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Final Report

CHEMISTRY OF BORON HYDRIDES AND RELATED HYDRIDES

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## FOREWORD

The work reported herein was conducted under Contract AF 33(616)-8 with the United States Air Force, the sponsoring agency being the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command. Direct technical responsibility for the investigation was vested in the Chemistry Research Branch of the Aeronautical Research Laboratory under the supervision of Dr. Lloyd A. Wood. Lt. David A. Fischer served as technical representative of the Government during much of this work. The authors wish to express their sincere appreciation to the scientists, officers, and men of WADC who provided an ideal situation for a productive scientific investigation.

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Last but not least, the authors wish to express to Prof. Kasimir Fajans of The University of Michigan their appreciation for his inspiring and iconoclastic views which served to promote this work in many ways. This investigation has been stimulated to a great degree by the "Quanticule Theory."

TABLE OF CONTENTS

	Page
LIST OF TABLES	vi
LIST OF FIGURES	x
ABSTRACT	xiii
I. INTRODUCTION	1
II. METHATHESIS REACTIONS OF BOROXYDRIDES IN LIQUID AMMONIA	2
A. BACKGROUND	3
B. THE PREPARATION AND PROPERTIES OF HEXAMINE COBALT (III) BOROXYDRIDE, HEXAMINE CHROMIUM (III) BOROXYDRIDE, AND AMMONIUM BOROXYDRIDE	4
III. THE STRUCTURE AND CHEMISTRY OF THE DIAMMONIATE OF DIBORANE	16
A. BACKGROUND	17
B. CHEMICAL EVIDENCE FOR THE STRUCTURE OF THE DIAMMONIATE OF DIBORANE (I). EVIDENCE FOR THE BOROXYDRIDE ION AND FOR THE DIHYDRIDO-DIAMMINE-BORON (III) CATION	19
C. CHEMICAL EVIDENCE FOR THE STRUCTURE OF THE DIAMMONIATE OF DIBORANE (II). THE PREPARATION OF AMMONIA BORANE	31
D. CHEMICAL EVIDENCE FOR THE STRUCTURE OF THE DIAMMONIATE OF DIBORANE (III). THE REACTIONS OF BOROXYDRIDE SALTS WITH LITHIUM HALIDES AND ALUMINUM CHLORIDE	43
E. CHEMICAL EVIDENCE FOR THE STRUCTURE OF THE DIAMMONIATE OF DIBORANE (IV). THE REACTION OF SODIUM WITH LEWIS ACIDS IN LIQUID AMMONIA	54
F. A TRACER STUDY OF THE REACTION BETWEEN SODIUM AND THE DIAMMONIATE OF DIBORANE	68
G. MOLECULAR-WEIGHT MEASUREMENTS IN LIQUID AMMONIA. THE MOLECULAR WEIGHTS OF THE METHYLAMINE BORANES, THE DIAMMONIATE OF DIBORANE, AND AMMONIA BORON TRIFLUORIDE	82
H. THE RAMAN SPECTRUM OF THE BOROXYDRIDE ION AND EVIDENCE FOR THE CONSTITUTION OF THE DIAMMONIATE OF DIBORANE	92
IV. UNUSUAL COMPOUNDS RESULTING FROM THE BORANE GROUP	102
A. BACKGROUND	103
B. PREPARATION AND PROPERTIES OF TRIMERIC N-METHYL-AMINOBORANE	104
C. THE PREPARATION AND PROPERTIES OF PHOSPHORUS TRIFLUORIDE—BORANE AND PHOSPHORUS TRIFLUORIDE—BORANE-d <sub>3</sub>	108



TABLE OF CONTENTS  
(Concluded)

	Page
V. THE REACTIONS OF DIBORANE WITH HYDROXYLAMINE AND ITS METHYL DERIVATIVES	117
A. THE PHYSICAL AND CHEMICAL PROPERTIES OF THE HYDROXYLAMINES	118
B. THE REACTION OF HYDROXYLAMINE AND ITS N-METHYL DERIVATIVES WITH DIBORANE	134
C. THE REACTION OF O-METHYLHYDROXYLAMINE AND ITS N-METHYL DERIVATIVES WITH DIBORANE	147
VI. THE REDUCTION OF CHLOROPHOSPHINES WITH LITHIUM ALUMINUM HYDRIDE AND WITH LITHIUM HYDRIDE	161
APPENDIX. THE ISOTOPE EFFECT IN THE TRACER STUDIES OF THE "DIAMMONIATE OF DIBORANE"	171

## LIST OF TABLES

<u>Section II-B</u>	Page
I. Effect of pH of Original Solution on the Composition of the $[\text{Co}(\text{NH}_3)_6] \text{F}_3$ Crystals	8
II. Analysis of Borohydrides	11
 <u>Section III-B</u>	
I. Reaction of the Diammoniate of Diborane with Sodium Borohydride or Ammonium Bromide and of Sodium Borohydride with Ammonium Bromide	21
II. X-Ray Powder Patterns for $\text{H}_2\text{B}(\text{NH}_3)_2\text{Br}$ and $\text{NH}_4\text{Br}$	23
III. The Reaction in Liquid Ammonia Between Na and the Product Obtained from the Action of $\text{NH}_4\text{Br}$ on $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$	24
 <u>Section III-C</u>	
I. The Reaction Between the "Diammoniate of Diborane" and Ammonium Chloride Slurried in Ether	34
II. The Reaction Between Lithium Borohydride and an Ammonium Salt Slurried in Ether	35
III. Comparison of the Properties of Ammonia-Borane with Those of the "Diammoniate of Diborane"	36
 <u>Section III-D</u>	
I. The Reaction Between the "Diammoniate of Diborane" and Aluminum Chloride in Ether	46
 <u>Section III-E</u>	
I. The Reaction of Ammonium Carbamate with Sodium in Liquid Ammonia	56
II. A Comparison of the Results of Schlesinger and Burg with Those from This Laboratory	58
III. The Reaction of the Diammoniate of Diborane with Sodium in Liquid Ammonia	60

LIST OF TABLES  
(Continued)

<u>Section III-E (Cont'd)</u>	Page
IV. The Reaction of Sodium with Diborane-Ammonia Systems from Which Ammonia Was Never Removed	60
 <u>Section III-F</u>	
I. A Tracer Study of the Reaction of the "Diammoniate of Diborane" with Sodium in Liquid Ammonia	70
II. A Tracer Study of the Reaction of Sodium with Solutions of Diborane in Ammonia	72
III. A Tracer Study of the Reaction of "Mistreated Diammoniate of Diborane" with Sodium in Liquid Ammonia	74
IV. Ammonolysis Reactions	75
 <u>Section III-G</u>	
I. Molecular Weights of Urea	84
II. Molecular Weights of $\text{NH}_4\text{Br}$ , $\text{NH}_4\text{BF}_4$ , and $\text{NaBH}_4$ in Liquid Ammonia	86
 <u>Section III-H</u>	
I. Raman Frequencies (in $\text{cm}^{-1}$ ) and Assignments for Lithium, Sodium, Potassium, and Ammonium Borohydrides and for Lithium and Potassium Borodeuterides Dissolved in Liquid Ammonia	96
II. Raman Frequencies (in $\text{cm}^{-1}$ ) of the Diammoniate of Diborane Dissolved in Liquid Ammonia	98
 <u>Section IV-B</u>	
I. Analysis for $(\text{CH}_3\text{NHBH}_2)_3$ , %	105
II. Interplanar Spacings ( $d$ Values) and Relative Line Intensities of Trimeric N-Methylaminoborane	107

LIST OF TABLES  
(Continued)

<u>Section IV-C</u>	Page
I. Comparison of the Properties of Carbon Monoxide—Borane and Phosphorus Trifluoride—Borane	112
II. Data on Reactions Between Phosphorus Trifluoride and Diborane	114
III. Vapor Pressures of Phosphorus Trifluoride—Borane	115
IV. Vapor Pressures of Phosphorus Trifluoride—Borane-d <sub>3</sub>	115
 <u>Section V-A</u>	
I. Melting Points of Hydroxylamine and Its Methyl-Substituted Derivatives	122
II. The Vapor Pressure of O-Methylhydroxylamine	124
III. The Vapor Pressure of O,N-Dimethylhydroxylamine	125
IV. The Vapor Pressure of O,N,N-Trimethylhydroxylamine and N-Methylhydroxylamine	126
V. The Vapor Pressure of N,N-Dimethylhydroxylamine	127
VI. Melting Points, Boiling Points, Heats of Vaporization, and Trouton Constants of Methyl-Substituted Hydroxylamines	127
VII. pKa Values for Ammonia, Hydroxylamine, and Methyl-Substituted Hydroxylamines	129
VIII. A Comparison of the "Trouton Constant" at a Pressure of 200 mm with the Hildebrand-Trouton Constant at a Uniform Vapor Concentration of 0.00507 Mole/Liter for a Series of Amines	133
 <u>Section V-B</u>	
I. Summary of the Properties of the Borane Addition Compounds of Hydroxylamine and Its N-Methyl Derivatives	135
II. Reaction between N,N-Dimethylhydroxylamine and Excess Diborane	139
III. Catalytic Decomposition of Pure N,N-Dimethylhydroxylamine-Borane by Diborane at 25°C	139

LIST OF TABLES  
(Concluded)

<u>Section V-C</u>	Page
I. Summary of the Properties of the Borane Addition Compounds of Hydroxylamine and its Methyl-Substituted Derivatives	152
II. Characterization of $\mu$ -Monoaminodiborane	159
 <u>Section VI</u>	
I. Vapor Pressures of Mono- and Diethyl Phosphines	165
II. The Reaction of Phosphines and Amines with $\text{LiAlH}_4$	169

## LIST OF FIGURES

<u>Section II-B</u>	Page
1. Apparatus for the preparation of hexamine metal (III) borohydrides.	10
2. Molecular weight of the "diammoniate of diborane" as compared to that for the decomposition product from $\text{NH}_4\text{BH}_4$ .	14
3. Molecular-weight data for $\text{NH}_4\text{Br}$ , $\text{NH}_4\text{BF}_4$ , and $\text{NaBH}_4$ in liquid ammonia as a function of solution concentration.	15
 <u>Section III-C</u>	
1. The reaction between ammonium chloride and the "diammoniate of diborane" in an ether slurry.	33
2. Apparatus for the reaction between ammonium chloride and the "diammoniate of diborane" in an ether slurry.	40
 <u>Section III-D</u>	
1. The decomposition of the "diammoniate of diborane" in the presence of a lithium halide.	45
2. Apparatus for the preparation of solutions of aluminum chloride in ether.	49
3. Reactor tube for the decomposition of the "diammoniate of diborane" in the presence of a lithium halide.	51
4. Apparatus for the reaction between the "diammoniate of diborane" and aluminum chloride in ether.	52
 <u>Section III-E</u>	
1. Bulb crusher for reactions with sodium in liquid ammonia.	65
 <u>Section III-F</u>	
1. Sodium still.	78
2. Schematic diagram of system for tracer studies.	80

