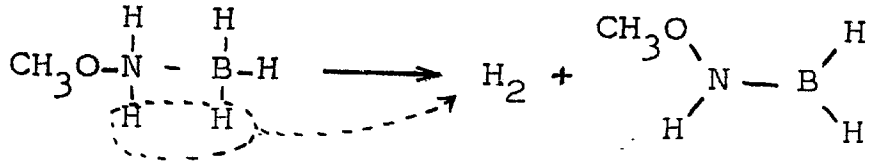
The empirical formula for the residue is, therefore, $B_1N_{1.12}(OCH_3)_{0.1}H_{1.3}$.

The sharp break in the rate of hydrogen evolution after loss of two thirds of one mole was difficult to correlate with a reasonable decomposition mechanism. Therefore, pure samples of methoxyamine-borane were prepared and the rate of decomposition at 55° studied as a function of dilution. Diethylene glycol dimethylether was chosen as a solvent because its vapor pressure (3 mm., 20°) is high enough to

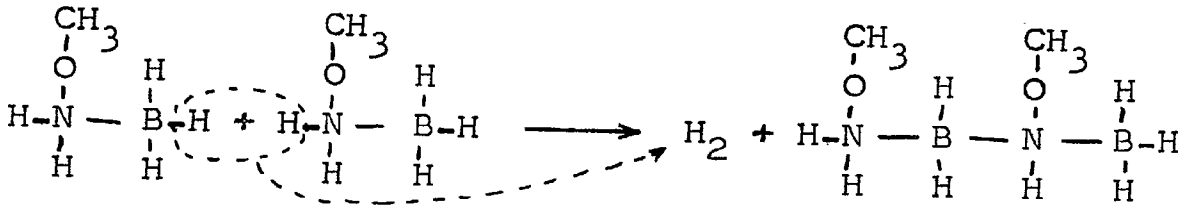
permit slow movement at room temperature in the vacuum line and yet low enough so that only small amounts would distill into the cooler portions of the reaction system. This solvent also has the advantage of dissolving both methoxyamine-borane and its decomposition products.

Figure 2 illustrates the decomposition of the pure compound, a 50% solution, and an approximately 10% solution as a function of time at 55.0°. It is at once apparent that the sharp break in the curve at two-thirds of one mole of hydrogen disappears when a solvent is introduced.

These data can be used to consider possible decomposition mechanisms. If the liberated hydrogen was produced by an intramolecular reaction between the protonic hydrogens on the nitrogen and the hydridic hydrogens on the boron, the reaction would be first order and one mole of hydrogen would be evolved per mole of borane adduct.



Another possibility would be an intermolecular loss of H_2 which would follow second order kinetics.



Since the resulting dimer has hydridic and protonic hydrogens on the end atoms, it could react further to increase the chain length. If the resulting chains were long or could

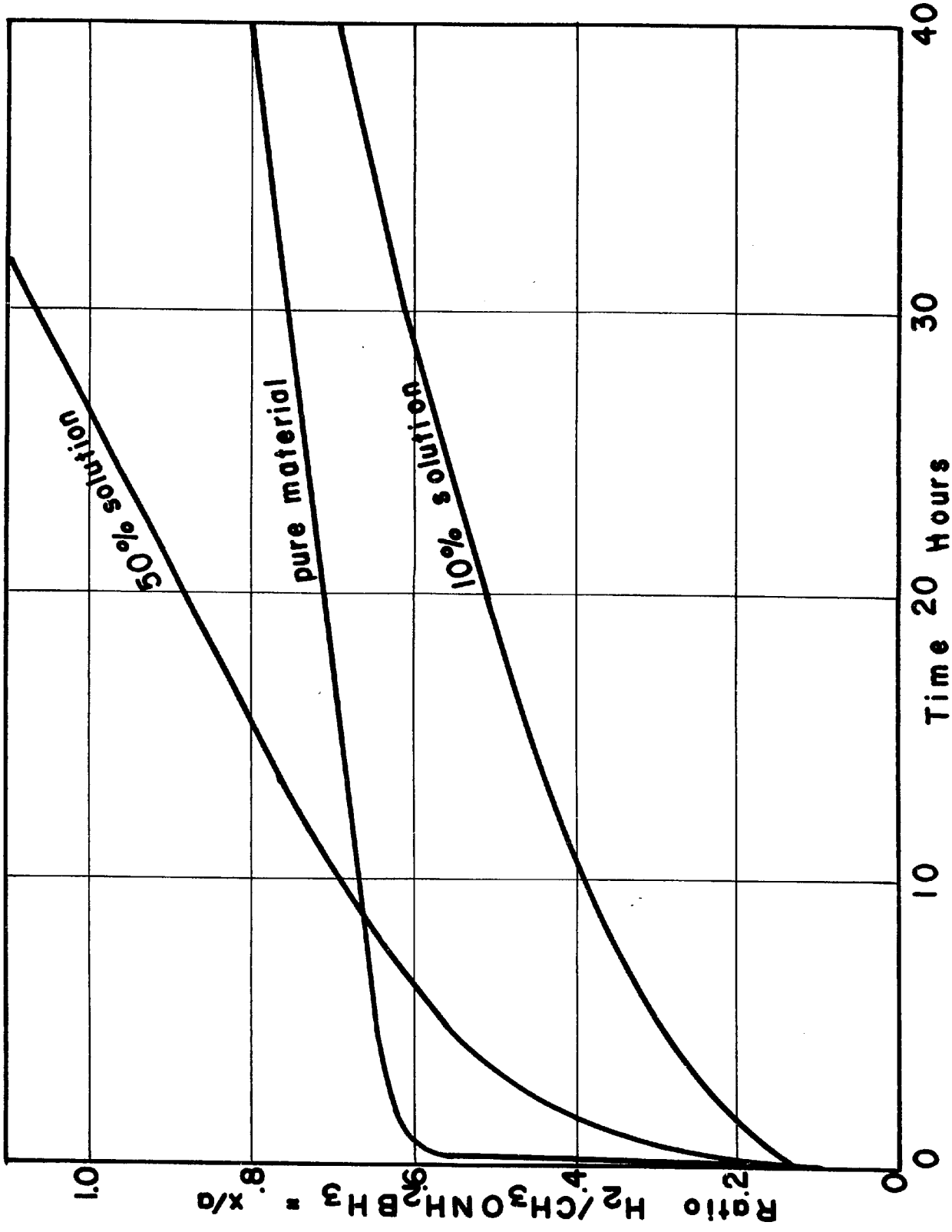


Figure 2. Decomposition of $NH_2OCH_3 \cdot BH_3$ at 55.0° C.

cycle, the over-all stoichiometry would be the same as for the postulated first order reaction, i.e., one mole of hydrogen liberated per mole of starting material.

Both of these mechanisms would be complicated by the partial loss of a second mole of hydrogen since both protonic and hydridic hydrogens are still available. This would result in unsaturated bonds within the polymer or cross-linking between chains.

In Figure 2 the fraction decomposed, x/a, is plotted as a function of time, where x is the number of moles of hydrogen at time t, and a is the initial number of moles of $CH_3ONH_2BH_3$. Assuming that one mole of hydrogen is liberated for each mole of starting material decomposed, the order of the reaction was considered. The first order rate equation is $-dc/dt = kc$, where c is the concentration of $CH_3ONH_2BH_3$ expressed as moles per unit volume of solution. Substituting $(a-x)/v$ for c yields:

$$-\frac{d[(a-x)/v]}{dt} = k\frac{(a-x)}{v}$$

Multiplying both sides of the equation by the constant v and dividing by the constant a converts the rate equation to the form:

$$\frac{d(x/a)}{dt} = \frac{k(a-x)}{a}.$$

In other words, the per cent decomposed at any time would be independent of the volume of the solution if the reaction were first order. The observed decomposition curves

show that this is not the case. The rates of decomposition of the two solutions were calculated at about 40% decomposition. The rate for the more dilute solution was 2.4×10^{-2} moles/liter/hour at a concentration of 1.0 mole/liter, while the rate for the concentrated solution was 52×10^{-2} moles/liter/hour at a concentration of 4.1 moles/liter, corresponding to an order of 2.2 for the reaction.

When 1/c is plotted against time for the 10% solution a straight line was obtained up to about 60% decomposition. Beyond this point, the amount of hydrogen obtained was greater than would be expected for a second order reaction. The partial liberation of a second mole of hydrogen would increase the amount of hydrogen observed, especially during the later stages of the decomposition. This secondary reaction becomes quite significant, as can be seen from the fact that the decomposition curves cross the line where $x/a = 1$ without an appreciable change in slope, and explains the apparent deviation from a second order reaction as the ratio x/a approaches 1.

The decrease in the rate of decomposition $[d(x/a)/dt]$ with dilution is a very large effect and could not be mistaken experimentally. It is, therefore, concluded, from the limited data available, that the decomposition of methoxyamine-borane involves an intermolecular loss of hydrogen in the concentrated solutions which were studied. In dilute solution it is still possible that an intramolecular splitting out of hydrogen could be the predominant mechanism.

Such an intermolecular reaction would produce a polymerization, correlating the visual observation of the increase in viscosity of the residue. The sharp break at two thirds of one mole of hydrogen for the pure compound is attributed to this polymerization, which increases the viscosity to such an extent that the unreacted methoxyamine-borane is trapped in the polymeric network, and the reaction with another molecule of the same becomes greatly hindered. The fact that the curve for the 50% solution crosses the curve for the pure compound substantiates this explanation, since the solvent reduces the viscosity to a point where this intermolecular reaction is not hindered.

The volatile solids, which are given off in the decomposition of $CH_3ONH_2BH_3$, were found to be a complex mixture of NH_3, $B(OCH_3)_3$, and on occasion CH_3OH. The chief component of the mixture is the weakly associated compound $NH_3 \cdot B(OCH_3)_3$. In the vapor phase this system exists entirely as NH_3 and $B(OCH_3)_3$. The identification of this mixture was approached in several ways. The mixture does not give off any hydrogen when it is hydrolyzed, and traces of methyl alcohol were qualitatively identified in the hydrolysis products. An examination of a potentiometric titration curve showed that no methoxyamine was present but rather that the nitrogen was present as ammonia. Goubeau (57) has studied the reaction of ammonia and the methylamines with trimethoxyborane. He used two equations to account for the decomposition of the compound $NH_3 \cdot B(OCH_3)_3$.

1) $NH_3B(OCH_3)_3 \longrightarrow B(OCH_3)_3 + NH_3$ 90%

2) $2\ NH_3B(OCH_3)_3 \longrightarrow (CH_3O)_3BNH_2B(OCH_3)_2 + NH_3 + CH_3OH$ 10%

The second equation could account for the observation made in this research that the material cannot be transferred quantitatively in the vacuum line, and that white solids are always left in the traps after the mixture had been stored in them for a period of time.

The molecular weight, by vapor density, was measured on a portion of this volatile solid and a value of 70.3 was obtained. The same sample was then hydrolyzed and analyzed for boron and nitrogen. The results were 9.22% B and 7.52% N. This is equivalent to 88.4% $B(OCH_3)_3$ and 9.15% NH_3; a mixture of which, if completely dissociated in the vapor phase, would have a calculated molecular weight of 70.0. This agreement with the observed molecular weight was a strong confirmation of the identity of the mixture.

As a final check on the identity of the volatile solid, mixtures of NH_3, $B(OCH_3)_3$ and CH_3OH were made and studied. The trimethoxyborane was prepared by refluxing four moles of absolute methyl alcohol with one mole of meta boric acid. The resulting trimethoxyborane - methyl alcohol azeotrope was separated by adding anhydrous lithium chloride (58). The final purification step was a fractional distillation in the vacuum line. A boron analysis indicated that the resulting ester was 98% pure.

When an excess of anhydrous ammonia, distilled from

sodium, was added to $B(OCH_3)_3$ a solid product was formed. After removing the excess ammonia by fractional condensation, it was found that 2.60 mmoles of NH_3 had reacted with 2.64 mmoles of $B(OCH_3)_3$. The $NH_3 \cdot B(OCH_3)_3$ had a dissociation pressure of 31.2 mm. at 0° and was completely dissociated in the vapor phase since the apparent molecular weight was 61.4 (theory 121.05/2 or 60.5).

When NH_3 was allowed to react with an excess of $B(OCH_3)_3$, the addition compound could not be completely separated from the excess trimethoxyborane, since the vapor pressure of this ester is 37.3 mm. at 0° (59). The vapor tension exerted by this mixture was very slow in coming to equilibrium and values from 42 to 27 mm. at 0° were measured.

When small amounts of methyl alcohol, which has a vapor pressure of 29 mm. at 0°, were added to the $NH_3 \cdot B(OCH_3)_3$, there was, of course, a decrease in the apparent molecular weight of the mixture but very little change in the physical appearance. The vapor pressure was about 29 to 30 mm. at 0°. When there were small amounts of CH_3OH or excess $B(OCH_3)_3$ present with the $NH_3 \cdot B(OCH_3)_3$, it was very difficult to distinguish a liquid phase. These mixtures appeared visually to be a volatile solid over a large range of compositions.

In terms of physical appearance, vapor pressures, and dissociation in the vapor phase, these mixtures appeared in every way identical to the volatile solid isolated as one of the decomposition products of methoxyamine-borane.

The B/N ratio in the volatile products obtained from the decomposition was always greater than one. This checked with the fact that the B/N ratio in the solid residue (page 36) was less than one.

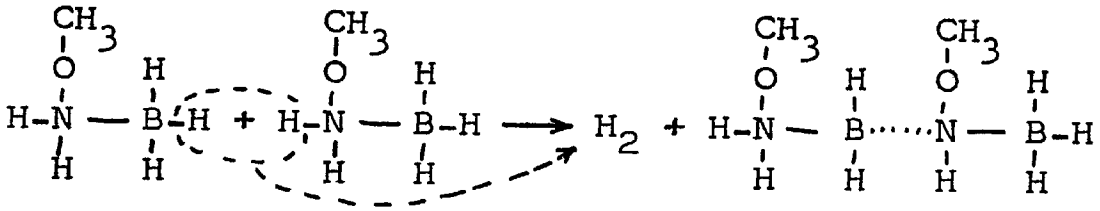
The isolation of trimethoxyborane demonstrated that the methoxy group which had been originally on the nitrogen had shifted to the boron. The amount to which this shift occurred was dependent on the amount of hydrogen lost from the methoxyamine-borane. Further data showed that a hydridic hydrogen from the boron had shifted over to the nitrogen. These shifts can be summarized as follows:

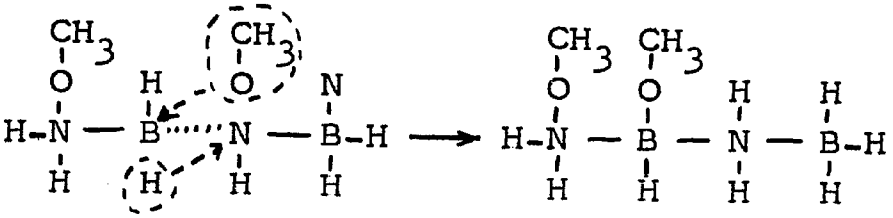
1. Before loss of H_2, hydrolysis of $CH_3ONH_2BH_3$ should liberate three moles of hydrogen and one mole of methoxyamine.