LIST OF FIGURES  
(Continued)

<u>Section III-G</u>	Page
1. Molecular-weight apparatus.	85
2. Determination of the molecular weight of $\text{NH}_3\text{BF}_3$ in liquid ammonia.	87
3. Molecular weights of the methylamine boranes in liquid ammonia.	89
4. Molecular-weight measurements on the "diammoniate of diborane."	91
 <u>Section III-H</u>	
1. Apparatus for purification and loading of samples in a Raman tube.	94
2. The B-H stretching region in the Raman spectra of some borohydrides dissolved in liquid ammonia. Tracing 1, $\text{LiBH}_4$ ; 2, $\text{NaBH}_4$ ; 3, the diammoniate of diborane. (Frequency in $\text{cm}^{-1}$ )	99
 <u>Section IV-C</u>	
1. Decomposition of $\text{OCBH}_3$ and $\text{PF}_3\text{BH}_3$ at room temperature.	110
 <u>Section V-A</u>	
1. The pKa values for $\text{CH}_3$ , $\text{OH}$ , and $\text{OCH}_3$ substituted amines.	132
 <u>Section V-B</u>	
1a. Mole ratio of hydrogen to $\text{H}_2\text{NOH}\text{BH}_3$ .	137
1b. Decomposition curves of hydroxyl- and methyl-substituted hydroxyl-amine boranes.	137
2. Special weighing unit for hydroxylamine.	143
3. Reaction of diborane with hydroxylamine at $-112^\circ\text{C}$ .	146

LIST OF FIGURES  
(Concluded)

<u>Section V-C</u>	Page
1. Decomposition of $\text{NH}_2\text{OCH}_3 \cdot \text{BH}_3$ at $55^\circ\text{C}$ .	150

<u>Section VI</u>	
1. Apparatus for production of phosphines by reduction of chlorophosphines with $\text{LiAlH}_4$ .	167

<u>Appendix</u>	
1. An approximation of $\alpha_0$ for the reaction of $\text{B}_2\text{D}_6 \cdot 2\text{ND}_3$ with sodium in ammonia- $\text{d}_3$ .	174



## ABSTRACT

The types of coordination compounds formed by diborane with various Lewis bases have been explored and the reactions of such coordination compounds have been delineated. The bases studied were: ammonia, methylamine, dimethylamine, trimethylamine, phosphorus trifluoride, nitrogen trifluoride, carbon monoxide, hydroxylamine, N-methylhydroxylamine, N-N dimethyl hydroxylamine, O-methyl hydroxylamine, O,N-dimethyl hydroxylamine, and trimethyl hydroxylamine.

The hexammine metal (III) borohydrides have been prepared and it has been shown that the "diammoniate of diborane" has the structure  $[\text{H}_2\text{B}(\text{NH}_3)_2]^+(\text{BH}_4)^-$ . The decompositions of the borane adducts of the methyl hydroxylamines have been studied in some detail, and mechanistic arguments for the decompositions have been considered.

The reduction of phosphorus trichloride by lithium aluminum hydride has been studied.

Results of the diborane reaction are interpreted in terms of symmetrical and non-symmetrical cleavage of the double-bridge bond in diborane.



## I. INTRODUCTION

Boron compounds, particularly the hydrides, have been recognized as theoretical puzzles for many years. Recent interest in the large-scale synthesis of certain boron-hydrogen compounds has transformed the theoretical puzzle into a large-scale practical problem. Methods used in developing chemical processes usually owe their success to an application of appropriate theoretical guides. For example, a truly amazing theoretical framework guides the organic chemist in his work. On the other hand, conventional chemical theories, particularly those developed for carbon chemistry, usually fail miserably when applied to boron hydrides. As an example, consider the simplest of the free boron hydrides, diborane— $B_2H_6$ . The organic chemist pictures a covalent chemical bond as arising from the sharing of an electron pair, yet  $B_2H_6$  has more apparent bonds than electron pairs. It is frequently referred to as an "electron-deficient" molecule. Such electron deficiency has been treated extensively in theoretical papers but the results offer very little help in correlating the reactions of boron hydrides. In general, the reactions of carbon cannot be transferred to a study of boron hydrides; hence, it is now painfully apparent that the laws and generalizations correlating the chemistry of boron compounds must be developed independently. The studies described herein were conducted in the hope that a useful reaction pattern for certain boron compounds might be evolved.

A number of seemingly separate studies have been conducted during the course of this work, yet all are related through their contribution to an understanding of the reaction pattern of boron hydrides. It appears to be convenient to discuss the various facets of the work as individual units and then to correlate the pertinent observations. For this reason the report will take the form of a series of separate papers, all of which are germane to the announced objective. The credit and responsibility for each set of data are also indicated more precisely using this pattern.

## II. METATHESIS REACTIONS OF BOROHYDRIDES IN LIQUID AMMONIA

## A. BACKGROUND

Ever since the first description of aluminum borohydride by Schlesinger and his co-workers,<sup>1</sup> the synthesis, by metathesis reactions in suitable solvents, of new and potentially interesting borohydrides has seemed worthy of study. It should be noted that the borohydride ion has much in common with the better known complex fluoroborate ion although several important differences do exist.

The stability of the alkali metal borohydrides increases as the size of the cation increases. On the other hand, it is normally assumed that the presence of protonic or acidic hydrogens in the cation reduces the stability of the borohydride. For these reasons it seemed to be relevant to study the stability characteristics of the hexammine metal (III) borohydrides. The hexammine metal (III) cation is large, yet it contains potentially acidic hydrogens attached to the coordinated ammonia.

The remote possibility of putting the borohydride ion in the coordination sphere of the Co (III) seemed worthy of consideration and the possibility of obtaining interesting metal-nitrogen-boron polymers offered some additional justification for the study.

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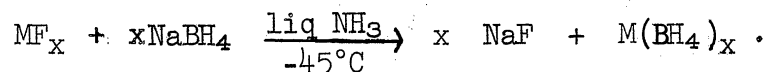
1. H. I. Schlesinger, R. I. Sanderson, and A. B. Burg, J. Am. Chem. Soc., 61, 536 (1939).

B. THE PREPARATION AND PROPERTIES OF HEXAMMINE COBALT (III) BOROHYDRIDE, HEXAMMINE CHROMIUM (III) BOROHYDRIDE, AND AMMONIUM BOROHYDRIDE (R. W. Parry, D. R. Schultz, and P. R. Girardot)

Abstract

The methods for the preparation of hexamine cobalt (III) borohydride, hexamine chromium (III) borohydride, and ammonium borohydride are described. Hexamine chromium (III) borohydride is a stable compound up to 60°C, the cobalt compound decomposes at 25°C under high vacuum, and ammonium borohydride is unstable above -40°C. The thermal decomposition of these compounds, as well as their decomposition in aqueous solution, has been studied.

The synthesis of penetration-type metal ammine borohydrides may be achieved by metathesis reactions in liquid ammonia of the general type



This reaction has been effected for those cases in which M is the hexamine chromium (III) ion, the hexamine cobalt (III) ion, and the ammonium ion. The resulting new compounds, hexamine chromium (III) borohydride and hexamine cobalt (III) borohydride, are described herein. Although ammonium borohydride was mentioned briefly by Armstrong<sup>1</sup> in a previously classified industrial report, little information on its properties was available. In a study of the "diammoniate of diborane" the properties of this compound became important, and a more thorough investigation was warranted. From the philosophical standpoint ammonium borohydride is interesting since it represents borohydric acid in liquid ammonia.

Ammonium Borohydride.—If the reaction between ammonium fluoride suspended in liquid ammonia and sodium borohydride is carried out at -40°C, or below, and this temperature is carefully maintained during all filtration and transfer operations, no noncondensable gas is evolved. Pure ammonium borohydride may be obtained from the reaction as a white crystalline solid. Above about -40°C slow decomposition of the solid begins with liberation of hydrogen. At 25°C one sample of ammonium borohydride was 50% decomposed in about six hours.

The Raman spectrum of a liquid ammonia solution of ammonium borohydride compared favorably in every detail, including the shape of the envelope and intensity of lines, with the spectrum of a liquid ammonia solution of sodium borohydride. A detailed consideration of the Raman spectra of a number of borohydrides in liquid ammonia will be deferred to later publications;<sup>2</sup> however, the data now available offer convincing evidence of the presence of the borohydride group in the compound. The molecular

1. Aerojet Engineering Corp., Biennial Report No. 420, January 26, 1950; RTM-66 May 26, 1950.

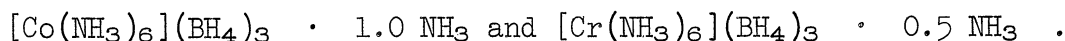
2. R. C. Taylor, D. R. Schultz, and A. E. Emery, this Report p. 92.

weight of the compound in liquid ammonia solution was measured by vapor-pressure depression. Some difficulties were encountered in the experiment due to decomposition and other factors; however, the data are sufficiently precise to indicate that the molecule is monomeric and undissociated in 1-molar liquid ammonia solution; the apparent molecular weight was about 34 as compared to a theoretical value of 32.89. Other salts such as sodium borohydride and ammonium bromide likewise exist as undissociated ion pairs<sup>3</sup> in 1-molar liquid ammonia solution.

At room temperature ammonium borohydride loses one mole of hydrogen per mole of salt to give a relatively stable material of empirical composition  $\text{BNH}_6$ . An earlier report<sup>4</sup> on this substance, which has the same empirical formula as the "diammoniate" of diborane, indicated that it could not be the classical "diammoniate." It was reported that the new solid did not yield borazene on thermal decomposition while the classical "diammoniate" gives borazene in yields approaching 50%.

In the present investigation a portion of the  $\text{BNH}_6$  produced from ammonium borohydride was pyrolyzed at  $180^\circ\text{C}$  for 2-1/2 hours to give a 15% yield of recovered borazene. The very small scale of the reaction undoubtedly contributed to the low yield (i.e., .04 mmole of borazene recovered). The isolation of borazene indicates that the  $\text{BNH}_6$  could be the same species as the classical "diammoniate of diborane." Molecular-weight measurements in liquid ammonia for the compound  $\text{BNH}_6$  compared favorably with values for samples of the "diammoniate." Values were not in agreement with results found for the recently discovered monomer,  $\text{H}_3\text{NBH}_3$ .<sup>5</sup> In evaluating the molecular-weight data certain anomalous features of the vapor-pressure depression measurements on systems of this type prevented one from using the evidence as conclusive proof of the identity of the two materials. Additional evidence was sought in a study of Raman spectra. The Raman spectrum of  $(\text{H}_3\text{NBH}_3)_n$  obtained by the decomposition of ammonium borohydride was almost the same<sup>2</sup> as the spectrum of the "diammoniate of diborane." Results are discussed elsewhere (see p. 82).

Hexammine Cobalt (III) Borohydride and Hexammine Chromium (III) Borohydride.— A metathesis reaction in liquid ammonia between a suspension of the ammonia insoluble hexammine metal (III) fluoride and ammonia soluble sodium borohydride produced ammonia insoluble sodium fluoride and ammonia soluble, yellow complexes of composition  $[\text{M}(\text{NH}_3)_6](\text{BH}_4)_3$ . The reaction appeared to go to completion at  $-63.5^\circ\text{C}$  in about two hours, but longer reaction times were generally used. NaF was identified by fluoride analysis. Ordinarily an excess of  $\text{M}(\text{NH}_3)_6\text{F}_3$  was used in the reaction in order to remove all of the ammonia soluble sodium borohydride. When reaction was complete, the insoluble NaF and excess  $[\text{M}(\text{NH}_3)_6]\text{F}_3$  were filtered from the system to leave a relatively pure solution of  $[\text{M}(\text{NH}_3)_6](\text{BH}_4)_3$  in liquid ammonia. After evaporation of the solvent, long yellow needle-like crystals of the pure complexes were obtained. Analysis of the yellow crystals indicated the formulas



3. See page 82 of this report.

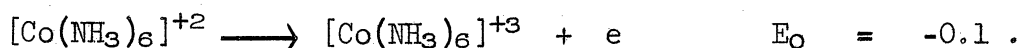
4. Aerojet Engineering Corp. Annual Report No. 367, March 11, 1949.

5. S. G. Shore and R. W. Parry, J. Am. Chem. Soc., 77, 6084 (1955).

Since attempts to remove excess ammonia always resulted in some darkening and decomposition of the solid, particularly for the cobalt complex, the excess ammonia was not removed.

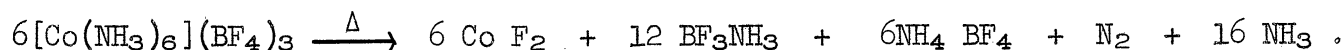
The Thermal Decomposition of the Hexamine Metal (III) Borohydrides of Cobalt and Chromium.—Dry hexamine cobalt (III) borohydride loses ammonia and undergoes irreversible decomposition when the ammonia pressure is reduced below 50 mm at 25°C. In contrast, the dry hexamine chromium (III) borohydride is remarkably stable at 25°C even under high vacuum; the decomposition under these conditions was less than 2% as measured by hydrogen evolution. When the chromium complex was heated in vacuum to 60°C, its decomposition became comparable to that of the cobalt complex at 25°C.

Data now available indicate that the instability of the cobalt complex is to be associated with the strong reducing properties of the borohydride group and with the fact that  $[\text{Co}(\text{NH}_3)_6]^{+3}$  is reduced more easily than its chromium counterpart. The latter fact is indicated by the value for the standard electrode potential of the oxidation reaction in aqueous solution:

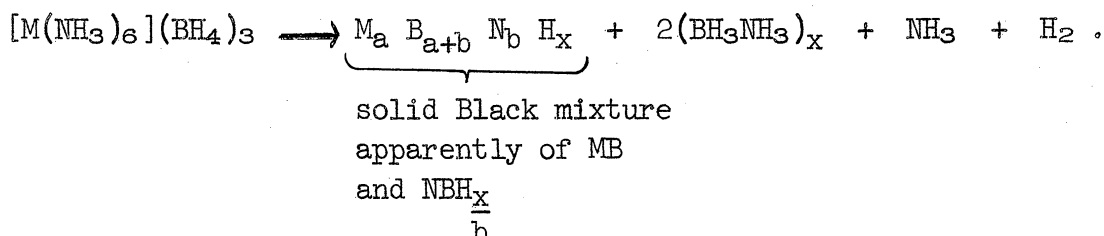


The value for the corresponding chromium couple is not available, but qualitative considerations indicate that it must be more positive than +0.5 since ammoniacal solutions of  $\text{Cr}(\text{NH}_3)_6^{+2}$  liberate hydrogen rapidly from water in the presence of finely divided platinum.<sup>6</sup>

As would be expected, the reducing properties of the borohydride group cause a different type of thermal decomposition than is observed with the hexamine complexes containing a nonreducing anion. The hexamine cobalt (III) fluoroborate, which is formally analogous to the complex borohydride, decomposes in accordance with the equation<sup>7</sup>



The thermal decomposition of the dry hexamine metal (III) borohydrides differs from that described above in that the borohydride group is oxidized instead of the ammonia. Otherwise certain elements of similarity may be noticed. Although the decomposition is complex, the equation which best describes the main process is



The hydrogen and ammonia were identified positively as gaseous decomposition products.

6. R. W. Parry and D. A. Berman, to be published.

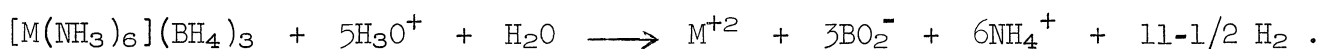
7. Baly, Von Günther, and Zinser, Z. anorg. allgem. Chem., 221, 225-48 (1935).



The compound  $(H_3BNH_3)_x$  was extracted from the solid residue with liquid ammonia and the empirical formula was established by analysis. During the slow decomposition of  $[Cr(NH_3)_6](BH_4)_3$  two relatively large clear crystals of solid formed in the cold trap through which gases were removed. Although these crystals were not identified at the time, more recent experience with the new crystalline compound  $H_3NBH_3$  suggests that the crystals were probably this monomeric species. The bulk of the material of composition  $(H_3NBH_3)_x$  remained in the reaction vessel, however, and was apparently the diammoniate of diborane. The overall composition of the ammonia insoluble, solid black residue suggested a mixture of metal boride and polymeric  $BNH_x$ , where  $x$  ranged from 0 to 4. Unequivocal identification of separate phases in this solid was never achieved.

The Reaction Between Water and the Hexammine Metal (III) Borohydrides of Chromium and Cobalt.—The hexammine cobalt (III) borohydride dissolved in water to give a yellow solution which decomposed rapidly. A black ferromagnetic precipitate was obtained which gave cobalt (II) ion when acidified. The same black solid was also observed when sodium borohydride was added to a hexammine cobalt (III) chloride solution. Hydrogen was always liberated.

The chromium complex borohydride reacted very slowly with water to liberate a small amount of hydrogen, but no precipitate appeared during this period. In the absence of air, the blue chromous ion was produced upon acidification. It is consistent with the above observation to note that hexammine chromium (III) chloride and sodium borohydride gave no apparent reaction in water solution except for the very slow evolution of hydrogen. Reaction ensued, however, when acid was added. Data for the overall hydrolysis reactions of both complex borohydrides in acid solution are consistent with the following equation:



The role of  $H^+$  in promoting reduction of the chromic complex is apparent from the equation.

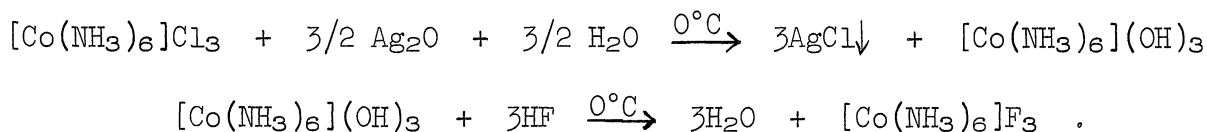
### Experimental.—

#### a. Materials.

1. Ammonium fluoride was Baker's Analyzed grade.  $NH_4HF_2$  was of course eliminated when the solid was placed in liquid ammonia.

2. Sodium borohydride was obtained from Metal Hydrides, Inc., and recrystallized twice from liquid ammonia before use.

3. Hexammine cobalt (III) fluoride—the pure complex was prepared by the following reactions:



Silver nitrate (0.38 mole) was dissolved in distilled water and treated with 50% NaOH. The precipitated  $Ag_2O$  was filtered on a Büchner funnel and

washed thoroughly with distilled water. Hexammine cobalt (III) chloride (0.1 mole) from laboratory stock was placed in a mortar which had been cooled in ice water, and wet Ag<sub>2</sub>O filter cake was added. The mixture was ground for about one hour. During this time the mortar was placed in an ice-water bath. The cold mixture was filtered and washed on a Büchner funnel. The filtrate was transferred to a polyethylene beaker, and reagent grade HF was added until the pH of the filtrate was seven, as measured by a Beckman, Model H-2 pH meter. The neutral solution was placed in a vacuum desiccator over concentrated sulfuric acid and periodically evacuated. After drying about one week the crystals were filtered on a sintered glass frit using a drying train to exclude moisture. The solid was washed with a very small amount of cold distilled water, and finally with absolute alcohol. The crystals were dried overnight at 105°C.

The solid product was identified as [Co(NH<sub>3</sub>)<sub>6</sub>]F<sub>3</sub> by measuring the absorption spectrum of its aqueous solution and by analysis. The spectrum was that of the Co(NH<sub>3</sub>)<sub>6</sub><sup>+++</sup> ion. The analysis of the solid showed Co-26.9%, NH<sub>3</sub>-46.6%, F-26.4%, and HF-0.13%; calculated for [Co(NH<sub>3</sub>)<sub>6</sub>]F<sub>3</sub>: Co-27.02%, NH<sub>3</sub>-46.84%, and F-26.13%.

Since the neutral salt [Co(NH<sub>3</sub>)<sub>6</sub>]F<sub>3</sub> is hygroscopic and very soluble in water, while the acid salt [Co(NH<sub>3</sub>)<sub>6</sub>](HF<sub>2</sub>)<sub>3</sub> is insoluble in acid solution, pH must be carefully controlled in preparing the neutral salt to prevent bifluoride contamination. The effect of pH on the composition of the resultant salt is shown in Table I.

TABLE I

EFFECT OF pH OF ORIGINAL SOLUTION ON THE COMPOSITION OF THE [Co(NH<sub>3</sub>)<sub>6</sub>]F<sub>3</sub> CRYSTALS

pH	% HF in Salt*	pH	% HF in Salt*
4.6	12.7	7.5	0.36
5.7	0.52	8.9	0.30
7.0	0.39		

\*Estimated by titration of salt to pH 7.0 using NaOH.

4. Hexammine chromium (III) fluoride, which has not been previously reported, cannot be prepared in the same manner as the cobalt complex because the hydroxide is too unstable. The following procedure does, however, yield the pure salt:



Hexammine chromium (III) chloride (0.034 mole) was dissolved in water in a polyethylene beaker. Silver fluoride solution was prepared in a separate polyethylene beaker by adding excess Ag<sub>2</sub>O to a dilute (6N) solution of HF. The excess Ag<sub>2</sub>O was filtered off and the silver fluoride solution was added carefully to the solution of the chromium complex until no excess Ag<sup>+</sup> or Cl<sup>-</sup>

could be detected. The silver chloride was filtered and the filtrate (pH = 6.3) was placed in a vacuum desiccator over concentrated sulfuric acid for one week. The crystals formed were filtered on a sintered glass frit with exclusion of air and dried in a vacuum desiccator over NaOH. The following analysis was obtained:

	Found	Theory		Found	Theory
Cr	24.1	24.63	F	27.0	26.99
NH <sub>3</sub>	47.0	48.38	HF	1.0	---

5. Liquid ammonia—commercial tank ammonia (Mathesson) was dried over sodium then distilled into the vacuum line.

b. Procedure for the Metathesis Reaction.