   $CH_3ONH_2BH_3 + 3\ H_2O \longrightarrow CH_3ONH_2 + B(OH)_3 + 3\ H_2$

   Run 9 in Table 11 illustrates this behavior.

2. After loss of one mole of H_2 by heating at 55° (equation (a)), the methoxy group shifts to the boron and a hydride unit shifts to the nitrogen (equation (b)). This hypothetical intermediate disproportionates at once to give the $NH_3 \cdot B(OCH_3)_3$ and a polymeric residue (equation (c)). As a result of the shift in equation (b), only one additional mole of hydrogen would be liberated by hydrolysis (equation (d)).

(a) 

(b) 

(c) $$\left[\begin{matrix} H & OCH_3 \\ | & | \\ N & B \\ | & | \\ H & H \end{matrix}\right]_x \longrightarrow 1/3\ NH_3 \cdot B(OCH_3)_3 + 1/3\ (HNBH)_x + 1/3\ (H_2NBH_2)_x$$

(d) $$1/3\ NH_3 \cdot B(OCH_3)_3 + 1/3\ (HNBH)_x + 1/3\ (H_2NBH_2)_x + 3\ H_2O \longrightarrow NH_3 + B(OH)_3 + CH_3OH + H_2$$

This "loss of an active hydrogen" is illustrated by the data in run 16 of Table 11 and is substantiated by the fact that the nitrogen has gained a hydrogen. Ammonia was shown to be present in the volatile solid produced in the decomposition. The presence of ammonia in the hydrolysis products was demonstrated by titration curves and by distillation of ammonia from the solution without prior reduction in the Kjeldahl analysis.

3. Upon heating the polymeric solid to higher temperatures, additional hydrogen is lost; the total approaching but never reaching two moles.

$$(HNBH)_x + (H_2NBH_2)_x \longrightarrow 2\ (BNH_z)_x + 3\text{-}z\ H_2$$

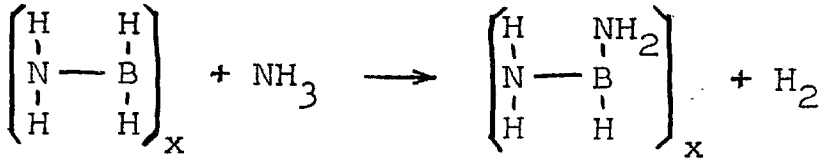
Runs 17 and 14 in Table 11 illustrate this behavior.

TABLE 11

DECOMPOSITION OF METHOXYAMINE-BORANE

Run No.	H_2 on Heating	Nitrogen as CH_3ONH_2	Further H_2 on Hydrolysis	Total H_2
9	0.016	0.93	2.80	2.82
16	0.97	0.02	0.99	1.96
17	1.59	0.02	0.34	1.93
14	1.70	0	0.13	1.83

These postulated reactions are not quantitative since a small amount of carbon was present in the residue after heating to 300°. Neither do they take into account the fact that the B/N ratio in the volatile solid was always greater than one. Part of the ammonia, instead of coming off with the $B(OCH_3)_3$, could have reacted with one of the polymeric species to form a diaminoborane unit.



The shift of a hydride unit to an adjacent atom is not unprecedented. Brown (24,25) reported several instances of the shift of a hydrogen from boron to an adjacent carbon atom. Also, the disproportionation reaction, in which three methoxy groups become attached to one boron atom, is common in boron compounds. Dimethoxyborane disproportionates reversibly (13).

$$6\ (CH_3O)_2BH \rightleftharpoons B_2H_6 + 4\ (CH_3O)_3B$$

The polymeric residue of "aminoborane" appears qualitatively similar to that reported by other investigators in that it is a nonvolatile solid which is insoluble in ether (23,60).

Methoxyamine has been shown to be a relatively weak base. The borane adduct was allowed to react with trimethylamine to see whether the methoxyamine could be replaced. The experiment was conducted by stirring pure methoxyamine-borane with an excess of trimethylamine for 17 hours in an ether solution at 0°. A 22% yield of trimethylamine-borane was isolated and identified by physical characteristics and analysis.

A competing reaction was the increased rate of decomposition of the $CH_3ONH_2BH_3$ in the presence of the $(CH_3)_3N$. As indicated by the evolution of hydrogen, 33% of the original compound had been decomposed in the same time.

When methoxyamine-borane is hydrolyzed by a base, the reduction of the nitrogen to ammonia and the loss of an "active" hydrogen are observed. In short, hydrogen shifts from boron to nitrogen as described previously for thermal decomposition. About 1 ml. of 50% KOH was added to a small amount of $CH_3ONH_2BH_3$. The resulting solution was heated up to assure complete hydrolysis. The $H_2/CH_3ONH_2BH_3$ ratio was found to be 2.12 instead of nearly 3 as when hydrolyzed with an acid. Also at least 62.5% of the original amine had been

reduced to ammonia. The NH_3 was purified by fractionation and characterized by its vapor pressure of 41 mm. at -80° and a molecular weight of 17.7. In order to eliminate the possibility that methoxyamine itself can be changed to ammonia by a strong base, 3.23 mmoles of methoxyamine and 1 ml. of 50% KOH were heated in a sealed tube at 100° for one hour. There were some losses in purifying and drying the amine but 2.46 mmoles or 76% of the amine was recovered in a pure condition. There was no compound more volatile than methoxyamine to suggest that any ammonia had been formed.

In some of the first attempts to prepare $CH_3ONH_2BH_3$, the adduct lost hydrogen at lower temperatures and a viscous liquid remained after the ether was removed. This was traced to a small amount of ammonia in the methoxyamine. When the methoxyamine was carefully purified, the borane addition compound was considerably more stable. This catalytic effect of an impurity was reproduced by adding 9% of ammonia to a carefully purified sample of methoxyamine and allowing the mixture to react with diborane as previously described. The resulting mixture of $CH_3ONH_2BH_3$ and $B_2H_6 \cdot 2NH_3$ changed into a liquid at room temperature and rapidly gave off hydrogen. After only one hour the ratio $H_2/CH_3ONH_2BH_3$ was 0.48.

Since boron trifluoride is a "stronger" Lewis acid than the borane group, the displacement of diborane from methoxyamine-borane was attempted using this reagent. Boron

trifluoride was prepared by heating ammonium tetrafluoroborate (III) with sulfuric acid (61). The method was scaled down to produce small quantities as needed. An ethereal solution of $CH_3ONH_2BH_3$ was prepared and a slight excess of BF_3 was added. The rate of decomposition of the $CH_3ONH_2BH_3$ was accelerated as evidenced by the hydrogen evolution, but the volatile materials upon examination consisted chiefly of ether and the boron trifluoride etherate. It was concluded that the BH_3 group could not be cleaved from the amine by the "stronger acid," BF_3.

Methoxyamine was found to explode both by spark and by heat. See Appendix B for details. It was, therefore, possible that the explosion of methoxyamine-borane at 90° was due solely to the amine part of the molecule. It was of interest to determine whether the attachment of a fourth group on the nitrogen increased or decreased the sensitivity of the amine to decomposition. The boron trifluoride addition compound with methoxyamine was prepared in benzene solution. This adduct was found to be a white solid melting at 86-88°. The compound was heated in a sealed tube up to temperatures of 300°. There was no violent decomposition but at the higher temperatures the solid turned dark. This evidence indicates that the explosive decomposition of methoxyamine-borane was associated with the reducing character of the BH_3 group.

Campbell, in his first reaction of methoxyamine with

diborane, obtained hydrogen evolution at a low temperature, and isolated a large yield of a liquid with a vapor pressure of 29 mm. at 0° and an apparent molecular weight of 62. This liquid slowly decomposed at room temperature to give diborane and a nonvolatile solid. In all his later runs he was unable to reproduce this material.

A number of trials using pure methoxyamine and various catalysts were unsuccessful. It was observed, however, that in his first reaction Campbell had not purified his methoxyamine from the ammonia which the crude material contained. In addition a portion of the methoxyamine had exploded and, as shown in Appendix B, one of the principal exposion products of methoxyamine is ammonia.

Therefore, various mixtures of methoxyamine and ammonia were allowed to react with diborane. It was found that small amounts of the same liquid could be isolated.

The volatile liquid was shown to be a weakly complexed mixture of diethyl ether and μ-monoaminodiborane. $H_2NB_2H_5$ can act as a rather strong Lewis acid since it contains a bridge hydrogen. For example, it has been shown that it forms very stable addition compounds with trimethylamine and ammonia (23). Although the complexing with ether has not been reported previously, it is not unexpected for the compound. Since the molecular weight of B_2H_7N is 42.7 and that of ether is 74.12, the apparent molecular weight of a 1-1 mixture which is completely dissociated in the vapor state

would be 58.4. This is close to the value observed by Campbell.

The μ-monoaminodiborane was characterized after separation from the ether. This was achieved by complexing the ether with stronger acids. Aluminum chloride and boron trifluoride were used with about equal success. In Table 12 are shown the results of analysis on a 7.7 mg. sample of the purified μ-monoaminodiborane. Since the weighing and quantitative transfer to a hydrolysis tube of such a small amount of this material was a very difficult experimental problem, only the B/N/"active" H ratio was obtained rather than the absolute percentages.

TABLE 12

CHARACTERIZATION OF μ-MONOAMINODIBORANE

	Observed	Literature (23)
Molecular Weight	46.6	42.7
Vapor Pressure -23°	7.8 mm.	7.64 mm.
0°	32.4 mm.	32.3 mm.
18.9°	85.4 mm.	86.8 mm.
Melting Point	above -78°	-66.4°
B/N/"active" H ratio	1/1.99/4.86	1/2/5

These observations, together with the disproportionation of the liquid to give B_2H_6 and a solid polymer, provide an unequivocal identification of this material. However,

all attempts to obtain a large yield such as was reported by Campbell were unsuccessful.

Reaction of O,N-Dimethylhydroxylamine with Diborane

The O,N-dimethylhydroxylamine was prepared as described previously. It was found that the procedure used for the reaction of methoxyamine with diborane would work very satisfactorily for the reaction of the O,N-dimethyl derivative. The use of ether as a solvent was necessary in the reaction with CH_3ONH_2 in order to obtain a stoichiometric reaction and to prevent hydrogen evolution at low temperatures. However, it was found that $CH_3ONHCH_3BH_3$ could be prepared more conveniently without the use of a solvent and good stoichiometry was always observed. A typical preparation of the addition compound with diborane without the use of a solvent is described below.

A quantity (0.2068 g. or 3.39 mmoles) of CH_3ONHCH_3 was weighed out in a weighing tube and distilled into a reaction tube. An excess of B_2H_6, 3.57 mmoles, was condensed in a ring above the frozen amine. The liquid nitrogen was then poured out of the Dewar flask and the flask replaced on the reaction tube. The reaction mixture was then allowed to warm up slowly to room temperature over a period of several hours. The tube was then frozen down and any hydrogen "Toeplerized" off. In this run 0.047 mmole of H_2 was obtained. This is slightly over 1% decomposition. A mixed pentane bath was placed on the tube and the excess diborane

distilled out and measured as 1.85 mmoles. This means that 1.72 mmoles of B_2H_6 had reacted, giving a ratio of CH_3ONHCH_3/B_2H_6 of 1.97.

The product, O,N-dimethylhydroxylamine-borane, is a liquid at room temperature. The melting point was determined visually as -23 to -21°. The vapor pressure of the adduct could not be measured with a mercury manometer, but the material could be transferred under high vacuum at room temperature without decomposition.

An analysis gave a B/N/"active" H ratio of 1/0.97/2.92. Upon hydrolysis, the original amine, O,N-dimethylhydroxylamine, can be recovered. The solution containing the hydrolysis products was placed in a micro Kjeldahl distillation apparatus and made alkaline with 50% KOH. The amine was then distilled out and collected in dilute HCl. This solution was evaporated to dryness in a vacuum desiccator and the hydrochloride salt recrystallized from absolute methyl alcohol by adding dry ether. The melting point of the salt was 114-115° as compared with the literature value of 115-116° (32) for $CH_3ONHCH_3 \cdot HCl$.

The addition compound appears to be largely monomeric as judged by vapor pressure depression measurements in diethyl ether. It is very soluble in this solvent. A value of 90 was obtained at a concentration of 4.6 grams per mole of solvent. The theoretical value for a monomer is 74.93.

$CH_3ONHCH_3BH_3$ is more stable than the methoxyamine adduct and only traces of hydrogen are liberated in its

preparation and upon standing for long periods at room temperature. Upon heating two different types of decomposition were observed as was the case for the previous compound. When heated rapidly to 100°, the compound undergoes explosive decomposition. It was found that a well-annealed bomb tube could withstand the shock of the explosion and the products could be isolated and identified.

A quantity (3.71 mmoles) of the compound was prepared in a bomb tube, which was sealed off and placed on a steam cone. In a short time it was noticed that the tube contained a solid material which ranged in color from yellow to black. The tube was then reopened to the line with a vacuum tube opener and the volatile products removed. A total of 13.72 mmoles of noncondensable gases was collected. From the molecular weight and combustion over hot CuO, the components were: 9.24 mmoles H_2, 0.32 mmole N_2 and 4.16 mmoles CH_4. Further details of the gas analysis techniques are described in Appendix B.

The condensable portions of the volatile materials were separated by fractional distillation, and 0.107 mmole of impure C_2H_6 and 0.84 mmole of HCN were found. The HCN was characterized by molecular weight, melting point, vapor pressures, and reaction with silver nitrate (see Table 13).

TABLE 13

CHARACTERIZATION OF HYDROGEN CYANIDE

		Observed	Literature
Molecular Weight		29.7	27.03*
Vapor Pressure	0°	257.1 mm.	264 mm.
	-22.8°	76.4 mm.	77 mm.
	-45.2°	14.5 mm.	14 mm.
Melting Point		-14.6°	-13.2°

*The observed molecular weight would be expected to be somewhat high since HCN is reported to be 18% associated at the boiling point and one atmosphere (62).

The solid nonvolatile residue from the explosion was scraped out and analyzed. The composition was found to be:

B 24.8%
N 22.7%
C 4.99%
H 2.97%
O remainder or 44.5% .

The carbon is probably present as free carbon since after boiling some of this residue with dilute nitric acid, a black flocculent solid remained.