The metathesis reaction could be carried out at any desired low temperature by means of the apparatus shown in Fig. 1. Stoichiometric amounts of the appropriate dry fluorides<sup>8</sup> and sodium borohydride were weighed out in a controlled-atmosphere gloved box and placed in tube T. The remaining portion of the apparatus had previously been attached to the high-vacuum line at the  $\text{S } 14/35$  joint. Final assembly of tube T to the rest of the apparatus was made as rapidly as possible to avoid contact with the atmosphere. After evaluation, ammonia was condensed into tube T and the reaction was carried out at  $-65^{\circ}$  to  $-45^{\circ}\text{C}$ . The mixture was agitated by an electromagnetic plunger-type stirrer which was actuated 60 times per minute. The reaction was allowed to proceed for 3 to 5 hours, and the mixture was then frozen with liquid nitrogen. The apparatus was inverted by turning through  $180^{\circ}$  about the  $\text{S } 14/35$  joint. At this point a metal can with a hole cut in the bottom was placed on the inverted tube T in place of the solenoid. The hole in the can was just large enough to permit a snug fit around the tube and was placed 1-1/2 inches from its end. Dry Ice and i-propyl alcohol were placed in this can and in the cup on R. The remainder of the tube T was wrapped with glass wool. If necessary, additional cooling of the tube could be effected by pouring a small amount of liquid N<sub>2</sub> over this glass wool.

The solid reaction mixture gradually melted, ran down the sides, and was held on the filter frit in R. As the pressure increased a Dry Ice i-propyl alcohol bath was placed around section S and the solution filtered through the frit. Effective washing of the precipitate and the sides of the reactor could be accomplished by placing an empty Dewar flask around S, opening the stopcock in the by-pass on R, and adding more Dry Ice to the can on T. Then the stopcock on the by-pass was closed and when S was cooled, the solution would filter again. Usually five washings were required to extract all of the product. The solvent ammonia was carefully evaporated, leaving the complex borohydride in S. The apparatus was finally "filled" with dry nitrogen and taken off the line. The products were removed and handled in the dry box. The observed and theoretical compositions for the compounds assumed are summa-

<sup>8</sup>. The actual apparatus used to prepare NH<sub>4</sub>BH<sub>4</sub> differed somewhat from that described here, but the essential principles of operation are the same. Details of the other apparatus are available in the doctoral dissertation of D. R. Schultz, Univ. of Mich., Ann Arbor.

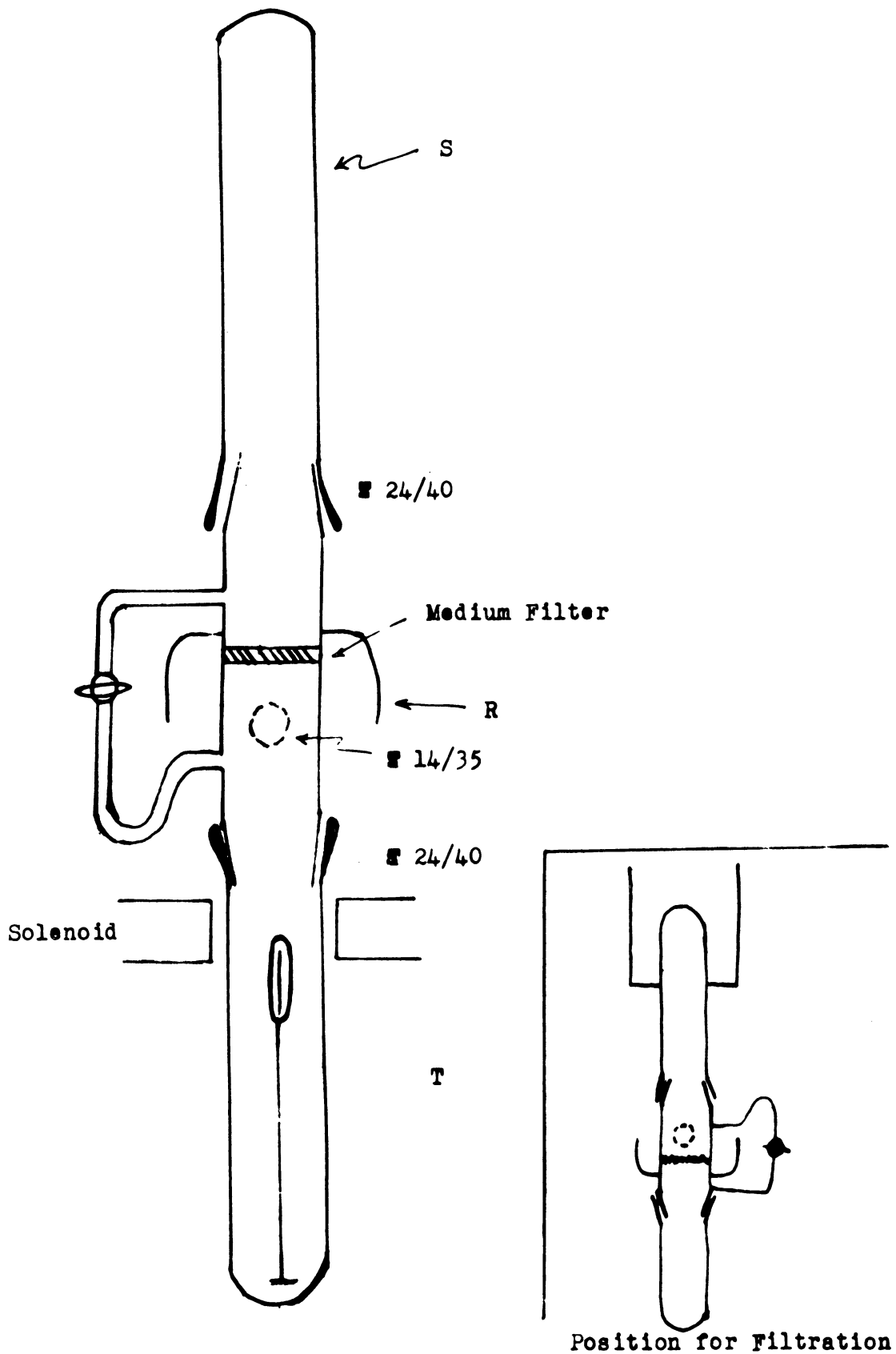


Fig. 1. Apparatus for the preparation of hexammine metal (III) borohydrides.

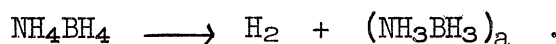
rized in Table II. Standard methods of analysis were used with minor modifications. Details are available elsewhere.<sup>9</sup>

TABLE II  
ANALYSIS OF BOROHYDRIDES

Compound	% NH <sub>3</sub>		% B		Hydridic H		% Co		% Cr	
	Obs.	Theor.*	Obs.	Theor.*	Obs.	Theor.*	Obs.	Theor.*	Obs.	Theor.*
NH <sub>4</sub> BH <sub>4</sub> **	51.6	51.79	31.4	32.91	9.10 <sup>4</sup>	12.20	--	--	--	--
[Co(NH <sub>3</sub> ) <sub>6</sub> ](BH <sub>4</sub> ) <sub>3</sub> · 1.0 NH <sub>3</sub>	53.8	53.5	14.2	14.6	5.0	5.4	26.6	26.4	--	--
[Co(NH <sub>3</sub> ) <sub>6</sub> ](BH <sub>4</sub> ) <sub>3</sub> · 0.5 NH <sub>3</sub>	53.3	53.3	15.6	15.7	5.7	5.8	--	--	25.3	25.1

\*Theoretical value for compound in left-hand column.

\*\*The identity of this compound was also confirmed by the stoichiometry of its formation from a known weight of NaBH<sub>4</sub> and an excess of NH<sub>4</sub>F which could be filtered off. For 2.45 mmoles of NaBH<sub>4</sub>, 2.48 mmoles of H<sub>2</sub> were evolved in the reaction



For 10.8 mmoles NaBH<sub>4</sub>, 10.77 mmoles of H<sub>2</sub> were obtained.

<sup>4</sup>Values for active hydrogen on B<sub>2</sub>H<sub>6</sub> · 2NH<sub>3</sub> also low by method used.

c. The Thermal Decomposition of Hexammine Metal (III) Borohydrides of Cobalt and Chromium.

Thermal decomposition of a sample was carried out in the vessel which had been used earlier for synthesis (Fig. 1). The sample, placed in section T, was frozen with liquid nitrogen and the system was evacuated.

Decomposition was accomplished by increasing the temperature or by pumping on the solid. Exit gases were passed through a trap cooled with liquid N<sub>2</sub> to remove condensable products. Hydrogen was identified by measuring its molecular weight; ammonia was characterized by molecular-weight and vapor-pressure measurements. After essentially complete gas removal, liquid ammonia was condensed into the tube T and mixed with the solid black residue. The ammonia soluble portion was filtered through the frit R and the residue was washed with liquid ammonia.

After removal of the ammonia the residues were removed in the dry box for

9. R. W. Parry, D. H. Campbell, D. R. Schultz, S. G. Shore, T. C. Bissot, and R. C. Taylor, "Chemistry of Boron Hydrides and Related Hydrides," Annual Report for 1953, Eng. Res. Inst., Univ. of Mich., Proj. 1966-1-P (May, 1954).

analysis. The colorless ammonia soluble residue contained boron and nitrogen in a ratio of 1 to 1.08.  $H_2$  was the only other element present. The solubility of the residue in liquid ammonia and its B/N ratio suggested the material  $(BNH_6)_x$ . The ammonia insoluble residue consisted of 4.40 matoms H, 0.879 matoms Cr, 2.42 matoms N, 3.29 matoms B. Such a mixture would correspond to .18 mmole CoB and 0.22 mmoles  $(BNH_x)_n$ . For the chromium salt, the ammonia soluble portion was stained with a trace of undecomposed  $[Cr(NH_3)_6](BH_4)_3$ . After correcting for this contaminant about 0.35 mmole of  $BNH_6$  was found. B/N ratio found was 1.02. The ammonia insoluble fraction contained 0.88 matoms Cr, 2.42 matoms N, and 3.29 matoms B. Such a mixture would correspond to 0.88 mmoles CrB and 2.41 mmoles  $(BNH_x)_n$  where  $x = 0$  to 4.

d. Thermal Decomposition of Ammonium Borohydride.

Ammonium borohydride was prepared in a tube attached to the vacuum system. The white crystalline solid, obtained by evaporation of the solvent ammonium decomposed slowly just above  $-40^\circ C$  and quite rapidly at  $0^\circ C$ ; upon loss of  $H_2$  the crystalline solid became an amorphous mass. The system was filled with dry  $N_2$  and the apparatus was transferred to the dry box for dismantling. A 25.6-mg sample of the decomposition product was transferred in the dry box to a 20-mm, 8-inch tube equipped with an inner Standard Taper joint. The tube was opened and stoppered, removed from the dry box, then quickly fastened to the vacuum system. After evacuation, the tube was enclosed in an electric furnace made by wrapping four feet of No. 22 nichrome wire over an asbestos coating on the tube. The wire was covered with more asbestos. Pressure in the reaction vessel was followed by a manometer and temperature by a thermocouple.