This explosive decomposition is obviously very complex and involves a number of simultaneous processes. The results may be summarized by the equation:

$$3.71 \text{ mmoles } CH_3ONHCH_3BH_3 \longrightarrow 9.24 \text{ mmoles } H_2 + 4.16 \text{ mmoles } CH_4 + 0.107 \text{ mmole } C_2H_6 + 0.32 \text{ mmole } N_2 + 0.84 \text{ mmole HCN} + x \text{ mmole } (B_{2.3}N_{1.62}O_{2.79}H_{2.97}C_{0.38}) .$$

The appearance of large amounts of H_2 is to be expected in view of the reaction between protonic hydrogen attached to nitrogen and the hydridic hydrogens attached to boron. Additional amounts of the hydrogen would also be expected from pyrolysis of BH_3 and cracking of hydrocarbon groupings at high localized temperatures. The cracking is also suggested by the presence of small amounts of carbon in the solid residue. N_2 is a normal explosion product of nitrogen containing compounds. The appearance of methane and ethane suggests the splitting off of some methyl free radicals in the decomposition, and subsequent reduction with hydrogen to give CH_4 or combination to give C_2H_6. The appearance of HCN in the products was rather unexpected, but can be accounted for in terms of the decomposition of the original H-C-N linkage in the molecule. Finally, the explosive nature of the reaction is to be associated with the rapid oxidation of the BH_3 group by the CH_3ONHCH_3. The energy released in formation of the B-O linkage would be large, which accounts for the observation that all of the boron and oxygen were present in the solid residue probably as B_2O_3. The rest of the boron was tied up as some $(BNH_z)_x$ polymer.

When the O,N-dimethylhydroxylamine-borane is heated at 65° for a period of time, the decomposition takes a different course. Approximately one mole of hydrogen is lost and the resulting unsaturated intermediate undergoes a shift and a disproportionation.

The shift of an "active" hydrogen was proved very conclusively. A sealed tube was made which had two break-tips. A quantity (3.345 mmoles) of $CH_3ONHCH_3BH_3$ was prepared in this tube. The tube was sealed off and heated at 65° for 48 hours. Upon opening the tube and "Toeplerizing," 3.12 mmoles of H_2 were found. Three milliliters of dilute HCl were then distilled into the tube. The side arm was sealed off again and the contents hydrolyzed for 39 hours at 100°. Upon opening the tube for the second time, an additional 3.79 mmoles of H_2 were recovered.

The results show that 3.12 mmoles of hydrogen were obtained upon pyrolysis; a corresponding amount of 3.12 mmoles of hydrogen shifted from boron to nitrogen and the remaining "active" hydrogen, 3.79 mmoles, was determined by acid hydrolysis. This gives a total of 10.03 mmoles of "active" hydrogen accounted for, in excellent agreement with the 3 x 3.34 or 10.04 mmoles in the original compound.

The methoxy group had simultaneously shifted from the nitrogen to the boron. An improved technique led to a good isolation and characterization of trimethoxyborane (methyl borate). Since the trimethoxyborane from the decomposition was weakly complexed with methyl- or dimethylamine as it was with ammonia in the decomposition of $CH_3ONH_2BH_3$, isolation by trap to trap distillation was impossible. Therefore, an excess of diborane was added to the volatile decomposition products. Since BH_3 is a much stronger

electron acceptor than $B(OCH_3)_3$, the amines were complexed as the amine-boranes. The problem of separating the excess diborane from the trimethoxyborane was then simple.

The characterization of the $B(OCH_3)_3$ isolated by this procedure is summarized in Table 14.

TABLE 14

CHARACTERIZATION OF TRIMETHOXYBORANE FROM THE DECOMPOSITION OF O,N-DIMETHYLHYDROXYLAMINE-BORANE

		Observed	Literature (59)
Vapor Pressure	-22.9°	9.7 mm.	9.4 mm.
	0°	36.8 mm.	37.3 mm.
	9.7°	60.8 mm.	62.6 mm.
	19.4°	98.9 mm.	101.3 mm.
Melting Point		-29.0°	-29.3 ± 0.1°
Molecular Weight		114.6	103.9
"Active" Hydrogen		0%	0%
Boron		10.05%	10.41%

An attempt was made to identify the amines which had been complexed with the $B(OCH_3)_3$. The borane adducts were hydrolyzed with dilute HCl. The resulting solution was made basic with KOH and the amines distilled out and dried over BaO. Vapor pressures and molecular weight showed that dimethylamine was the chief component, contaminated with what was probably a small amount of methylamine.

In addition to the hydrogen and the trimethoxyborane-amine complex, there was a liquid of low volatility and a

white crystalline solid produced in the decomposition of $CH_3ONHCH_3BH_3$. Since these white crystals appeared to be a definite chemical compound, a thorough investigation of their identity and properties was conducted.

$CH_3ONHCH_3BH_3$ was prepared and heated for at least 24 hours in a sealed tube at 65°. This length of time was found necessary to avoid the previously mentioned explosive decomposition. The temperature was then raised to 100° for several hours. Upon cooling, white needles appeared in the liquid on the bottom of the tube. The sealed tube was opened to the vacuum line with the vacuum tube opener and the hydrogen and volatile materials removed. A beaker of boiling water was placed on the bottom of the tube and the white solid sublimed under high vacuum. A ring of white needles collected on the walls of the tube just above the level of the heating bath. The tube was removed from the line, broken on each side of the ring of crystals, and the product scraped off the glass.

This procedure was repeated a number of times to obtain sufficient material for characterization. The maximum yield obtained was about 22%. Chemical analysis indicated that the compound was composed of the (CH_3NHBH_2) unit (see Table 15).

Once the unit was known it was apparent that the product could be prepared more conveniently by heating methylamine-borane (16). Such was found to be the case and yields of 80 to 90% were obtained. The crystals from both

methods of preparation were shown to be identical by comparing their X-ray powder patterns.

In a typical preparation starting from methylamine, 3 mmoles of diborane were condensed with liquid nitrogen together with a small excess of anhydrous methylamine (7 mmoles). The mixture was then allowed to warm up to room temperature over a period of about 3 hours. A small amount of hydrogen is produced in this preparation of methylamine-borane. 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 the 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 transferred to 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 material sublimed under high vacuum. The product collected as a ring of fine needles and was removed as previously described. The yield was about 0.22 gram or 85%.

The analysis on the material is summarized in Table 15.

The methylamine preparation gave enough material to use conventional macro scale molecular weight methods. All previous attempts using modifications of the micro-Rast method were unsuccessful. The cryoscopic depression of the freezing points of benzene and nitrobenzene were determined

TABLE 15

ANALYSIS OF TRIMERIC N-METHYLAMINOBORANE

	Observed	Calculated for (CH_3NHBH_2)
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

using a conventional 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 depression of liquid ammonia, in which the compound is quite soluble. The apparatus designed by Schultz (21a) was modified by using a large slush bath of 1,2-dichloroethane 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.

The molecular weight measurements in liquid ammonia were rechecked independently in this laboratory after the introduction of several improvements in the molecular weight apparatus. The precise values which were obtained in dilute solutions demonstrated unequivocally that the material was trimeric.

The compound may be recrystallized from methyl or ethyl alcohols 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, but is insoluble in carbon tetrachloride, petroleum ether, and water. The insolubility in the latter may be primarily a wetting problem.

The density of the compound is 0.90 g./cc., 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./cc.

A sample of the solid was allowed to stand exposed to the moist air of the laboratory for months, after 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.

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 H_2, identified by a molecular weight of 2.07 were found. This gives a ratio of hydrogen per mole of $(CH_3NHBH_2)_3$ 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

$$(CH_3NHBH_3)_2 \xrightarrow{200°} 3\ H_2 + (CH_3NBH)_3 .$$

The characterization of the 1,3,5-trimethylborazene is summarized in Table 16.

TABLE 16

CHARACTERIZATION OF 1,3,5-TRIMETHYLBORAZENE

		Observed	Literature (17)
Vapor Pressures	50.6°	38.8 mm.	40.2 mm.
	55.2°	48.6 mm.	49.3 mm.
	60.3°	61.1 mm.	61.4 mm.
	64.8°	72.1 mm.	74.2 mm.
	70.0°	91.9 mm.	91.6 mm.
	74.8°	111.8 mm.	110.7 mm.
Molecular Weight of Vapor at 75°		126	122.5
Melting Point		-1 to 0°	-9°

The fact that the melting point is significantly higher is probably due to the higher purity since the isolation of the trimeric N-methylaminoborane would represent an additional purification step.

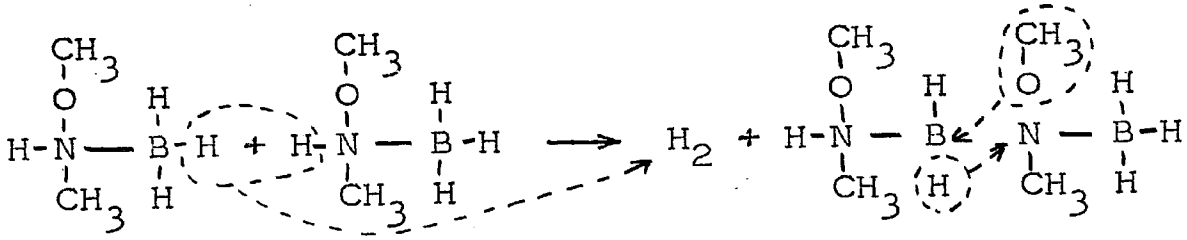
In Table 17 are listed the interplanar spacings ("d" values) and the relative line intensities found to be characteristic of the compound. Copper Kα radiation and a 57.2 mm. cylindrical camera were used. The capillaries were of low absorbing glass, 0.2 mm. in diameter with 0.01 mm. wall thickness.

TABLE 17

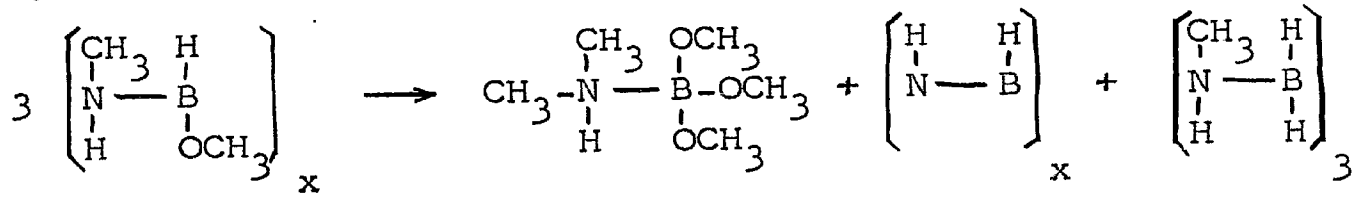
X-RAY POWDER DIFFRACTION DATA ON TRIMERIC N-METHYLAMINOBORANE

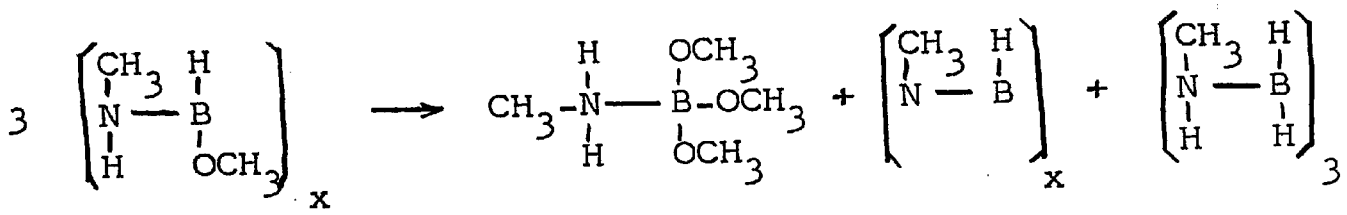
d Å	I	d Å	I	d Å	I
7.1	VS	2.68	VW	1.20	VW
4.26	VS	2.29	W	1.88	VW
4.00	MS	2.27	W	1.77	VW
3.45	M	2.19	W	1.70	VW
3.06	VW				

The isolation and identification of trimeric N-methylaminoborane provided the necessary information to write equations for the decomposition of the O,N-dimethylhydroxylamine-borane. The splitting out of hydrogen is immediately followed by a shift of a methoxy group and a hydride unit.



This hypothetical intermediate disproportionates at once to give the observed products. It can be noted that both methyl- and dimethylamines can be complexed to the trimethoxyborane as a result of the disproportionation.





Experimentally it was observed that more than one mole of hydrogen was produced in the decomposition at 100°. The amount found ranged between 1.1 and 1.2 moles per mole of compound. The additional hydrogen is produced in the secondary reactions

$$(HN - BH)_x \longrightarrow (NBH_z)_x + (1 - z/2)x\ H_2$$

and $(CH_3NHBH_2)_3 \longrightarrow (CH_3NBH)_3 + 3\ H_2$.

Small amounts of material having a vapor pressure close to that of the 1,3,5-trimethylborazene were isolated from the decomposition products. It was contaminated with other materials and attempts at purification by vacuum fractionation were unsuccessful.

The remaining experiments which were conducted with the O,N-dimethylhydroxylamine-borane included the reaction with trimethylamine and hydrolysis by a base. The decomposition with 50% KOH produced reduction of the nitrogen and "loss of an active hydrogen" just as was observed with the methoxyamine adduct. After preparing 1.463 mmoles of $CH_3ONHCH_3BH_3$ in a bomb tube, 2 ml. of 50% KOH were admitted through a side arm. The tube was evacuated, sealed and heated at 100°. On opening the tube, 3.04 mmoles of H_2 were found. The ratio H_2/compound is 2.08. (Acid hydrolysis gave a ratio of three.) The amines were distilled out of

the tube and dried over BaO. They appeared to be a rather complex mixture and the only compound which could be isolated in a reasonably pure state was methylamine (0.39 mmole).

The stability of the amine alone was demonstrated by heating CH_3ONHCH_3 with 50% KOH overnight at 100°. After separation and drying with BaO, 95% of the amine was recovered in pure form.

An ether solution of $CH_3ONHCH_3BH_3$ (3.14 mmoles) was stirred with an excess of trimethylamine (4.97 mmoles) at 0° overnight. The yield of trimethylamine-borane was 0.1970 g., or 86%. It was identified by "active" hydrogen analysis and recovery of the $(CH_3)_3N$. There was no hydrogen evolution in this displacement reaction, as there was in the similar experiment with $CH_3ONH_2BH_3$.

Reaction of O,N,N-Trimethylhydroxylamine with Diborane

The reaction between O,N,N-trimethylhydroxylamine and diborane was conducted without a solvent. The experimental details were the same as described for the previous compound. It was found that, as for the previous amines, two moles of the amine react with one mole of diborane. The experimental values were 1.98, 1.99, and 2.01. The addition compound was a liquid at room temperature. It has a melting point of -16.5 to -16.0°. The material could be moved readily in the vacuum line since the vapor pressure was 3.8 mm. at room temperature (26°).

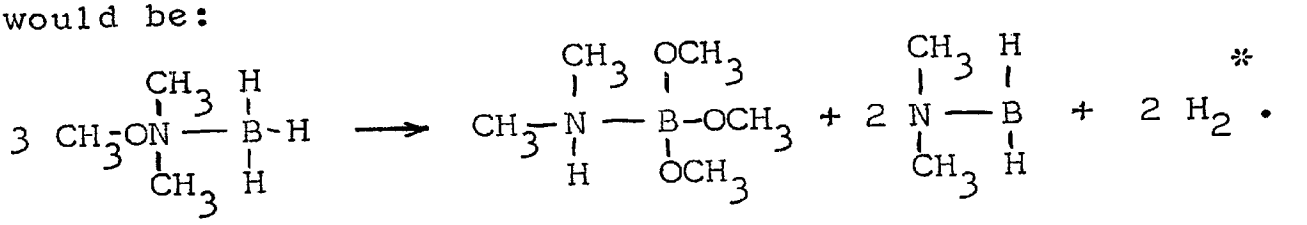
The $CH_3ON(CH_3)_2BH_3$ would not undergo an explosive

decomposition. A sealed tube containing the compound was heated up rapidly to 100°. It was only slowly decomposed at this temperature.

When 3.57 mmoles of $CH_3ON(CH_3)_2BH_3$ were heated at 100° for two hours, 2.29 mmoles of H_2 were produced. All of the remaining decomposition products were volatile and after a preliminary separation, trimethoxyborane was isolated and identified. The method of adding diborane to remove any weakly complexed amines was utilized.

The remainder of the volatile components were fractionated extensively but no fraction could be isolated which behaved like a pure compound. The reason was apparent after considering the possible decomposition products.

By analogy to the previous cases studied, the equation would be:



Burg and Randolph (20) report that N,N-dimethylaminoborane, in addition to participating in a monomer-dimer equilibrium, can enter into the reaction

$$3/2\ [(CH_3)_2NBH_2]_2 \longrightarrow [(CH_3)_2N]_2BH + (CH_3)_2NB_2H_5 \cdot$$

These investigators report that the mixture cannot be quantitatively separated into its components by conventional trap to trap distillation. The vapor pressure of

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*Details of probable mechanisms are considered in more detail on page 87.

decomposition products were in the same range as the above compounds.

The behavior of the O,N,N-trimethylhydroxylamine-borane toward trimethylamine was studied. Stoichiometric amounts were allowed to react at room temperature for a period of about 20 hours. A quantitative reaction resulted.

$$CH_3ON(CH_3)_2BH_3 + (CH_3)_3N \longrightarrow (CH_3)_3NBH_3 + CH_3ON(CH_3)_2$$

The O,N,N-trimethylhydroxylamine was recovered in 98% yield. The identity and purity were checked by the vapor pressures and molecular weight. The identity of the trimethylamine-borane was confirmed by its melting point.

Hydrolysis with 50% KOH gave distinctly different results from the two preceding cases. Four milliliters of 50% KOH and 4.15 mmoles of $CH_3ON(CH_3)_2BH_3$ were heated in a sealed tube at 100° for two hours. A total of 11.19 mmoles of hydrogen resulted from the hydrolysis. The ratio of $H_2/CH_3ON(CH_3)_2BH_3$ is 2.70 which is approaching the theoretical three. It may be recalled that for the two previous compounds the ratio was just slightly over two. The nitrogen component was not reduced but 92% of the original $CH_3ON(CH_3)_2$ was recovered in a pure form.

The Reaction of N-Methylhydroxylamine with Diborane

The preparation of N-methylhydroxylamine hydrochloride and its conversion to the free base were described previously. A quantity of the $HONHCH_3$, 4.15 mmoles, was weighed out after sublimation into a small weighing tube. This was transferred

to the reaction tube and 6.7 ml. of ether added. The mixture was stirred until the amine dissolved in the ether and the resulting solution was cooled to precipitate the amine out in a finely divided form. After adding 4.15 mmoles of diborane, the mixture was warmed to -112°. A clear solution resulted after stirring for two hours.

The temperature was then raised to -78° and the excess diborane and ether distilled out and fractionated. Since 1.99 mmoles of B_2H_6 were recovered, 2.16 mmoles had reacted, giving a ratio of $HONHCH_3/B_2H_6$ of 1.92.

The N-methylhydroxylamine-borane remained as a clear liquid which decomposed with the evolution of hydrogen as the temperature was raised.

TABLE 18

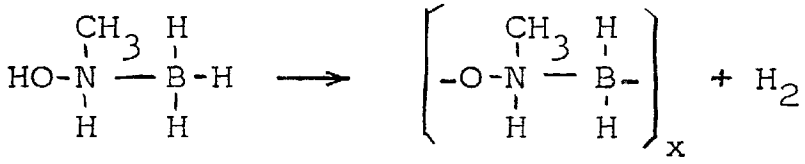
DECOMPOSITION OF N-METHYLHYDROXYLAMINE-BORANE--HYDROGEN EVOLUTION AS A FUNCTION OF TEMPERATURE

Temperature	Hrs. at Temp.	Mmoles H_2	Ratio H_2/Amine
-112	2	0.0	0.0
-78	2	0.512	0.123
-63	1	0.905	0.22
-23	1	0.98	0.24
0	12	1.36	0.33
28	5	1.95	0.47
28	13	2.23	0.54
28	24	2.38	0.57
65	4	3.14	0.76
100	3.5	5.25	1.26
100	6.5	5.40	1.30
220	1	7.10	1.71
220	11	7.12	1.72

The liquid became very viscous as hydrogen was lost, gradually turning into a solid at the higher temperatures. No volatile products other than the hydrogen were observed until the temperature was raised to 100° and above. The volatile material given off at the higher temperatures was found to be principally methylamine contaminated with what is believed to be a trace of ammonia. A total of 0.79 mmole of amines was collected. This is 19% of the total nitrogen content.

The residue in the reaction tube after the pyrolysis was a yellow solid. Upon hydrolysis with dilute HCl, an additional 1.17 mmoles of H_2 were obtained. This brings the ratio of total "active" hydrogen per amine to 2.00.

One may interpret these observations in the following manner. The initial step is the reaction of the protonic hydrogen on the oxygen with one of the hydridic hydrogens on the boron, of another molecule, to produce hydrogen gas. An oxygen-boron bond is formed, binding the two molecular species together.



This polymerization continues and long chain units are formed. As the polymerization proceeds, the viscosity of the mass increases tremendously and the remaining unreacted molecules are hindered in their ability to orient themselves in a position for reaction. This accounts for

the fact that, as the system is raised to progressively higher temperatures, the rate of hydrogen evolution is rapid at first but rapidly dwindles off to practically zero. Campbell (2) observed the same effect with the hydroxylamine-borane.

Before this primary reaction is completed, a secondary reaction, involving the acid hydrogen on the nitrogen and one of the hydridic hydrogens on the boron, begins to contribute to the amount of hydrogen which is liberated. This secondary step could produce either a double bond between the nitrogen and the boron or a cross-linking between chains. The reason that a definite break at one mole of hydrogen is not observed is because of the overlapping of this primary and secondary reaction.

At temperatures of 100° and above, there is a third reaction which reduces the nitrogen to the primary amine. This may also be looked upon as a shift of hydrogen from the boron to the nitrogen, and is one of the reasons why only 2.00 of the three "active" hydrogens were accounted for. Another very likely possibility is loss of hydrogen from the breaking of B-H bonds at the high temperatures, such as is observed in the pyrolysis of diborane. Evidence for the latter possibility was found when extra hydrogen was produced from the pyrolysis of $HON(CH_3)_2BH_3$, as described in the following section.

Reaction of N,N-Dimethylhydroxylamine with Diborane

The N,N-dimethylhydroxylamine was prepared by displacement from the hydrochloride salt with ammonia. The experimental details of the reaction with diborane were the same as those previously described. The addition reaction was conducted both with and without ether as a solvent. The stoichiometry of the addition was not as good as those observed with the methoxy type amines. There is some secondary reaction which consumes small amounts of diborane. The deviation from a 2/1 ratio is definitely greater than the experimental error in measuring the amounts of the reactants. This is a general observation for the hydroxylamines and contrasts sharply with the methoxyamines in which excellent stoichiometry was always obtained. This evidence for a secondary reaction which consumed small amounts of excess diborane was supported by further studies of this addition compound.

TABLE 19

REACTION BETWEEN N,N-DIMETHYLHYDROXYLAMINE AND DIBORANE

	Run Number 1	2	4
Solvent	ether	none	ether
$HON(CH_3)_2/B_2H_6$	1.94	1.91	1.91
$H_2/HON(CH_3)_2$	0.426	0.72	0.315
Yield $HON(CH_3)_2BH_3$	50%	30%	64%

The N,N-dimethylhydroxylamine-borane is a liquid with a vapor pressure of 6 mm. at room temperature and, hence, could be purified by vacuum distillation. The melting point was not sharp and was observed visually to be over the range of 2 to 4°. An analysis, after hydrolyzing the purified compound in a sealed tube with dilute HCl, gave very good results: 3.92% "active" H, 14.4% B, and 18.6% N. The theoretical values are 4.04% "active" H, 14.44% B, and 18.69% N.

The initial preparations were conducted using an excess of diborane and there was always some hydrogen evolution before the excess diborane and solvent could be removed, even at low temperatures. The hydrogen evolution became more vigorous during the time that the reaction tube was warmed up enough to distill the addition compound away from its decomposition products. Once it was purified, the $HON(CH_3)_2BH_3$ was surprisingly stable at room temperature. A sample standing at room temperature for five days was less than 5% decomposed.

The yield of $HON(CH_3)_2BH_3$ obtained from its preparation with excess diborane was found to correlate with the amount decomposed before purification, as measured by the amount of hydrogen evolved. The results shown in Table 19 also show the advantage of a solvent.

The decomposition of the N,N-dimethylhydroxylamine-borane was shown to be catalyzed both by its decomposition products and by diborane. When a sample of the purified compound was returned to the tube which contained the solid

decomposition products produced during the preparation, hydrogen evolution began at once at room temperature. The studies illustrating the catalysis by diborane are summarized in the following table.

TABLE 20

CATALYTIC DECOMPOSITION OF N,N-DIMETHYLHYDROXYLAMINE-BORANE BY DIBORANE

	Trial 1		Trial 2
Mmole $HON(CH_3)_2BH_3$	1.18		2.66
Mmole B_2H_6 added	0.92		0.37
Temperature °C.	25°		25°
Time, hours	0.5	4	28
Mmole H_2 liberated	0.965	1.27	2.84
Ratio $H_2/HON(CH_3)_2BH_3$	0.82	1.08	1.07
Mmole B_2H_6 recovered	0.84		0.13
Mmole B_2H_6 consumed	0.08		0.24
Ratio H_2/B_2H_6 consumed	16		12

The high ratio of H_2/B_2H_6 consumed indicates that the B_2H_6 is acting catalytically and is not being used up in any obvious stoichiometric process. Rather there is a secondary reaction which uses up small amounts of excess diborane and is responsible for the small quantity of hydrogen liberated in excess of the expected one mole. This same side reaction is probably the reason for the poor stoichiometry observed in all the reactions of the OH hydroxylamines with diborane.

In Run 5 the compound was prepared using an excess of the amine rather than an excess of B_2H_6. Five mmoles of $HON(CH_3)_2$ were weighed out and dissolved in 2.8 ml. of ether. After adding 2.39 mmoles of diborane, 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 addition compound and the excess amine. In this preparation only 0.11 mmole of hydrogen was obtained. The fact that only 2.3% decomposition had occurred demonstrated the catalytic effect of the excess diborane in the earlier runs. The excess amine could not be fractionated quantitatively from the desired product since their vapor pressures are not far enough apart. The yield of pure $HON(CH_3)_2BH_3$ was only 70% because of fractionation losses.

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

$$\left[-O-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{N}}-\underset{\displaystyle H}{\overset{\displaystyle H}{B}} \right]_x .$$

The material is believed to be a high polymer, but the value of x could not be directly determined since the polymer is

insoluble in solvents such as ether and liquid ammonia, and hydrolyzes readily in more protonic solvents.

The $[-ON(CH_3)_2BH_2-]_x$ polymer undergoes further decomposition upon heating to higher temperatures. A sample of $HON(CH_3)_2BH_3$ upon prolonged pyrolysis at 100° yielded 1.25 moles of hydrogen plus a trace of material of very low volatility which was not identified. The hydrogen in excess of one mole could only have been formed by the breaking of B-H bonds. The type of thermal decomposition which might be expected of this polymer, at temperatures of 100° and above, is the reaction:

$$3\ [-ON(CH_3)_2BH_2-]_x \longrightarrow B[N(CH_3)_2]_3 + 3\ H_2 + B_2O_3\ .$$

The tris(dimethylamino)borane is reported as a liquid with a vapor pressure of 5 mm. at 25° (63).

There is no shift of a hydride unit in the decomposition of $HON(CH_3)_2BH_3$ to form the polymeric solid. The sample, which had liberated one mole at 55°, yielded another 1.6 moles upon acid hydrolysis. The failure to achieve the full additional two moles on hydrolysis was due to experimental difficulties.*

The decomposition of the N,N-dimethylhydroxylamine-borane is different in several respects from that of $HONH_2BH_3$

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*The $[-ON(CH_3)_2BH_2]_x$ polymer is formed as a thin layer on the walls of the tube. When the dilute HCl was distilled in, the material on the walls of the tube above the level of the liquid nitrogen was partially hydrolyzed by the acid vapors. This hydrogen had to be pumped away in order to continue distilling the acid and was not measured.

and $HONHCH_3BH_3$. In the case of the latter 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, no definite break in the amount of hydrogen was observed after the liberation of one mole of gas. Pure $HON(CH_3)_2BH_3$, on the other hand, was relatively stable at 25° and when heated up another 30°, produced exactly one mole of H_2. One of the reasons for this difference is the fact that the latter addition compound is volatile. In addition $HON(CH_3)_2BH_3$ and its decomposition product do not appear to be very soluble in each other but separate as distinct phases. Therefore, the polymerization which accompanies the loss of hydrogen does not impede the decomposition of the unreacted material. Furthermore, the decomposition of the dimethyl compound is not complicated by the loss of a second mole of hydrogen as was the case for the other two, since it contains only one protonic hydrogen. Therefore, a temperature-decomposition curve would show a distinct break after the loss of one mole of hydrogen.

Since $HON(CH_3)_2BH_3$ has 6 mm. vapor pressure at room temperature, a crude estimate of the molecular weight by vapor density was attempted. The value of 70 observed was sufficiently accurate to distinguish between a monomer (mol. wt. 74.9) and a dimer. However, due to the small weight of the gas at such low pressures, the measurement was not sensitive enough to detect possible dissociation in the vapor phase.

$$2\ HON(CH_3)_2BH_3 \rightleftharpoons B_2H_6 + 2\ HON(CH_3)_2$$

The reason is that the N,N-dimethylhydroxylamine itself is highly associated in the gas phase (see page 15).

A sample of the N,N-dimethylhydroxylamine-borane was allowed to react with a small excess of trimethylamine. The reaction did not go to completion but an 80% yield of $(CH_3)_3NBH_3$ was obtained. The amine displaced was identified as the N,N-dimethylhydroxylamine. There were only traces of noncondensable gas produced in this displacement reaction.