The sample was heated for 2-1/2 hours at  $180^\circ C$ . The pressure developed rapidly during the first half hour then leveled off. The sample was subsequently frozen with liquid nitrogen and the noncondensable gas was Toeplerized and measured (1.53 mmoles). A molecular-weight value of 2.18 by vapor density indicated  $H_2$ .

A volatile product was vaporized from the reaction tube and fractionated in the vacuum line. Its vapor pressure and molecular weight, tabulated below, indicate borazene:

T $^\circ C$	Vapor Pressure		
	Observed	Borazene	
-78.5	0.5 mm	0.5 mm	Molecular weight by vapor density (obs.) = 77
-63.5	1.0 mm	1.0 mm	
-45.2	5.0 mm	5.0 mm	Theory for borazene = 80.5
-22.9	23.5 mm	23.5 mm	

e. Molecular-Weight Measurements.

Molecular weight was determined by measuring vapor-pressure depression in liquid ammonia solutions. Apparatus and general procedure are described elsewhere.<sup>4</sup> Special techniques were required for ammonium borohydride since it decomposes above

-40°C. The sample was prepared as described earlier, except that the receiver on the filtration apparatus (Fig. 1) was replaced by the sample bulb used for molecular-weight determinations. The product was washed carefully into the bulb and the solvent ammonia was removed slowly at -45°C to prevent spattering. The decomposition at this point, as measured by H<sub>2</sub> evolution, was less than 2%. The vacuum apparatus was filled with dry nitrogen and the chilled sample vessel was transferred rapidly to the molecular-weight apparatus. The ammonium borohydride was then frozen with liquid nitrogen, the system was evacuated, then known amounts of solvent ammonia were condensed on the sample and the vapor-pressure depressions were measured. Temperature was always maintained below -40°C.

After making measurements on the ammonium borohydride, the solvent ammonia was removed and the sample was warmed to room temperature. The hydrogen evolved was measured. The value (2.11 mm H<sub>2</sub>) permitted an estimate of the amount of ammonium borohydride present. Following H<sub>2</sub> evolution known amounts of ammonia were condensed on the resulting BNH<sub>3</sub> residue, and molecular-weight measurements were made.

After completion of the molecular-weight measurements, ammonia was removed under high vacuum at room temperatures, the apparatus was filled with nitrogen, transferred to a dry box, and the sample bulb was weighed (76.0 g solid). Hydrolysis of the sample and subsequent Kjeldahl analysis (29.6 mg N) indicated the amount of BNH<sub>3</sub> present. The value (2.11 mm) confirmed the earlier estimate of NH<sub>4</sub>BH<sub>4</sub> based on H<sub>2</sub> evolution. The difference in total weight based on analysis and direct weighting (6.7 mg) was attributed to NaBH<sub>4</sub>. By use of this value and the previously determined curve for the molecular weight of NaBH<sub>4</sub> in liquid ammonia, the results were corrected for the small NaBH<sub>4</sub> contamination. Results are summarized in Figs. 2 and 3. In Fig. 3 the curves for NH<sub>4</sub>BF<sub>4</sub> and NH<sub>4</sub>Br are shown for comparison.

The amazing rise in apparent molecular weight as the solution approaches infinite dilution leaves some uncertainty as to the real value for the molecular weight but the most reasonable extrapolations consistent with data on other compounds indicate that NH<sub>4</sub>BH<sub>4</sub> was undissociated and monomeric. More extensive data and treatment of molecular-weight measurements are given elsewhere.

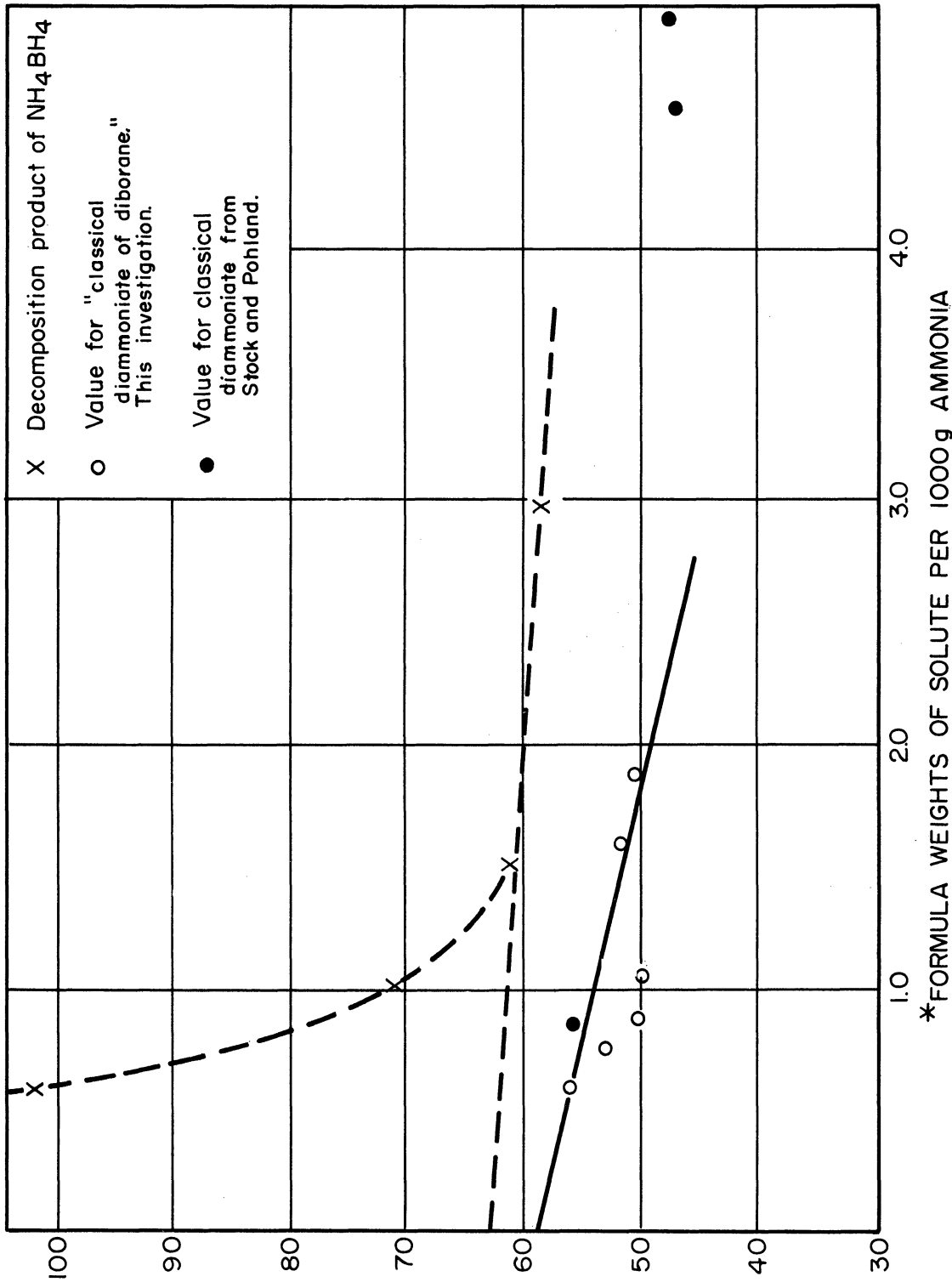


Fig. 2. Molecular weight of the "diammoniate of diborane" as compared to that for the decomposition product from  $\text{NH}_4\text{BH}_4$ .



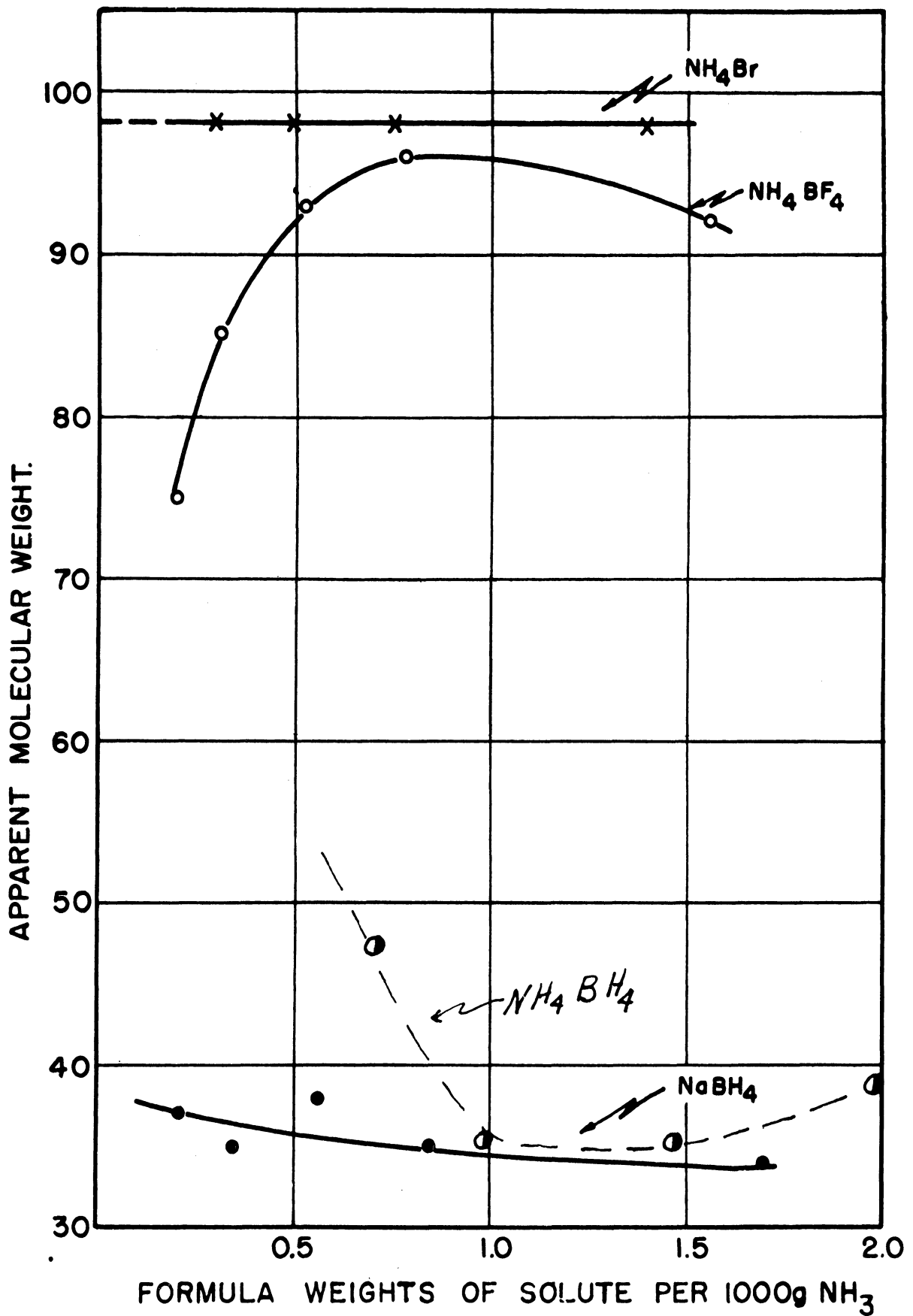
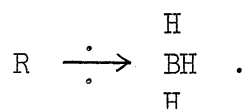


Fig. 3. Molecular-weight data for NH<sub>4</sub>Br, NH<sub>4</sub>BF<sub>4</sub>, and NaBH<sub>4</sub> in liquid ammonia as a function of solution concentration.

### III. THE STRUCTURE AND CHEMISTRY OF THE DIAMMONIATE OF DIBORANE

## A. BACKGROUND

In many of its reactions the molecule  $B_2H_6$  cleaves smoothly to give two  $BH_3$  groups which then react independently with Lewis bases to give regular coordination compounds such as



Reactions of the foregoing type are considered normal for the diborane molecule. It was then somewhat surprising for Stock and Pohland<sup>1</sup> to find that the reaction between the Lewis base ammonia and the Lewis acid, diborane, did not follow this normal pattern but gave instead a compound whose molecular weight in liquid ammonia corresponded to that of a dimer  $(H_3BNH_3)_2$ . In order to rationalize this unexpected dimeric formula, Stock<sup>2</sup> assumed that two of the hydrogen atoms of diborane are acidic in character. Such an assumption leads to the representation of the diammoniate as an ammonium salt,  $(NH_4)_2 B_2H_4$ .

Schlesinger and Burg<sup>3</sup> questioned the formulation of Stock and proposed instead the formula  $NH_4(H_3BNH_2BH_3)$ . This new representation, showing only a single ammonium ion and requiring no acid hydrogens for diborane, was based on the fact that only one equivalent of hydrogen was liberated when they allowed sodium to react with  $B_2H_6 \cdot 2NH_3$  in liquid ammonia at  $-77^\circ C$ .

Additional evidence bearing on the question of acid hydrogens in diborane was presented by Burg.<sup>4</sup> It has been shown that when the Brønsted-Lowry acid  $NH_4Cl$  is dissolved in liquid ammonia, a rapid interchange of protons between the acid and the solvent molecule occurs.<sup>5</sup> Burg conducted experiments with  $ND_3$  and  $B_2H_6 \cdot 2NH_3$  which showed that H-D interchange occurs only with the hydrogen of the ammonia and not with that of the  $B_2H_6$  in the diammoniate. He interpreted his results as proof of the assumption that the hydrogens of diborane have no acidic character. Insofar as exchange experiments can be accepted as a criterion of acidic character, Burg's evidence is convincing, although his isotope analysis was based only on differences in vapor pressure between  $ND_3$  and  $NH_3$ .

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1. A. Stock and E. Pohland, *Ber.*, 58, 657 (1925).

2. A. Stock. Hydrides of Boron and Silicon. Ithaca: Cornell Univ. Press, 1933.

3. H. I. Schlesinger and A. Burg, *J. Am. Chem. Soc.*, 60, 290 (1938).

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

5. C. J. Nyman, Si-Chang Fung, and H. W. Dodger, *ibid.*, 72, 1033 (1950).

Still another possibility has been considered in recent times. Wiberg, Bolz, and Buckheit<sup>6</sup> and others<sup>7</sup> have suggested that the compound is indeed a monomer,  $H_3BNH_3$ , and the salt-like character and dimeric nature in liquid ammonia are due to dipole-dipole attraction and hence to systematic errors in molecular-weight measurement in liquid ammonia.

The enigma presented by the diammoniate of diborane offered a real challenge to anyone attempting a systematic treatment of boron hydride chemistry. In an effort to rationalize the chemistry and structure of this substance, a detailed study of its nature has been conducted. Results are summarized in the following papers.

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6. E. Wiberg, A. Bolz, and P. Buckheit, *Z. anorg. Chem.*, 256, 287 and footnote p. 301 (1948).

7. L. J. Agronomow, *J. Chim. gen.*, 9 (71), 1389 (1939); *Chem. Zbl.*, 1941 I, 2362; Gmelin's Handbuch der anorganischen Chemie, 8. Auflage. System 13, pp. 100-101 (1954).

B. CHEMICAL EVIDENCE FOR THE STRUCTURE OF THE DIAMMONIATE OF DIBORANE (I). EVIDENCE FOR THE BOROHYDRIDE ION AND FOR THE DIHYDRIDO-DIAMMINE-BORON (III) CATION (D. R. Schultz and R. W. Parry)

Abstract

New chemical evidence is cited to support the following points: (1) the proposed existence of an ammonium ion in the diammoniate is inconsistent with its chemical properties; (2) there is strong chemical evidence for the borohydride ion in the diammoniate of diborane; (3) data available are consistent with the formula  $[\text{H}_2\text{B}(\text{NH}_3)_2](\text{BH}_4)$ .

The most widely accepted present-day structure for the diammoniate of diborane,  $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ , is the ammonium model of Schlesinger and Burg,<sup>1</sup>  $\text{NH}_4(\text{H}_3\text{BNH}_2\text{BH}_3)$ . The principal evidence for this formulation was the stoichiometry of the reaction between the diammoniate and sodium in liquid ammonia.



Evolution of only one-half mole of hydrogen per mole of diammoniate was cited as evidence for the presence of a single ammonium ion per molecule.<sup>1</sup> It is only fair to note that the foregoing ammonium model was proposed before the discovery of the borohydride ion and represented the structure which was most consistent with facts then available.

After discovery of the borohydride ion by Schlesinger and his co-workers<sup>2</sup> a new structure was equally plausible,  $[\text{H}_2\text{B}(\text{NH}_3)_2](\text{BH}_4)$ . This moiety was mentioned briefly in the literature of 1947 but was rejected without serious examination.<sup>3</sup>

A more careful experimental study of the diammoniate has revealed that the stoichiometry of the sodium reaction is very sensitive to the experimental conditions, hence the ammonium model still leaves many facts unexplained. A more complete report of this work is contained elsewhere.<sup>4</sup> In this paper additional independent chemical evidence pertinent to the structure of the diammoniate (prepared under very carefully controlled conditions) is examined in relation to the two foregoing models--the ammonium structure,  $\text{NH}_4(\text{H}_3\text{BNH}_2\text{BH}_3)$ , and the borohydride structure,  $[\text{H}_2\text{B}(\text{NH}_3)_2](\text{BH}_4)$ .

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1. H. I. Schlesinger and A. B. Burg, *J. Am. Chem. Soc.*, 60, 290 (1938).

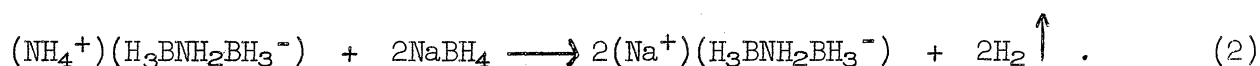
2. H. I. Schlesinger, R. J. Sanderson, and A. B. Burg, *ibid.*, 61, 536 (1939); 62, 3421 (1940); A. B. Burg and H. I. Schlesinger, *ibid.*, 62, 3425 (1940); H. I. Schlesinger and H. C. Brown, *ibid.*, 62, 3429 (1940).

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

4. S. G. Shore and R. W. Parry, this Report, p. 54.

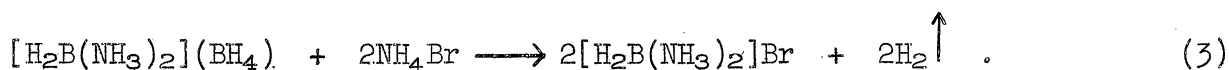
The Reactions of the Diammoniate of Diborane with Ammonium Bromide and Sodium Borohydride.—Although the stoichiometry of the reaction between sodium and the diammoniate of diborane in liquid ammonia is consistent with the presence of an ammonium ion in liquid ammonia, it is important to note that such a reaction is definitely not proof of the existence of an ammonium ion in the solid state. Rather it is evidence for the presence of any Brönsted-Lowry acid which can oxidize the active sodium metal in liquid ammonia solution. For example, the acid behavior of aluminum sulfate in water solution (e.g., reaction with carbonate to liberate CO<sub>2</sub>) is not evidence for the existence of hydronium ion, H<sub>3</sub>O<sup>+</sup>, in solid aluminum sulfate hydrate, but is, instead, evidence for the existence of water molecules whose proton-donor qualities have been enhanced by coordination of the water molecule to an ion of relatively high field strength. The proton-donor properties of ammonia can likewise be increased by coordination.

An independent, though still not conclusive, test for the ammonium ion would be its reaction with borohydride at room temperature to give hydrogen. The validity of this test is indicated by the earlier data on the instability of ammonium borohydride.<sup>5</sup> The overall reaction should be

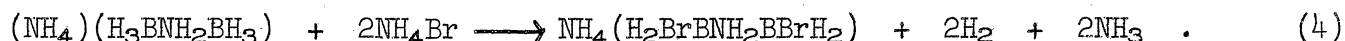


To test for the ammonium ion, sodium borohydride was added to the diammoniate in two separate experiments, under conditions which resulted in vigorous hydrogen evolution from mixtures of authentic ammonium salts and NaBH<sub>4</sub>. Results in Table I show that hydrogen evolution did not proceed as demanded by the ammonium formulation. Since the formula (NH<sub>4</sub>)(H<sub>3</sub>BNH<sub>2</sub>BH<sub>3</sub>) does not permit easy treatment as an un-ionized solid structure, one would assume that the behavior of an ammonium ion, if present, should be typical of other authentic ammonium salts.