Discussion

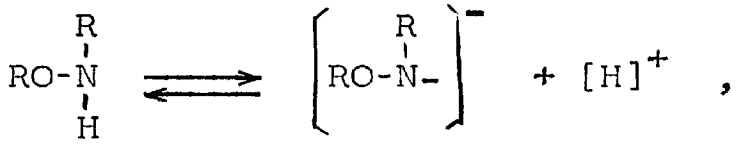
The Reactions of the Methyl Substituted Hydroxylamine-boranes

Before attempting to establish a correlation between the properties of the substituted hydroxylamines and their reactions with diborane, it is necessary to make a distinction between the first and second acid ionizations of the amine. The Ka values which were measured are the equilibrium constants for the reaction

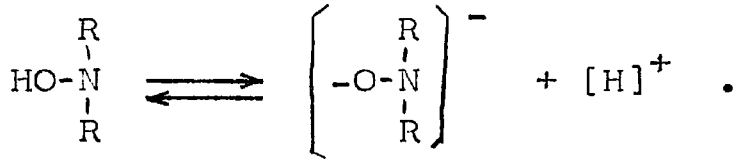
$$\left[\begin{array}{c} R \\ | \\ RO\text{-}N\text{-}H \\ | \\ R \end{array}\right]^+ \rightleftharpoons \begin{array}{c} R \\ | \\ RO\text{-}N \\ | \\ R \end{array} + [H]^+ \ ,$$

in which R is either hydrogen or a methyl group. This shall be considered the first ionization of the amine. The Ka values are related to the extent to which the nitrogen can donate its lone pair of electrons.

The second ionization is the loss of a proton from the amine to form an amido group



or,



It must be recognized that the base strengths which were measured are for the proton as the reference acid and were in an aqueous solution, where there is the possibility of strong solvation effects. It does not necessarily follow that these values determine the strength of coordination using borane as the reference acid. Brown (53), however, found that the series of methylamines display the same order of base strengths with both the proton in aqueous solution and with trimethylborane in the vapor phase. The displacement reactions with trimethylamine demonstrate that these hydroxylamines are weaker bases than $(CH_3)_3N$ when the borane group is used as the reference acid. The displacements of the substituted hydroxylamine from $CH_3ONH_2BH_3$, $CH_3ONHCH_3BH_3$, and $HON(CH_3)_2BH_3$ were not quantitative; on the other hand, the displacement went easily and quantitatively in the case of $CH_3ON(CH_3)_2BH_3$. The foregoing result is what might be expected from the pKa values, since the O,N,N-trimethylhydroxylamine was the weakest electron donor of the series.

In any case, the base strengths of these hydroxylamines lie in a very narrow range when considered as part of

the variety of bases to which borane can coordinate. The important fact is that the secondary reactions, such as splitting out of hydrogen, occur at a much lower temperature than any observable dissociation of the adduct back into diborane and the amine.

Campbell (2) reported that the reaction between diborane and hydroxylamine was somewhat reversible at -112°, but it is now believed that his observations are interpreted more easily without assuming reversibility of the addition reaction. The reaction between hydroxylamine and diborane was very slow at -112°, since both the amine and its borane adduct are insoluble in ether. The diborane, which he was able to recover by long distillation from -112°, had not reacted with the amine but was weakly complexed with the ether. It has has been found that distilling diborane out of an ether solution at -112° is an extremely slow process.

In the reaction of hydroxylamine and methyl substituted hydroxylamines with diborane there is the possibility of the coordination of a borane group to an electron pair on the oxygen. A comparison of nitrogen and oxygen coordination compounds with boron acids indicates that nitrogen is the stronger donor. Dimethylether-borane, for example, has a dissociation pressure of 18 mm. at -78.5° (6). Since only one BH_3 unit was complexed for each hydroxylamine, the coordination is undoubtedly to the nitrogen alone.

The temperature at which these borane adducts will

decompose by hydrogen evolution is dependent on the relative acidity of the hydrogens in the amine. This relative acidity is related to the ease of the second ionization. If one assumes the usual correlation between protonic character of a hydrogen and its ability to form a hydrogen bond, the physical properties (such as boiling point, melting point, Trouton constant, etc.) should provide a measure of this acidity. The data presented in Table 21 divide the series of the six amines into two groups, since a hydrogen attached to oxygen is always more acidic than a comparable hydrogen attached to nitrogen. The OH hydroxylamines show a high degree of hydrogen bonding. They have high melting points, boiling points, and Trouton constants as compared to unassociated compounds of similar molecular weight. The OCH_3 hydroxylamines show much less hydrogen bonding and are low melting and boiling materials. The completely methylated derivative has no protonic hydrogens available and has a "normal" boiling point and Trouton constant as compared to unassociated compounds of similar molecular weight such as hydrocarbons.

In both of these groups of hydroxylamines, the replacement of one of the hydrogens on the nitrogen by a methyl group lowers the Trouton constant, and, with one exception, the boiling point. A major reason is that the replacement reduces the number of hydrogens available for hydrogen bonding. In addition, if one assumes the usual electron donating power

attributed to alkyl radicals, the inductive effect of the methyl groups would reduce the protonic character of the remaining hydrogens.

Trends in the boiling points of the OCH_3 hydroxylamines and in the boiling points of the N- and N,N-methylhydroxylamines offer strong support for Campbell's contention that the reported boiling point of $HONH_2$ is too low and its entropy of vaporization much too high. An extrapolation of the above data suggests a boiling point of about 125° for the pure hydroxylamine.

The second acid ionization provides a basis for interpreting the temperatures at which the borane adducts of these hydroxylamines lose hydrogen. The OH hydroxylamine-boranes should be less stable than the OCH_3 hydroxylamine-boranes with respect to the temperature at which hydrogen is evolved. The column in Table 22 which lists the approximate temperature at which 50% decomposition would occur in 24 hours, shows that this is the case. Also, in Figure 3 are some experimental results plotted as a function of the ratio H_2/compound versus temperature. The curves are only qualitative since the times that the compounds were heated at a particular temperature were not the same. The curve for the N,N-dimethylhydroxylamine-borane is taken from a run in which the material was prepared with excess diborane, and was in the presence of its decomposition products. It is to be noted that these curves lie in the same order as the Trouton constants of the

TABLE 21

SUMMARY OF THE PROPERTIES OF HYDROXYLAMINE AND ITS METHYL SUBSTITUTED DERIVATIVES

	Melting Point	Boiling Point	ΔH/T	pKb
$HONH_2$	33°	110°	43.3	8.03
$HONHCH_3$	38.5°	115°	30.6	8.04
$HON(CH_3)_2$	17.5°	100.7°	25.6	8.80
CH_3ONH_2	-86.4°	48.2°	23.8	9.40
CH_3ONHCH_3	-97.0°	42.4°	23.4	9.25
$CH_3ON(CH_3)_2$	-97.2°	30.2°	20.8	10.35

TABLE 22

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

	Melting Point	Volatility	Ratio amine/B_2H_6 in preparation	Approx. Temp. at which 50% decom. in 24 hrs.
$HONH_3BH_3$	solid decom.	nonvol.	1.80	-75°
$HONHCH_3BH_3$	liquid	nonvol.	1.92	15°
$HON(CH_3)_2BH_3$	2-4°	6 mm. 25°	1.92	25° as prep. 55° pure
$CH_3ONH_2BH_3$	55°	slightly vol. 40°	2.00	55°
$CH_3ONHCH_3BH_3$	-23 to -21°	slightly vol. 25°	1.97	65°
$CH_3ON(CH_3)_2BH_3$	-16.5°	3.8 mm. 26°	1.99	90°

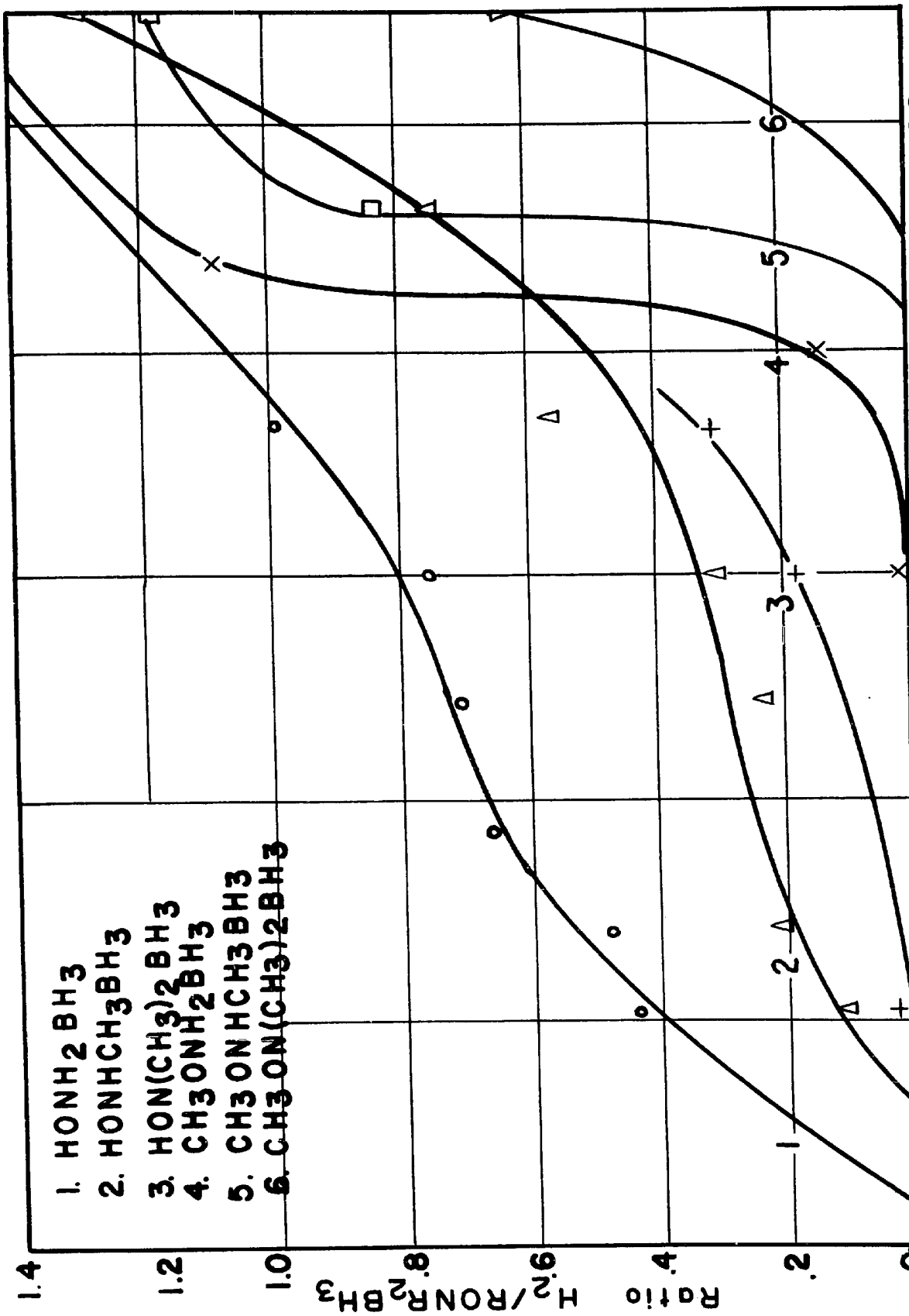
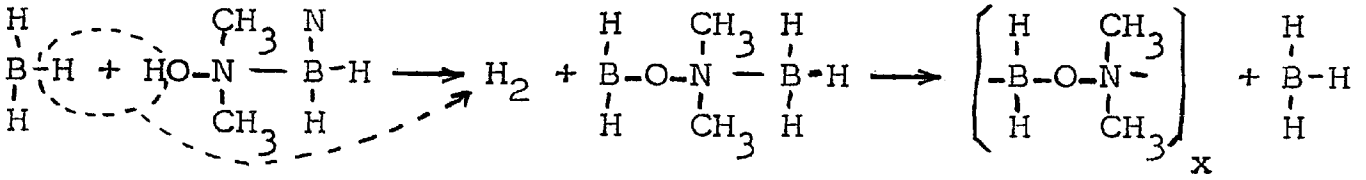


Figure 3. Decomposition Curves of Hydroxyl and Methyl Substituted Hydroxylamine-Boranes

corresponding amine. The methoxyamine- and the N,N-dimethylhydroxylamine-boranes occupy an intermediate position and when pure, their stabilities were comparable. When carefully purified, the latter was amazingly stable for a compound which contained a hydroxyl group and hydridic hydrogens in the same molecule.

The stability of $HON(CH_3)_2BH_3$ and the catalysis of its decomposition by diborane, illustrate the deactivation of the hydridic hydrogens by coordination. The degree of this deactivation is dependent on the strength of the coordinate link which is formed. For example, a weakly complexed addition compound such as PF_3BH_3 was found to be almost as reactive as diborane itself, since it inflamed spontaneously in moist air. Complexing with a strong base like trimethylamine reduces the activity of the hydridic hydrogens to the point where the adduct is stable indefinitely in dry air and is only slowly hydrolyzed by water. In $HON(CH_3)_2BH_3$ the hydridic hydrogens are sufficiently deactivated through coordination to make the compound stable at room temperature. An (+I) inductive effect of the two methyl groups could also reduce the protonic character of the acid hydrogen on the oxygen atom. However, the unstabilized hydrogens on diborane are basic enough to react readily with this protonic hydrogen. The BH_3 group which was originally attached to the amine could then be released to reform B_2H_6 and attack another molecule.



The same effect of catalysis by diborane and by the decomposition products was probably present in hydroxylamine-borane and its N-methyl derivative, but was not observed because of the low decomposition temperature and the non-volatility of the adduct. The catalysis by diborane was not observed in any of the OCH_3 hydroxylamine-boranes at room temperature or below.

A possible explanation for the poor stoichiometry of the reactions of the OH hydroxylamines with diborane could be based on the assumption that the second step was not quantitative.

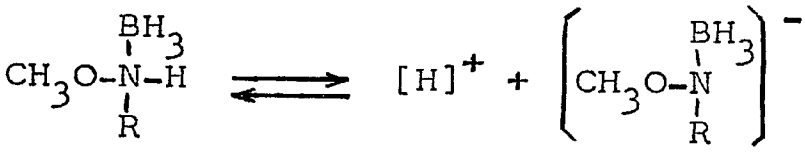
The shift of a methoxy group and a hydride unit in the decomposition of the OCH_3 hydroxylamine-boranes is an interesting reaction. The shift of these groups in $CH_3ONH_2BH_3$ and $CH_3ONHCH_3BH_3$ is preceded by hydrogen evolution. This was observed experimentally, and it is easier to visualize the shift of these groups in the resulting unsaturated intermediate. Another way of looking at these shifts is in terms of an internal oxidation-reduction reaction. The breaking of a B-H and an N-O bond to form an N-H and a B-O bond is very favorable thermodynamically and is accompanied by the release of a large amount of heat. The violent explosion of these compounds on being heated rapidly is this same oxidation-reduction reaction which has gotten out of control. The

explosion products of $CH_3ONHCH_3BH_3$ show that all of the B-H bonds have been broken and that boron and oxygen are combined in the residue.

The trimethylhydroxylamine-borane was also shown to undergo this shift. In this case there can be no shift of the groups over an unsaturated intermediate, since the compound did not contain any protonic hydrogens. Any mechanism which would impose a coordination number of five for boron or nitrogen is highly unlikely. The decomposition occurred at high temperatures where there would be partial dissociation of the compound. The BH_3 group could then recombine to the amine by attachment to the electron pair on the oxygen. The momentary existence of such an intermediate could permit a hydridic hydrogen to shift to the nitrogen and the boron to retain the methoxy group. A disproportionation of the methoxyborane to trimethoxyborane and diborane would give the observed products. The rate for such a mechanism would be relatively slow compared to a shift over an unsaturated intermediate, and would not be expected to achieve explosion proportions. This was found to be the case since $CH_3ON(CH_3)_2BH_3$ would not explode on rapid heating to 100°.

Another significant difference between this adduct and the other two is the products upon hydrolysis with 50% KOH. When $CH_3ONH_2BH_3$ and $CH_3ONHCH_3BH_3$ were hydrolyzed by 50% KOH only a little over 2 moles of hydrogen were recovered and the amine had lost the methoxy group. Hydrolysis of the

trimethyl compound gave nearly three moles of hydrogen and almost complete recovery of the original O,N,N-trimethylhydroxylamine. The reason the basic hydrolysis promotes the shift of the methoxy group and a hydride unit in the first two compounds is suggested by their ammonium type structures. In a strongly alkaline solution the following equilibrium would be displaced to the right.



The resulting ion could then rearrange by the shift of a hydride unit to the nitrogen and the methoxy group to the boron. Since the hydrolysis of B-H bonds in alkaline solutions is a rather slow reaction, this reduction of the nitrogen could occur before the original compound was decomposed. This explanation is supported by the fact that $CH_3ON(CH_3)_2BH_3$ did not suffer the shift of a methoxy group and a hydride unit upon hydrolysis by a base. Since there are no hydrogens on the nitrogen the above ionization would be impossible.

The N-methyl and the N,N-dimethylhydroxylamine-boranes do not have to shift any groups to form a boron-oxygen bond. The interaction between the hydrogen of the hydroxyl group and a hydridic hydrogen on the boron of another molecule to produce hydrogen gas results directly in the formation of a B-O bond. This reaction takes place smoothly as the temperature is raised, and no explosions were ever encountered in

heating an OH hydroxylamine-borane. A sample of the N,N-dimethyl derivative was heated directly up to 100°, a procedure which would have detonated $CH_3ONH_2BH_3$ or $CH_3ONHCH_3BH_3$.

Physical Properties of the Methyl Substituted Hydroxylamine-boranes

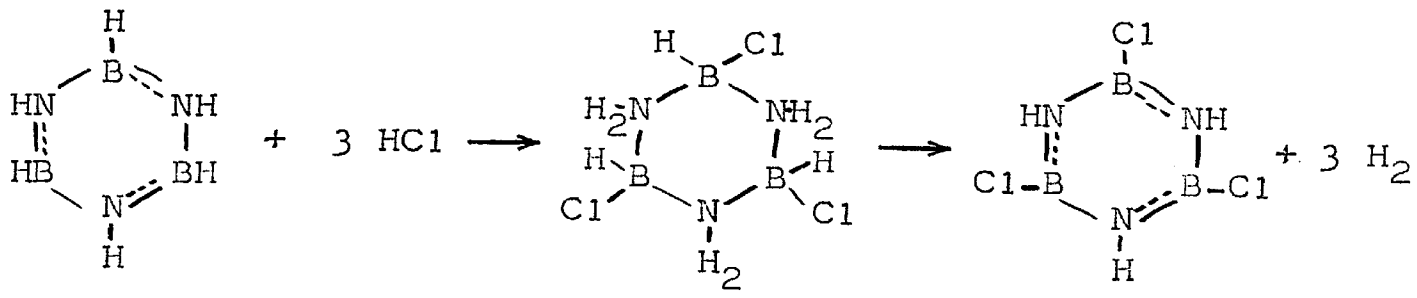
The boiling points, melting points and heats of vaporization for the methyl substituted hydroxylamines are those expected from simple considerations of the hydrogen bond. In contrast, the physical properties of the hydroxylamine-boranes cannot be treated so easily. The melting points, for example, do not show any apparent trends. The OCH_3 hydroxylamine-boranes show low vapor pressures when considered only in terms of their molecular weights and normal hydrogen bond possibilities. The slight increase in volatility with alkyl substitution on the nitrogen suggests that hydrogen bond formation is still of some importance for these compounds. Nevertheless, this effect must be of minor importance in determining properties since CH_3ONHCH_3, with relatively good possibilities for hydrogen bond formation, is much more volatile than $CH_3ONHCH_3BH_3$ in which hydrogen bonding possibilities are reduced somewhat by coordination of the BH_3 group. The effect due to the increased mass of the BH_3 group could not account for the very large difference in volatility. (Compare boiling points in a homologous hydrocarbon series.) The foregoing suggests that the above compounds have relatively large dipole moments which reduce

volatility. Such a postulate is further supported by the fact that $HON(CH_3)_2BH_3$ is more volatile than $CH_3ON(CH_3)_2BH_3$. This observation which is contrary to the expected results of hydrogen bond formation, suggests a large dipole contribution.

Trimeric N-Methylaminoborane

The trimeric N-methylaminoborane, which was first isolated as one of the decomposition products of $CH_3ONHCH_3BH_3$, is in all probability a six-membered ring composed of alternating boron and nitrogen atoms. 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 (19,20), while CH_3NHBH_2 (16) and H_2NBH_2 (23,60) have been reported as higher polymers.

The only previous examples of a saturated boron-nitrogen ring are the compounds formed when borazene takes up in the cold three molecules of HCl, HBr, H_2O or CH_3OH to give a symmetrically trisubstituted "inorganic cyclohexane." These molecules lose three molecules of hydrogen at 50-100° to form the corresponding substituted "inorganic benzene."



The trimeric P-dimethylphosphinoborane and the trimeric As-dimethylarsinoborane recently reported by Burg and his coworkers (8,9) are examples of saturated six-membered rings containing boron. Although $(CH_3NHBH_2)_3$ does not display their extreme stability toward heat and hydrolysis, it is very stable for a boron-nitrogen compound containing both hydridic and protonic hydrogens.

EXPERIMENTAL RESULTS--PHOSPHORUS TRIFLUORIDE

Preparation*

The PF_3 was prepared by the reaction between PCl_3 and ZnF_2. The method consisted of adding PCl_3 slowly to ZnF_2 and passing the volatile materials through a reflux column at about -78° in order to conserve the unreacted PCl_3. (The reaction is exothermic.) The PF_3 passed through the column and was retained in a liquid nitrogen trap. The gas was stored in a small stainless steel cylinder, from which small quantities could be removed as needed. The PF_3 was purified by low temperature fractionation before it was used.

Reaction of Phosphorus Trifluoride with Diborane

Preparation of PF_3BH_3

The experimental details of the reaction between phosphorus trifluoride and diborane were patterned after those used for the preparation of carbon monoxide-borane (4,64). A measured amount of diborane, together with a large excess of PF_3, was condensed in a heavy wall Pyrex bomb tube of about 60 ml. capacity. The bomb tube was then allowed to stand at room temperature for a period of time. It was determined that maximum yields were obtained after four days. Longer periods of time promoted a secondary reaction, which led to other products.

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*The author is indebted to Dr. H. M. Dess for the preparation of the PF_3 used in this investigation.

The bomb tube and its contents were then frozen with liquid nitrogen and the tube opened to the line by means of the vacuum tube opener. Any noncondensable gases were removed with the Toepler pump and measured with the gas burette. The condensable portions were distilled through a trap at -155°, at which temperature the PF_3BH_3 is quantitatively retained. The excess B_2H_6 and PF_3 was measured and analyzed by a sealed tube hydrolysis, using the amount of hydrogen generated to determine the portion of B_2H_6 in the mixture. The PF_3BH_3 was freed from less volatile impurities by distilling through a trap at -128°. The uniformity of the phosphorus trifluoride-borane was observed by a consistent checking of its vapor pressure at -111.8° as 23.0 mm.

The extent of the secondary reaction, which produced hydrogen and less volatile materials, increased with the time that the bomb tube was allowed to stand at room temperature. Upon hydrolysis of this less volatile material, only small amounts of hydrogen were liberated. After oxidation of the resulting solution, phosphorus was qualitatively identified by the yellow precipitate of ammonium phosphomolybdate. In Run 5 the less volatile materials were separated by fractional condensation and a liquid with a vapor pressure of 5 mm. at -80° was isolated. A measurement on the molecular weight of this liquid gave a value of 120. It appeared stable in the vapor phase but polymerized in the liquid state to give a nonvolatile liquid. No hydrogen was liberated upon addition

of water, indicating that it contained no "active" hydrogens. On the basis of these limited data a possible formula for this liquid would be F_2P-BF_2. A more complete characterization was not undertaken because of the small amount of material available.

TABLE 23

DATA ON REACTIONS BETWEEN PHOSPHORUS TRIFLUORIDE AND DIBORANE

	Run Number				
	3	4	5	6	8
Conditions					
Volume of bomb, ml.	62.5	62.9	63.5	61.7	61.7
Initial mmoles B_2H_6	3.28	3.20	3.16	3.22	5.42
Initial mmoles PF_3	19.21	18.18	19.10	17.92	10.71
Initial pressure, atm.	8.72	8.30	8.57	8.36	6.40
Time at 25°, days	2	4	7	22	25
Products					
Mmoles B_2H_6	1.24	0.69	0.27	0.44	2.12
Mmoles PF_3	14.65	13.17	11.37	12.31	4.87
Mmoles PF_3BH_3	4.26	5.01	4.34	4.73	4.50
Mmoles less volatile impurities	0.01	0.08	1.40	0.38	0.84
Mmoles H_2	0.03	0.55	-	1.29	2.10
Yield PF_3BH_3 based on B_2H_6	65%	78.3%	68.7%	73.5%	41.5%
Apparent equilibrium constant Katm.	5.73	1.86	0.71	1.18	0.98

The true equilibrium constant for the reaction

$$2\ PF_3BH_3 \longrightarrow 2\ PF_3 + B_2H_6$$

is estimated to lie in the range K atm. = 1.0 ± 0.3. One of the reasons the determination of this constant was not very reproducible was because the bomb tubes were not thermostated. The values in Table 23 were calculated on the assumption that room temperature was constant at 25°. In addition, there were a number of problems involved in the quantitative separation of the large excess of PF_3 from the product and the unreacted diborane. This problem was simplified in the case of carbon monoxide-borane since the CO is noncondensable.

Analysis and Molecular Weight

The molecular weight was determined by vapor density as 102.7. This agrees very well with the theoretical value of 101.82 for PF_3BH_3.

The "active" hydrogens in the compound were determined by condensing a weighed sample of the gas in a tube and then distilling in an excess of water. The sealed tube was allowed to stand at room temperature for one day, and then the tube was opened to the vacuum line and the amount of hydrogen measured. The 0.4207 gram sample yielded 12.09 mmoles of hydrogen. This is 2.89% "active" hydrogen. Theoretical for PF_3BH_3 is 2.97%.

The PF_3 is partially hydrolyzed by this procedure, and the attack of the resulting HF on the glass precludes the chance of obtaining a boron analysis. Small amounts of

of PF_3 were recovered from the hydrolysis and they were contaminated with what appears to be SiF_4.

The addition compound was hydrolyzed by 40% NaOH as the first step in obtaining a phosphorus analysis, since the P-F bond is rapidly cleaved in alkaline solutions (65). The resulting solution was acidified and the phosphorus acid was oxidized to the phosphoric by evaporating the solution almost to dryness with aqua regia. The precipitation of the ammonium phosphomolybdate was carried out in the usual manner. Considering the precision of the methods for determining phosphorus in compounds of this type, the result, 29.87% P, is in good agreement with the formulation PF_3BH_3 (30.43% P).

Physical Constants of PF_3BH_3

Phosphorus trifluoride-borane is a colorless gas which is spontaneously inflammable in air. The melting point was determined on three separately purified samples, using the magnetic plunger method of Stock (39). An ethylene vapor pressure thermometer was used to measure the temperatures. The values observed were -116.1°, -116.3°, and -115.9°.

The vapor pressures of PF_3BH_3 were measured and in the liquid range can be described by the equation,

$$\mathrm{Log}_{10}P = -1038.9/T + 7.8061 \ .$$

Since the material decomposes so readily, it was necessary to purify the compound before each reading and to achieve temperature equilibrium rapidly.

TABLE 24

VAPOR PRESSURES OF PHOSPHORUS TRIFLUORIDE-BORANE

Slush Bath	Vapor Pressure Thermometer	Temp. °C.	Observed Pressure mm.	Calcd. Pressure mm.	ΔP Cal.-Obs.
Methyl cyclohexane	C_2H_4	-127.7	4.1 (s)		
Ethyl bromide	C_2H_4	-119.7	11.4 (s)		
Carbon disulfide	C_2H_4	-111.8	23.0	23.4	+0.4
Methyl formate	CO_2	-101.5	56.6	57.0	+0.4
Methyl alcohol	CO_2	-98.1	76.4	74.6	-1.8
Toluene	CO_2	-95.7	90.6	89.7	-0.9
Ethyl acetate	CO_2	-87.6	162.1	161.6	-0.5
Dry Ice-isopropyl alcohol	CO_2	-79.9	267	270	+3.0

These data extrapolate to give a boiling point of -61.8°, a heat of vaporization of 4760 cal./mole, and a Trouton constant of 22.5. The slightly high value of the Trouton constant might indicate that the complete curve of Log P - 1/T would be slightly concave downward, making the true boiling point one or two degrees higher.

Rate of Decomposition of PF_3BH_3

In order to be able to compare the stability of PF_3BH_3 with that of carbon monoxide-borane, the rate of decomposition at room temperature was measured. The decomposition reaction,

$$2\ PF_3BH_3 \longrightarrow B_2H_6 + 2\ PF_3\ ,$$

produces an increase in pressure. Since the system was not thermostated and there was a volume correction for the manometer with changes in pressure; the amount of gas decomposed at any time was calculated by the equation:

$$\% \text{ decomposed} = \frac{2\ (\text{mmoles gas} - \text{initial mmoles } PF_3BH_3) \times 100}{\text{initial mmoles } PF_3BH_3} .$$

The early data of Burg and Schlesinger (4) on the decomposition of carbon monoxide-borane are included for comparison purposes in Figure 4. The similarity of the rates is very apparent. An attempt was made to use these data to compare the decomposition of PF_3BH_3 with the mechanism which has been proposed by Burg (64) as a result of his kinetic studies on the decomposition of carbon monoxide-borane. He proposed that the rate determining step is

$$BH_3 + OCBH_3 \longrightarrow B_2H_6 + CO ,$$

the BH_3 groups being furnished from an initial equilibrium

$$OCBH_3 \rightleftharpoons BH_3 + CO .$$

The rate of decomposition of PF_3BH_3 appeared to follow the same kinetics for the first few hours, which would imply that the same decomposition mechanism was operating for both of these compounds. However, a definite confirmation of this would require a careful kinetic study involving more elaborate equipment, with provisions for thermostating and rapid, accurate measurement of pressure.