The alternative borohydride structure suggests that the diammoniate should react with ammonium bromide rather than with sodium borohydride. The results of such an experimental test are summarized in Table I; they indicated a stepwise liberation of hydrogen which, as expected, eventually approached two moles of hydrogen per mole of diammoniate. In terms of the borohydride model the expected reaction may be written as



The Isolation and Properties of [H<sub>2</sub>B(NH<sub>3</sub>)<sub>2</sub>]Br.—Although several features are distasteful, one might still rationalize the reaction between ammonium bromide and the ammonium model of the diammoniate of diborane in terms of the following equation which is based on the suggestions of Stock:



The above process involves the inconsistency of a reaction between the ammonium salt anion and the ammonium cation in ammonium bromide. More significant, however, is the composition of the product formed. The product expected from the borohydride structure

5. R. W. Parry, D. R. Schultz, and P. R. Girardot, this Report, p. 4 .

TABLE I

REACTION OF THE DIAMMONIATE OF DIBORANE WITH SODIUM  
BOROHYDRIDE OR AMMONIUM BROMIDE AND OF SODIUM  
BOROHYDRIDE WITH AMMONIUM BROMIDE

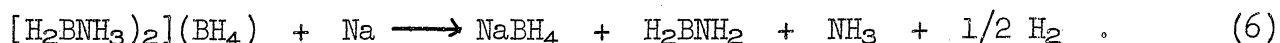
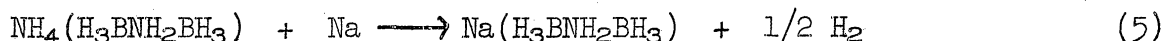
	<u>Run No. 1</u>	<u>Run No. 2</u>	<u>Run No. 3</u>
<u>A. Diammoniate Reactions</u>			
Ratio $\text{NH}_3/\text{B}_2\text{H}_6$ in prep	1.99	2.00	2.01
Temp. x's $\text{NH}_3$ removed	-45° C	-78.5° C	-45° C
$\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ (mmoles)	0.97	2.11	1.735
$\text{NaBH}_4$ (mmoles)	2.7	4.35	0
$\text{NH}_4\text{Br}$ (mmoles)	0	0	3.47
$\text{NH}_3$ (ml liquid)	5	5	5
Reaction temp.	25°	45°	25°
Reaction time	5 hr	3 hr	5 hr
$\text{H}_2$ evolved (mmoles)	0.069	0.166	3.41
Mmoles $\text{H}_2/\text{mm B}_2\text{H}_6 \cdot 2\text{NH}_3$	0.071	0.079	1.965
<u>B. Sodium Borohydride Reactions</u>			
$\text{NaBH}_4$ (mmoles)	3.98		
$\text{NH}_3\text{Br}$ (mmoles)	6.95		
$\text{NH}_3$ (ml liquid)	5		
Reaction temp.	25° C		
$\text{H}_2$ evolved (mmoles)	6.70		
$\text{H}_2/\text{NaBH}_4$	1.68		

is  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{Br}$  (see Equation 3). The total amount of boron in the product is determined by the amount of  $\text{B}_2\text{H}_6$  originally used. This value also fixes the amount of active hydrogen remaining in the product if appropriate correction is made for the gaseous hydrogen evolved. It will be noticed, however, from Equations 3 and 4 that the principal point of difference in the stoichiometry of the two overall processes is the evolution of two moles of ammonia in the reaction of the ammonium salt, but the evolution of no ammonia in the reaction of the borohydride salt. In consequence, the molar N/Br ratio expected in the case of the ammonium salt would be 1 to 1;—  $\text{NH}_4(\text{BrH}_2\text{BNH}_2\text{BBrH}_2)$ . On the other hand, the N/Br ratio expected in the case of the borohydride salt would be 2 to 1;—  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{Br}$ . Analysis of the product of the ammonium bromide "diammoniate" reaction gave a molar ratio of 2.02  $\text{NH}_3$  per bromide. The observed percentage of N was 22.1 as opposed to theoretical values of 22.09 for  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{Br}$  and 12.75 for  $(\text{NH}_4)(\text{BH}_2\text{BrNH}_2\text{BH}_2\text{Br})$ . The observed bromide value was 62.3 as compared to 63.01 expected for  $\text{H}_2\text{B}(\text{NH}_3)_2\text{Br}$  and 72.70 for the ammonium salt formulation. Both hydridic hydrogen and boron were low when the sample was hydrolyzed with 20%  $\text{H}_2\text{SO}_4$  at room temperature. Values are: observed  $\text{H}^- = 0.27\%$ , theoretical for  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{Br} = 1.59$ , theoretical for  $(\text{NH}_4)(\text{H}_2\text{BrBNH}_2\text{BBrH}_2) = 1.84$ ; observed B = 6.77%, theoretical for  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{Br} = 8.54$ , for ammonium structure = 9.86.

Analysis of the microcrystalline compound,  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{Br}$ , by x-ray diffraction indicated a complicated structure with interplanar spacings as shown in Table II. The "d" values indicate absence of ammonium bromide, hence the possibility of an  $\text{H}_2\text{BNH}_2\text{-NH}_4\text{Br}$  mixture instead of  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{Br}$  appears small. This is particularly true since it is already known that the  $\text{H}_2\text{BNH}_2\text{-NaBH}_4$  and  $\text{H}_2\text{BNH}_2\text{-NaBr}$  mixtures show the x-ray powder patterns for  $\text{NaBH}_4$  and  $\text{NaBr}$ , respectively, and a mixture of  $\text{H}_2\text{BNH}_2\text{-NH}_4\text{Cl}$ , resulting from the decomposition of  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{Cl}$ , shows the lines for  $\text{NH}_4\text{Cl}$  clearly. In view of the foregoing evidence it appears that a serious alteration of the  $\text{NH}_4\text{Br}$  lattice by polymeric  $\text{H}_2\text{BNH}_2$  would require totally unexpected and unprecedented behavior.

The compound  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{Br}$  is a white solid, soluble in ammonia, and is slowly hydrolyzed by water. It reacts with sodium in liquid ammonia as shown in the next section. It can be prepared by the reaction between  $\text{NaBH}_4$  and  $\text{NH}_4\text{Br}$  (see Table I).

The Reactions of the Diammoniate of Diborane and of  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{Br}$  with Sodium in Liquid Ammonia.—Carefully prepared  $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$  reacts rapidly with sodium in liquid ammonia to liberate one-half mole of hydrogen per mole of "diammoniate." Such a process is consistent with either model for the diammoniate:



Again, however, the nature of the reaction products provides a means for differentiation. In the ammonium case the solid residue should contain the complex salt  $\text{Na}(\text{H}_3\text{BNH}_2\text{BH}_3)$ , whereas in the borohydride model the solid should contain  $\text{NaBH}_4$ . X-ray powder data of Schaeffer, Adams, and Koenig<sup>6</sup> indicate that  $\text{NaBH}_4$  is indeed present as a major component of the solid phase.

6. G. W. Schaeffer, M. D. Adams, and F. J. Koenig, J. Am. Chem. Soc., 78, 725 (1956).

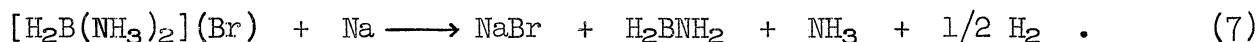


TABLE II

X-RAY POWDER PATTERNS FOR  $\text{H}_2\text{B}(\text{NH}_3)_2\text{Br}$  AND  $\text{NH}_4\text{Br}$ 

d Value (Angstroms)	Relative Intensity	d Value (Angstroms)	Relative Intensity
<u>A. Interplanar Spacings (d Values) for <math>[\text{H}_2\text{B}(\text{NH}_3)_2]\text{Br}</math> from Debye-Scherrer Powder Patterns</u>			
5.27	vs	1.80	vW
4.60	w	1.71	m
4.00	w	1.65	m
3.70	m	1.62	m
3.42	vs	1.55	w
2.88	vs	1.45	vW
2.61	s	1.43	vW
2.32	s	1.38	m
2.26	s	1.33	vW
2.07	s	1.31	vW
1.93	w	1.26	w
1.85	w	1.21	w
<u>B. Principal Lines for <math>\text{NH}_4\text{Br}</math> (compare above)</u>			
2.832	vs	1.639	m
2.303	w	1.413	w
1.991	w	1.327	w
1.785	m	1.241	w

The reaction of the complex dihydrido-diammine boron (III) cation  $[\text{H}_2\text{B}(\text{NH}_3)_2]^+$  with sodium in liquid ammonia should be independent of the anion of the salt, hence by analogy to Equation 6 one might expect the following reaction for the bromide salt:



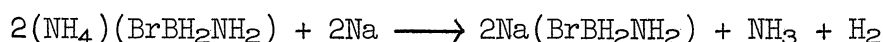
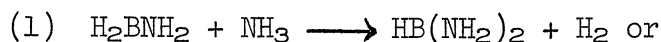
As shown in Table III, the reaction for the dihydrido-diammine boron (III) cation proceeded as expected and NaBr was identified in the solid product by x-ray powder methods.

Finally, brief mention should be made of an earlier argument<sup>3</sup> to the effect that in  $[\text{H}_2\text{B}(\text{NH}_3)_2]^+$  "the strong proton-donor character of the quaternary nitrogen atoms should render the proton-sensitive  $\text{BH}_4^-$  incapable of existence." Coordination theory indicates that the proton-donor characteristic of the nitrogen in  $[\text{H}_2\text{B}(\text{NH}_3)_2]^+$  should be less marked than those in  $\text{NH}_4^+$ . Furthermore, the existence of quaternary nitrogens

TABLE III

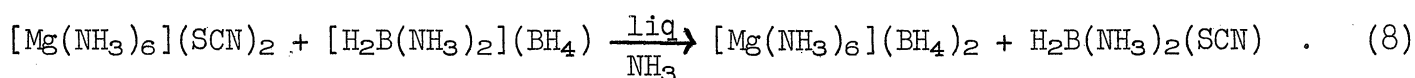
THE REACTION IN LIQUID AMMONIA BETWEEN Na AND THE  
 PRODUCT OBTAINED FROM THE ACTION OF  $\text{NH}_4\text{Br}$  ON  $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$   
 (A Comparison of Observed Stoichiometry with  
 That Expected from Two Models of the Diammoniate)

	Observed	Theory for $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{Br}$	Theory for $\text{NH}_4(\text{H}_2\text{BrBNH}_2\text{BBrH}_2)$
Mmoles salt on weight basis	--	1.04	0.60
Matoms Na	--	1.04	1.04
$\text{H}_2$ evolved in primary reaction (mm)	0.55	0.52	0.30
$\text{H}_2$ evolved in secon- dary reaction with ammonia <sup>(1)</sup>	1.06	1.04	0.52 (based on Na present)



in the stable compound  $[\text{Cr}(\text{NH}_3)_6](\text{BH}_4)_3$ <sup>5</sup> offers experimental contradiction to the above argument. Finally, sodium borohydride was crystallized from liquid  $\text{NH}_3$  with  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{Br}$  and no hydrogen was evolved. Comparable experiments with  $\text{NH}_4\text{Br}$  resulted in rapid  $\text{H}_2$  evolution.

The Precipitation of Hexammine Magnesium (II) Borohydride from a Liquid Ammonia Solution of the Diammoniate of Diborane.—One of the simplest tests for the presence of a borohydride ion in the liquid ammonia solution of the diammoniate of diborane would be the precipitation of ammonia insoluble hexammine magnesium (II) borohydride. When the diammoniate of diborane was mixed with a liquid ammonia solution of magnesium thiocyanate, hexammine magnesium (II) borohydride,  $[\text{Mg}(\text{NH}_3)_6](\text{BH}_4)_2$ , precipitated. A comparable reaction between  $\text{NaBH}_4$  and  $\text{Mg}(\text{SCN})_2$  gave a product whose x-ray powder pattern was identical to that obtained from the diammoniate of diborane. The equation for the precipitation is



The process appeared to be complicated by a secondary reaction involving the thiocyanate and the borohydride in solution, since the solution darkened a great deal during the course of the experiment.

Explanation of the foregoing results in terms of an ammonium model would require relatively rapid equilibrium shifts.