TABLE 25

RATE OF DECOMPOSITION OF PHOSPHORUS TRIFLUORIDE-BORANE

Time, minutes	total mmoles gas	% PF_3BH_3 decomposed
	Trial 1	
0	3.08	0
1	3.12	2.6
3	3.13	3.2
5	3.15	4.5
10	3.18	6.5
20	3.23	9.7
60	3.30	14.3
100	3.35	17.5
140	3.38	19.5
	Trial 2	
0	4.34	0
1	4.38	1.8
3	4.43	4.1
5	4.46	5.5
10	4.49	6.9
20	4.54	9.2
55	4.62	12.9
80	4.69	16.1
110	4.73	18.0
170	4.78	20.3
230	4.84	23.0
380	4.92	26.7
500	4.95	28.1
1100	5.07	33.6

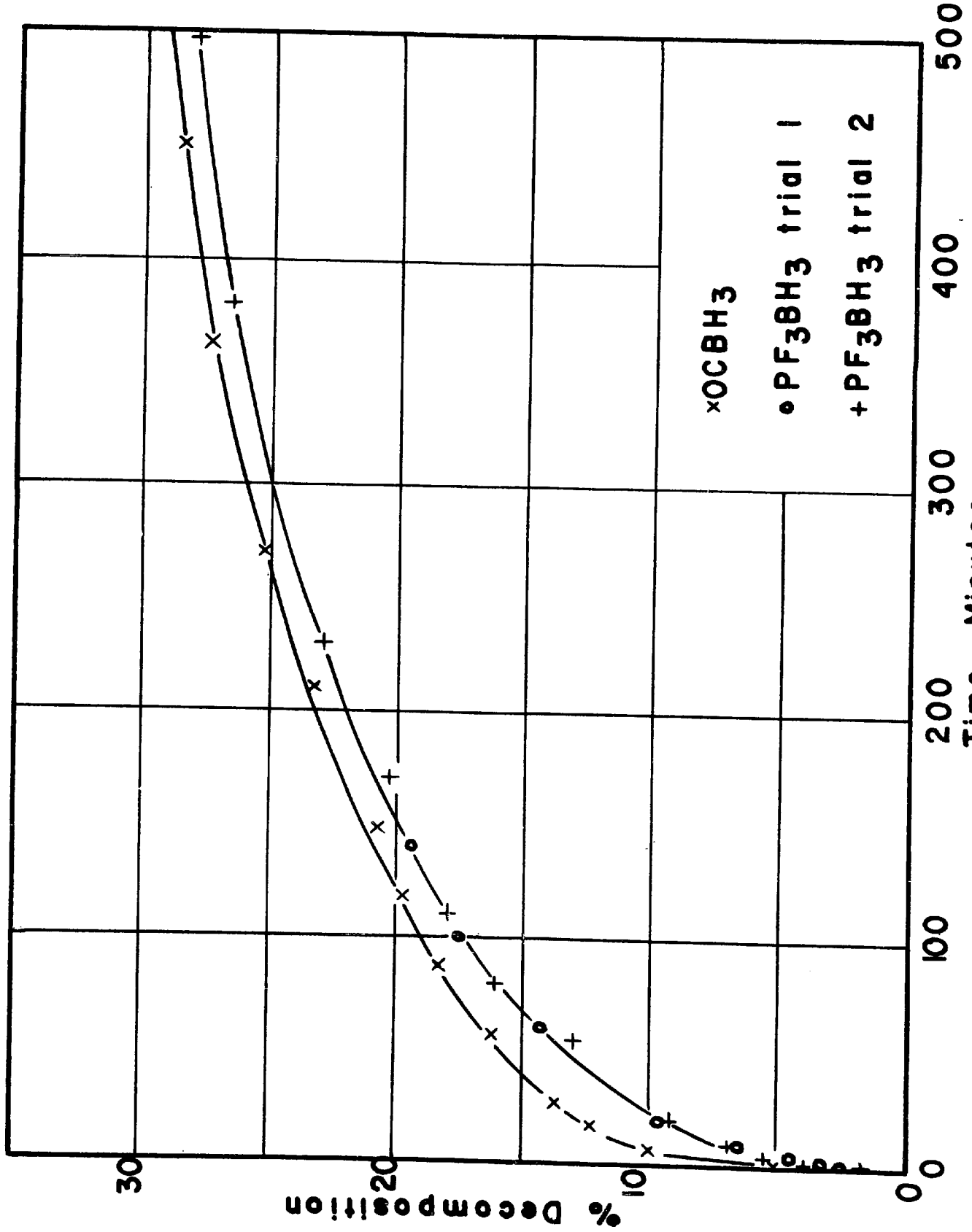


Figure 4. Decomposition of $OCBH_3$ and PF_3BH_3 at Room Temperature.

Reaction of PF_3BH_3 with Trimethylamine

PF_3BH_3 (1.93 mmoles) and a small excess of $(CH_3)_3N$ (2.31 mmoles) were condensed in a bulb of 250 ml. capacity. When the mixture was warmed to room temperature, there was an immediate reaction in which a white solid was produced. The more volatile products of the reaction were removed after cooling the bulb to -80°. The bulb was then weighed, the trimethylamine-borane sublimed out, and the bulb reweighed. A 97% yield, 0.1362 gram of $(CH_3)_3NBH_3$ was obtained. The excess amine had reacted with the PF_3 which was liberated to produce a nonvolatile solid and several unidentified gases. A 79.3% recovery of the PF_3 was obtained after purification. This PF_3 was characterized by a molecular weight of 87.6 (theory 87.98) and by its vapor pressures.

Temperature	Pressure Observed mm.	Observed for Pure PF_3 mm.
-128.3°	98.1	95.1
-119.5°	210.5	203.5
-111.8°	377.8	369.6

The postulate that the excess amine had reacted with the PF_3 was checked by allowing a small amount of trimethylamine to react with an excess of PF_3. An approximately one to one reaction occurred to produce a nonvolatile white solid and a mixture of gaseous products which were qualitatively the same as those observed previously.

Reaction of PF_3BH_3 with Ammonia

A quantity of dry ammonia, 14.70 mmoles, was condensed on the walls of a reaction tube. Then, 2.20 mmoles of PF_3BH_3 were added and the temperature raised from -128° to -80° over a period of 2-1/2 hours. The excess ammonia was then sublimed from the reaction tube at -80°. The amount of ammonia recovered was 3.69 mmoles, meaning that 5.0 moles of ammonia had reacted with one of PF_3BH_3.

The reaction product was a white solid which began to decompose at room temperature by turning yellow and giving off small amounts of hydrogen. Some ammonia was recovered by heating the reaction products up to 50-60° and trapping the less volatile materials out at -80°. The additional ammonia recovered brought the ratio NH_3/PF_3BH_3 down to 3.38.

During the decomposition a small amount of a white solid of very low vapor pressure was collected in the Dry Ice trap. It was thought at first that this might have been $NH_4F \cdot HF$, which would have accounted for the ammonia recovered upon decomposing the reaction products. This was discounted when it was observed that upon cleaning the traps, the white solid burst into flames upon contact with nitric acid.

In summary, the reaction between NH_3 and PF_3BH_3 is very complex. From the large amount of ammonia which is consumed at -80°, it is apparent that the fluorines of the phosphorus are participating in the reaction. An amino group is probably attached to the phosphorus with the formation of ammonium fluoride.

Discussion

The properties of the addition compound formed between phosphorus trifluoride and diborane are strikingly similar to the reported properties of carbon monoxide-borane. In Table 26 some of the properties of the two are compared.

TABLE 26

COMPARISON OF THE PROPERTIES OF CARBON MONOXIDE-BORANE AND PHOSPHORUS TRIFLUORIDE-BORANE

	$OCBH_3$	PF_3BH_3
Melting Point	-137.0°	-116.1°
Boiling Point	-64°	-61.8°
ΔH Vaporization	4750	4760
Trouton Constant	23.0	22.5
Dissociation Constant Katm. at 25°	2.5	1.0 ± 0.3
Per Cent Decomposed after 1 hr. at 25°	17%	14%

As seen from the decomposition curves and the equilibrium constant, the PF_3 compound appears to be slightly more stable. The same small difference in stability has been observed in the dichloroplatinous complexes. Lutton (66) reported that $PtCl_2 \cdot 2\ PF_3$ appeared to be somewhat more stable than the $PtCl_2 \cdot 2\ CO$ complex.

The isolation and characterization of PF_3BH_3 demonstrated that a P-B bond can be formed between PF_3 and a boron

Lewis acid, Therefore, theories (27) which are based on the nonexistence of such a bond must be re-evaluated in the light of this evidence.

SUMMARY

1. The melting points, vapor pressure curves, and Trouton constants were measured for all of the methyl substituted hydroxylamines. The values observed were what one would expect from the hydrogen bonding in these molecules. The base strengths of these compounds were measured in aqueous solution. The observed order can be explained in terms of an inductive effect of the methyl groups being opposed by a steric factor.
2. These methyl-substituted hydroxylamines react with diborane in a 2/1 ratio to form a borane addition compound. The stoichiometry of the reaction was very good for the OCH_3 hydroxylamines but small deviations from a 2/1 ratio were observed for the OH hydroxylamines. These addition compounds undergo secondary reactions before there is any observable dissociation back into the amine and diborane. It was found that the hydroxylamines could be displaced from their borane addition compounds by trimethylamine, the displacement being almost quantitative for the trimethyl derivative.
3. $CH_3ONH_2BH_3$ and $CH_3ONHCH_3BH_3$ explode upon rapid heating to 100° but decompose slowly at lower temperatures to liberate hydrogen gas. The hydrogen evolution is accompanied by a shift of the methoxy group from the nitrogen to the boron and the shift of a hydride unit from the

boron to the nitrogen. Following disproportionation, trimethoxyborane was isolated from the decomposition products. The trimethylhydroxylamine-borane also undergoes this shift and disproportionation but does not explode upon rapid heating. A different decomposition mechanism was proposed for this compound.

4. When $CH_3ONH_2BH_3$ and $CH_3ONHCH_3BH_3$ are hydrolyzed by 50% KOH, an "active" hydrogen is lost from the boron and reduction of the amine occurs. The behavior appears to parallel the thermal decomposition of these compounds. On the other hand, when $CH_3ON(CH_3)_2BH_3$ was hydrolyzed by a basic solution, three "active" hydrogens per boron were found and the original O,N,N-trimethylhydroxylamine recovered unchanged. The difference was ascribed to partial ionization of the ammonium type compounds in strongly alkaline solutions.

5. The OH hydroxylamine-boranes lose hydrogen at low temperatures when they are prepared with an excess of diborane. Since the N,N-dimethylhydroxylamine-borane was volatile, it could be distilled away from its decomposition products. It was found to be surprisingly stable at room temperature when it was pure. When $HON(CH_3)_2BH_3$ was heated to 55°, it lost exactly one mole of hydrogen to leave a $[ON(CH_3)_2BH_2]$ polymer. There was no shift of groups, except at high temperatures, in the decomposition of the OH hydroxylamine-boranes since a B-O bond can be

formed directly after the loss of hydrogen. The decomposition of $HON(CH_3)_2BH_3$ was catalyzed by diborane. In view of the stability of the pure adduct, this illustrates the deactivation of the hydridic hydrogens through coordination of the borane group.

6. The trimeric N-methylaminoborane which was first isolated as one of the decomposition products of $CH_3ONHCH_3BH_3$ is presumed to contain a six-membered ring of alternating boron and nitrogen atoms. This compound was extremely resistant to hydrolysis for a boron-nitrogen compound containing two "active" hydrogens per boron.

7. The compound PF_3BH_3 has been prepared by the reaction between phosphorus trifluoride and diborane. The properties of this compound are very similar to those reported for $OCBH_3$.

APPENDIX A

Analytical Methods

"Active" Hydrogen

The "active" hydrogen content of the boron hydride derivatives was determined by hydrolysis with 6 N hydrochloric acid. The hydrogen evolved was measured by use of a Toepler pump and a gas burette system. In most of the early work, the compound to be analyzed was either condensed or prepared in a tube on the vacuum line. A few milliliters of the acid were then distilled into this tube and condensed with liquid nitrogen above the compound containing "active" hydrogen. When the hydrolysis tube was warmed up, the acid melted and flowed down upon the compound. The last stages of the hydrolysis were assisted by heating the tube up to 50-60°. After freezing down the condensable vapors, the hydrogen was removed and measured. This method has its limitations because the hydrolysis is not quantitative for many compounds. In addition, there may be excessive foaming which scatters the other hydrolysis products outside the tube. This precludes the chance of obtaining a subsequent boron or nitrogen analysis.

Much better results were obtained when the compound to be analyzed was condensed or prepared in a tube which had a constriction for sealing off and a break tip for reopening. A few milliliters of hydrochloric acid were distilled into

the tube and it was sealed off under vacuum. Complete hydrolysis was assured by heating for several hours on a steam bath. The tube was then frozen with liquid nitrogen and the side arm with the break tip, sealed into the vacuum tube opener with Apiezon W black wax. After evacuating the tube opener, the break tip was snapped off and the hydrogen removed and measured as previously. The hydrolysis tube could then be removed, opened, and the contents rinsed out for further analysis.

Boron

The usual volumetric determination of boron, by titrating boric acid in the presence of a poly-alcohol, such as glycerol or mannitol, using phenolphthalein as an indicator, cannot be used in the presence of a weak acid such as ammonium chloride since high results will occur due to partial neutralization of the acidic salt. A modification of the so-called identical pH method proposed by Foote (67) was applied to this case for the micro determination of boron in nitrogen containing derivatives of diborane. The basic principle of this method is adjusting the solution to a pH value in the neighborhood of pH 7, then adding an amount of a complexing agent such as mannitol and titrating back to the same pH.

A few elementary considerations will indicate which pH value to select (see Figure 5). The pKa of boric acid is 9.234 (68), while that of the polyol complex in a saturated mannitol solution at 25° was observed to be about 4.2 from

the pH of the half neutralized solution. When the solution is adjusted to a pH near 7, a small amount of the boric acid is neutralized, while after adding the mannitol and titrating back to the identical endpoint, a small amount of the boric acid-mannitol complex is not neutralized. These two errors are in the same direction and make the value determined for boron too low. In order to reduce these errors to the smallest possible value, the identical pH chosen should lie exactly in the middle of the two pKa values, i.e., that of the boric acid and that of its polyol complex. This would be 1/2 x (9.234 + 4.2) or a pH of 6.72.

This fact can easily be shown as follows: if boric acid is represented as HA and the polyol complex as HB, the ionization equations can be written:

$$HA \rightleftharpoons H^+ + A^- \qquad K_a = \frac{[H]^+[A]^-}{[HA]}$$

$$HB \rightleftharpoons H^+ + B^- \qquad K_b = \frac{[H]^+[B]^-}{[HB]}$$

Since the error in the boron determination will be numerically equal to the sum of the boric acid titrated before addition of mannitol and the polyol complex not titrated at the pH chosen, the total error will be equal to $[A^- + HB]$ at the desired pH. Since from the above equations,

$$[A^- + HB] = \frac{K_a\,[1 - A^-]}{[H]^+} + \frac{[1 - HB]\,[H^+]}{K_b} \quad ,$$

$[A^- + HB]$ can be differentiated with respect to H^+ to obtain the pH of the minimum error. Since A^- will be small with

respect to 1 in the first term and HB will be small with respect to 1 in the second,

$$[A^- + HB] = \frac{K_a}{[H^+]} + \frac{[H^+]}{K_b}$$

and

$$\frac{d[A^- + HB]}{d[H]^+} = \frac{-K_a}{[H^+]^2} + \frac{1}{K_b} = 0$$

Then $[H^+] = \sqrt{K_a K_b}$, or for the minimum error

$$pH = \frac{pK_a + pK_b}{2}$$

The errors involved can now be calculated. In adjusting the solution to pH 6.72,

$$\frac{A^-}{HA} = \frac{K_a}{[H^+]} = \frac{5.82 \times 10^{-10}}{1.9 \times 10^{-7}} = 3.0 \times 10^{-3} =$$

0.30% of the boric acid already neutralized.

After saturating the solution with mannitol and titrating back to pH 6.72,

$$\frac{HB}{B^-} = \frac{[H^+]}{K_b} = \frac{1.9 \times 10^{-7}}{6 \times 10^{-5}} = 3.0 \times 10^{-3} =$$

0.30% of the boric acid-mannitol complex not neutralized.

Therefore, the total amount of boron determined by this method will be 0.60% low. Another error which tends to counterbalance this is the blank involved in the mannitol itself. Even C.P. grade mannitol contains traces of acidic substances and since five to ten grams are required to saturate the 20 to 40 ml. of solution used in the titrations, this

blank should be determined. This latter error tends to counterbalance the first mentioned error and in a number of standards which were run, they exactly balanced out. The error involved in changing the number of moles of water per liter in a saturated mannitol solution and, therefore, also the ion product of the water is small and can be neglected. The cooling of the solution upon dissolving the mannitol is considerable and in careful work the solution should be restored to the original temperature. Carbon dioxide does not appear to affect the results since the solution is acidic enough throughout most of the titration.

The samples were prepared by hydrolyzing a weighed amount of the material with water or dilute HCl. A brief heating period with nitric acid was necessary for some samples to convert all of the boron to boric acid. They were all diluted to about 30 ml. in a 150 ml. tall form beaker and boron-free 1 N NaOH was added dropwise until the pH was about 3.

The titrations were made using 0.05 N NaOH from a 5 ml. micro burette. A Beckman Model F, null-type, battery-operated pH meter with a glass electrode and a calomel reference electrode was used to follow the pH of the solution during a titration. The data were recorded pH versus ml. of standard base. The standard base was added in small increments until the pH of the solution was about 7. The solution was then saturated with C.P. grade mannitol and the standard

base added in increments until the pH is again about 7. The data were then plotted and the milliequivalents of base required to return the solution to a pH of 6.7 were determined. After the above corrections are applied, this figure represents the milliequivalents of boric acid in the sample.

The presence of buffering salts such as methoxyamine hydrochloride tend to decrease the slope of the pH versus ml. titrant curve at the identical pH point. When these salts are present in the same order of magnitude as the boric acid, the slopes of the curves in the region of pH 6.7 are still steep enough to determine the boron present with an accuracy of 1-4%. It was observed in all cases that the slopes of the curve before and after the addition of the mannitol are parallel in the region of pH 6.7 as is to be desired. A sample titration curve of boric acid in the presence of ammonium chloride is illustrated in Figure 6.

Carbon and Hydrogen

Carbon and hydrogen analyses were done by Mrs. Anna Griffin in the Micro-Analytical Laboratory of the Department of Chemistry of the University of Michigan.

Nitrogen

Nitrogen was determined using standard micro-Kjeldahl methods. The endpoints of the titration were observed with a Beckman Model F pH meter with a glass electrode, rather than with indicators. Solutions of 0.01 N sulfuric acid and

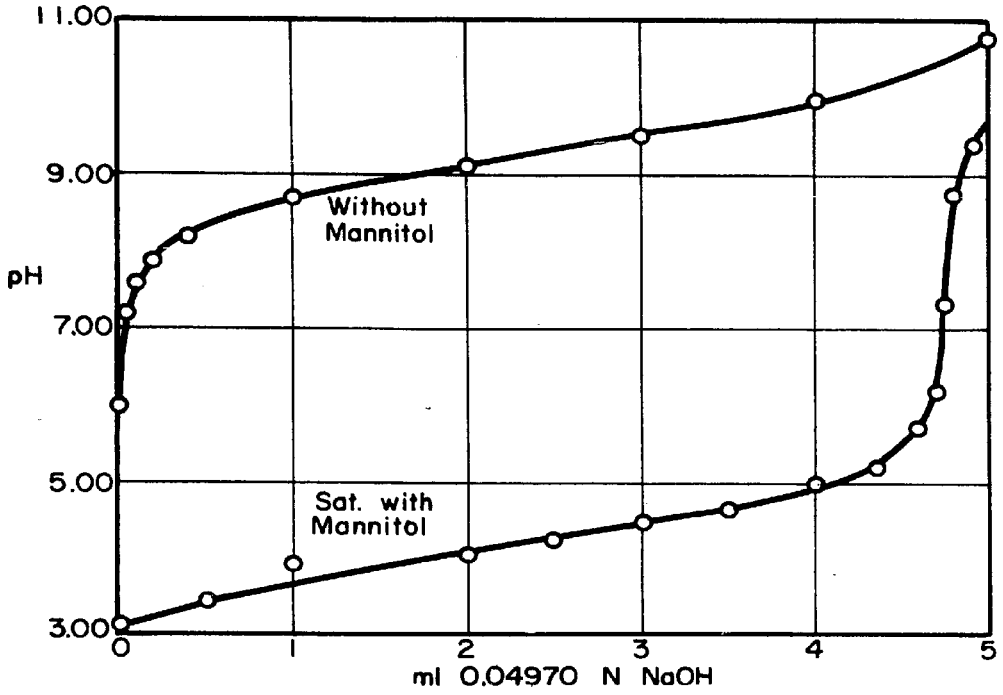


Figure 5. Titration of 0.2355 meq. Boric Acid.

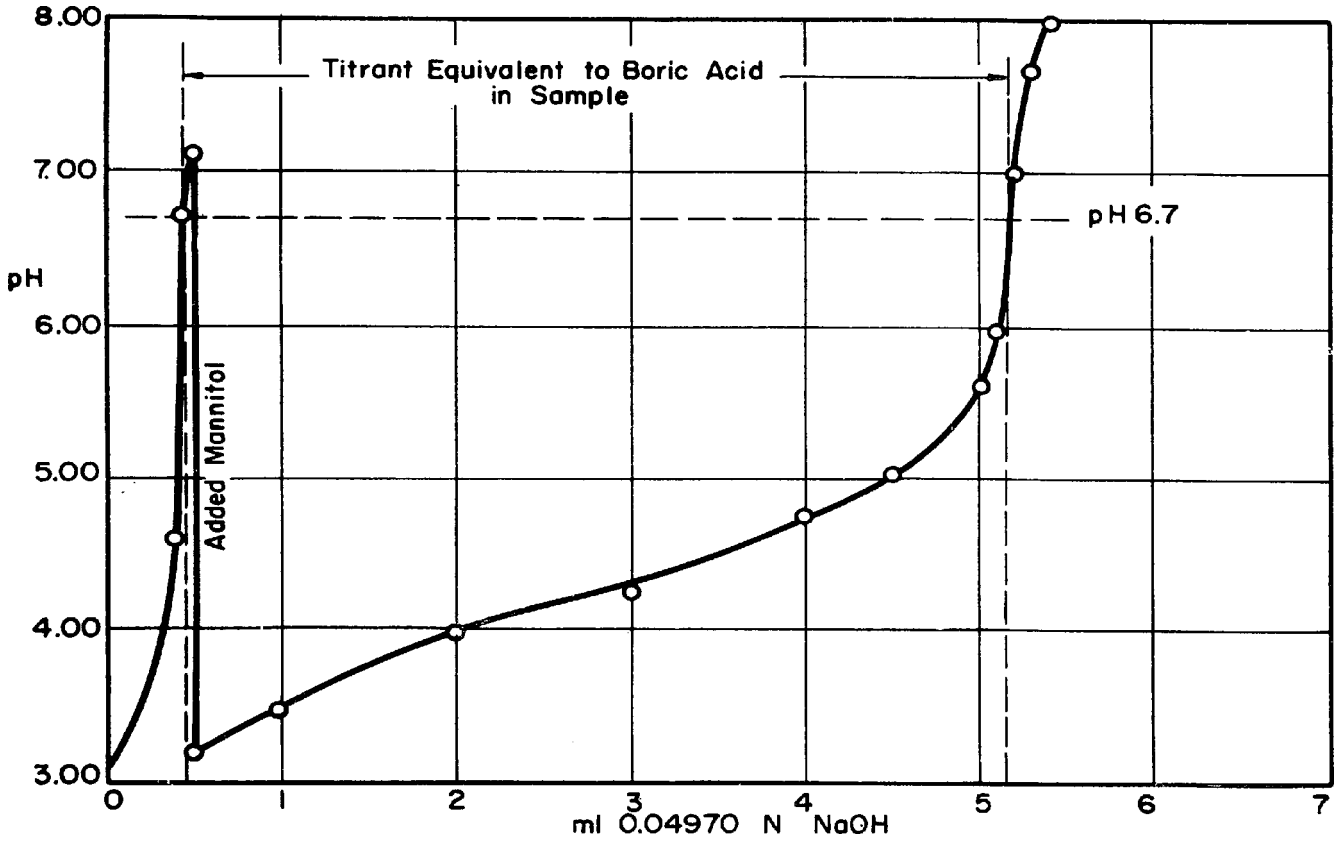


Figure 6. Titration of 0.2355 meq. Boric Acid in Presence of 0.25 meq. NH_4Cl.

0.05 N NaOH were used. The reduction of hydroxylamines was accomplished by digestion with glucose using a K_2SO_4-$CuSO_4$ catalyst.

The nitrogen content of $(CH_3NHBH_2)_3$ was determined by the micro-Dumas method. The sample was analyzed by Mrs. Anna Griffin in the Micro-Analytical Laboratory of the Department of Chemistry of the University of Michigan.

Phosphorus

Phosphorus was converted to phosphoric acid and determined as ammonium phosphomolybdate.

APPENDIX B

Thermal Stability and Explosion Products of Methoxyamine

Several explosions have occurred with methoxyamine in the high vacuum apparatus. Campbell reported an explosion when a portion of the line containing the amine was heated with a free flame. In this investigation a violent detonation occurred when a Tesla coil (the high frequency spark discharge coil used for locating leaks) was brought near a sample of methoxyamine. In the interest of safety and in the search for decomposition products which might have served as catalysts or reactants in Campbell's first reaction between methoxyamine and diborane, an investigation was made of the thermal stability and the explosion products of methoxyamine.

A sample of the amine was heated for 12 hours near its boiling point, 49.5°. After the CH_3ONH_2 was returned to the vacuum line, its vapor pressure at 0° showed that no decomposition had taken place. To check the stability in the vapor phase at higher temperatures, 0.1742 gram was sealed into a one liter bulb and heated at 195° for 10 hours. There was only about 3% decomposition, which produced traces of material both more and less volatile than the methoxyamine. In view of these experiments, it was concluded that the compound is quite stable at moderately high temperatures.

The conditions required to initiate an explosion by a high frequency spark were tested with sealed tubes of methoxyamine behind a safety shield. It was observed that

decomposition occurred only at low pressures where the spark produced a discharge in the vapor. This condition was brought about by allowing the amine to warm up slowly from liquid nitrogen temperature and applying the Tesla coil at intervals of time. A well-annealed sealed glass tube containing a limited amount of the amine was found to withstand the mechanical shock and pressure of the explosion products. The products were then introduced back into the vacuum line through a break tip on the tube and analyzed.

The explosion of 2.26 mmoles of methoxyamine produced 4.39 mmoles of noncondensable gases, with an apparent molecular weight of 14.42, in addition to a mixture of condensable materials. The amount of nitrogen in this mixture of noncondensable gases was determined by circulating an aliquot through a tube containing CuO at 420° with the Toepler pump. The amount of noncondensable gas recovered indicated that the mixture contained 13.9 mole per cent nitrogen. From the amount of CO_2 produced in the combustion it was calculated that there was 36.1 mole per cent of carbon-containing gases. This was found to be carbon monoxide by circulating another aliquot through a suspension of cuprous sulfate-β-naphthol in concentrated sulfuric acid (Cosorbant). The mole per cent of the gas absorbed was 35.6%. The remaining 50.6% of the mixture was apparently hydrogen since the average molecular weight of such a mixture would be 14.85, in good agreement with the measured value.

The largest component of the condensable fractions was ammonia. An 0.82 mmole sample was carefully purified and identified by molecular weight and vapor pressure. Another 0.51 mmole fraction consisted of impure ammonia. A small amount, 0.04 mmole, of a very volatile substance was obtained which had a vapor pressure close to that of ethane. The remainder was a mixture of less volatile materials which could not be separated and identified.

The explosive decomposition of methoxyamine can be represented approximately by the equation:

$$2\ CH_3ONH_2 \longrightarrow 1/2\ N_2 + NH_3 + 2\ H_2 + 4/3\ CO + 1/3\ (C_2H_9O_2)$$

where the last formula represents a mixture of materials such as ethane, methyl alcohol, water, etc.

The reason for this instability is the combination of oxidizing and reducing properties in the same molecule. The parent compound, hydroxylamine, is much more unstable and begins to decompose above 15° mainly by the equation (69):

$$3\ HONH_2 \longrightarrow NH_3 + N_2 + 3\ H_2O\ ,$$

and to a lesser extent:

$$4\ HONH_2 \longrightarrow 2\ NH_3 + N_2O + H_2O\ .$$

The principal difference in the decompositions of $HONH_2$ and CH_3ONH_2 is that the oxides of carbon are more stable than those of nitrogen. This accounts for the fact that no oxides of nitrogen were found among the explosion products of methoxyamine, but rather carbon monoxide was

identified. The hydrogen gas apparently came from the hydrogens which were originally attached to the carbon atom rather than from those on the nitrogen.

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