The Hydrolysis of the Diammoniate of Diborane.--One of the observations made repeatedly in this laboratory and confirmed elsewhere<sup>7</sup> was that hydrolysis of the diammoniate of diborane by 20% sulfuric acid at room temperature liberates approximately 2/3 of the hydridic hydrogen required by the formula  $B_2H_6 \cdot 2NH_3$ . Actual values for five separate experiments with temperatures up to 60°C show a hydridic hydrogen of  $66.1 \pm 6\%$ . High-temperature, sealed-tube reaction is required for complete hydrolysis and quantitative liberation of the boron and hydridic hydrogen. Such observations are consistent with a borohydride model inasmuch as 2/3 of the hydrogen (e.g., that present in borohydride) should be liberated easily while the remaining 1/3 (present in the complex cation) should hydrolyze with more difficulty. Difficult hydrolysis of the cation  $[H_2B(NH_3)_2]^+$  was confirmed by studies on the bromide salt  $[H_2B(NH_3)_2]Br$ .

Discussion.--The foregoing arguments offer support for a borohydride formulation of the diammoniate  $[H_2B(NH_3)_2](BH_4)$  as opposed to the currently accepted ammonium model,  $(NH_4)(H_3BNH_2BH_3)$ . An objective examination of the question demands, however, that data of previous investigators, particularly the earlier evidence for the ammonium model, be examined carefully in light of currently available information.

Five arguments were originally cited in support of the ammonium model.<sup>1</sup> Each of these (underlined below) can now be shown to be consistent with the borohydride representation.

1. The product (diammoniate of diborane) reacts with sodium in liquid ammonia at -77° to produce one equivalent of hydrogen per mole of diborane involved; it thus seems to contain one ammonium ion per pair of boron atoms.

It has been shown that oxidation of sodium ion in liquid ammonia solution with liberation of hydrogen is not a specific test for the ammonium ion. Tests on the compound  $[H_2B(NH_3)_2]Br$  show that the dihydrido-diammine boron (III) cation is likewise capable of reaction with sodium in an exactly analogous fashion. It is probable that the compound  $H_2B(NH_2)(NH_3)$  formed in the reaction loses ammonia to give polymeric  $(H_2BNH_2)$ . This explains the analytical results of Schlesinger and Burg on their product.

2. A slow secondary reaction of the product with ammonia and sodium, yielding barely 40% more hydrogen, is easily explained by assuming that ammonia removes a  $BH_3$  group from the above structure (ammonium model) by a reversible reaction, producing  $(NH_4)(BH_3NH_2)$ . This explanation is supported by the fact that trimethylamine reacts with the diammoniate of diborane to give borine trimethylamine. Neither reaction is easily explained by other structures (i.e., structures other than the ammonium model).

7. W. H. Schechter, R. M. Adams, and C. B. Jackson, "Boron Hydrides and Related Compounds," Callery Chemical Co., Contract NO a(s) 10992 (1951), Callery, Pa.

The question of excess hydrogen evolution is considered elsewhere<sup>4,6</sup> and is explained easily and quantitatively on the basis of the borohydride model. On the other hand, recent isolation of the compound  $H_3BNH_3$ ,<sup>8</sup> which presumably gives  $(NH_4)(BH_3NH_2)$  in liquid ammonia, shows definitely that it does not exist in labile equilibrium with the diammoniate; the postulated equilibrium is untenable.

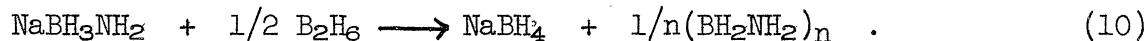
The fact that trimethylamine reacts with the diammoniate of diborane to give low yields of  $H_3BNR_3$  does not support the ammonium model, particularly when one realizes the supposed salt  $Na(H_3BNH_2BH_3)$  gives no reaction with trimethylamine. It is known that  $NaBH_4$  and  $H_2BNH_2$ , the actual components of this mixture, do not react with  $N(CH_3)_3$ . On the other hand, the  $BH_4^-$  ion in the field of the acidic, polarizing cation  $H_2B(NH_3)_2^+$  should react slowly with  $N(CH_3)_3$  to give low yields of  $H_3BNR_3$ . Such an argument is eminently reasonable when one considers the effect of cation field strength on the reactions of borohydrides. Both beryllium and aluminum borohydrides react with trimethylamine. The borohydride of the complex cation  $[H_2B(NH_3)_2]^+$  would probably fall in between the beryllium and alkali metal borohydrides in terms of borohydride polarization.

3. The reaction of the new compound  $(CH_3)_2OBH_3$  with ammonia and sodium produces the salt  $NaBH_3NH_2$ . The negative ion of this salt is considered to be an intermediate step in the formation of the above structure (ammonium structure).

This compound has no bearing on the structure since it is a substituted borohydride comparable to  $NaBH_3(OCH_3)$ . It appears to result from  $NH_3BH_3$  and sodium in liquid ammonia; it has been shown that  $NH_3BH_3$  is not in labile equilibrium with the diammoniate in anhydrous liquid ammonia,<sup>8</sup> hence this salt has little relationship to the structure of  $B_2H_6 \cdot 2NH_3$ .

4. The salt  $NaBH_3NH_2$  strongly absorbs diborane. This fact justifies the assumption that the negative ion of the above structure is easily formed by the addition of  $BH_3$  to the  $BH_3NH_2^-$  ion and is capable of existence.

The reaction involved in this argument is not one of formation of  $(H_3BNH_2BH_3^-)$ , but rather it appears to be similar to the acid-base reaction between diborane and  $NaBH_3OCH_3$ :<sup>9</sup>



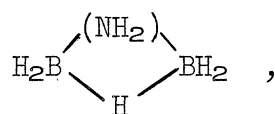
It has been shown<sup>6</sup> that the supposed salt  $Na(BH_3NH_2BH_3)$  is in reality a mixture of  $NaBH_4$  and  $BH_2NH_2$ . There is absolutely no evidence at the present time for the ion  $(H_3BNH_2BH_3^-)$ .

8. S. G. Shore and R. W. Parry, this Report, p. 31.

9. H. I. Schlesinger and H. C. Brown, et al., J. Am. Chem. Soc., 75, 186 (1953).

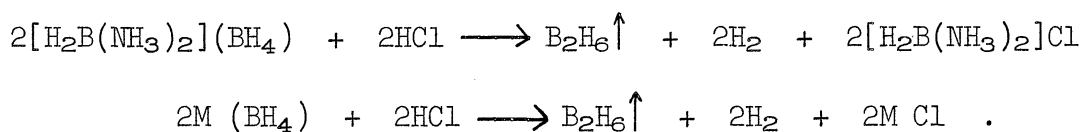
5. The new compound B<sub>2</sub>H<sub>7</sub>N, having a structural skeleton B-NB, is easily prepared from the diammoniate of diborane.

The linear structure, originally attributed to B<sub>2</sub>H<sub>7</sub>N, is now known to be incorrect. There is strong evidence<sup>10</sup> for a bridge structure,



which could easily result from the interaction of the complex cation [H<sub>2</sub>B(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> with BH<sub>3</sub> groups on B<sub>2</sub>H<sub>6</sub> molecules at the known high temperature (60°C) of the reaction. Alternatively, NH<sub>3</sub> might be displaced at high temperatures to react directly with B<sub>2</sub>H<sub>6</sub>. The original argument is equally good for the borohydride formulation and in no sense supports the ammonium model.

The new borohydride model also permits easy rationalization of earlier disturbing observations of Stock.<sup>11</sup> He found that gaseous HCl reacted with the diammoniate of diborane to yield hydrogen and diborane. Although these products were isolated in relatively large yield, they were considered as products of a side reaction since they were inconsistent with models for the diammoniate then available. The products are those expected from the borohydride model and have a formal resemblance to the reaction with the acid NH<sub>4</sub>Br in liquid ammonia; the reaction is directly analogous to the reaction of alkali metal borohydrides with gaseous HCl:



All of the foregoing properties of the diammoniate offer strong support for a structure containing a borohydride ion. The known instability of ammonium borohydride as well as other chemical properties of the diammoniate argue strongly against inclusion of ammonium and borohydride ions in the same molecule. A proposed<sup>6</sup> stabilizing effect due to H<sub>2</sub>BNH<sub>2</sub> has little experimental support. On the other hand, the new cation [H<sub>2</sub>B(NH<sub>3</sub>)<sub>2</sub>], which can be considered as an ammonia complex of boron (III), explains all properties formerly attributed to the ammonium ion and is itself consistent in every detail with the chemistry of the diammoniate.

### Experimental.—

#### a. Reagents.

1. Ammonia—The Matheson Co., Inc.—stored over and distilled from sodium before use.

10. K. Hedberg and A. J. Stosick, J. Am. Chem. Soc., 74, 954 (1952).

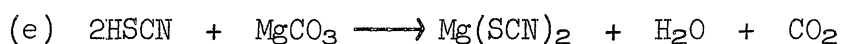
11. A. Stock. Hydrides of Boron and Silicon. Ithaca: Cornell Univ. Press, 1933.

2. Ammonium bromide—Baker and Adamson, reagent grade.
3. Sodium borohydride—Metal Hydrides, Inc.—recrystallized from liquid ammonia.
4. Diborane—prepared by reaction between boron trifluoride etherate and lithium aluminum hydride.<sup>12</sup>
5. Boron trifluoride etherate—Baker and Adamson, technical grade BF<sub>3</sub>—etherate was distilled just before use and the middle fraction used.
6. Lithium aluminum hydride—Metal Hydrides, Inc.
7. Magnesium (II) thiocyanate.

The following reactions were employed in synthesis:<sup>13</sup>



An excess of AgSCN in step (c) produced the soluble complex Mg[Ag(SCN)<sub>2</sub>]<sub>2</sub>. The complex was broken and the silver removed from solution by saturating the system with H<sub>2</sub>S. Ag<sub>2</sub>S was filtered off and excess H<sub>2</sub>S removed by boiling. Thiocyanic acid remaining in the solution was neutralized with MgCO<sub>3</sub>. The pertinent equations are:



The Mg(SCN)<sub>2</sub> was crystallized from neutral solution by evaporating the water at 35°C in a current of air. The product was recrystallized from distilled water and dried at about 50°C in the air. The air-dry product was very soluble in liquid ammonia; coordinated water around the Mg (II) cation was replaced by ammonia in the solution. The water in the system resulted in some H<sub>2</sub> evolution when the Mg(SCN)<sub>2</sub> solution was added to an ammonia solution of borohydride, but this side reaction did not interfere with the precipitation of Mg(NH<sub>3</sub>)<sub>6</sub>(BH<sub>4</sub>)<sub>2</sub>. Mg analysis: theory for Mg(SCN)<sub>2</sub>·5H<sub>2</sub>O = 10.45%; observed = 10.45-11.05% Mg.

8. The diammoniate of diborane—The procedure of Schlesinger and Burg<sup>1</sup> was used, except that known variations in the product could be introduced by removing excess ammonia at temperatures other than -78.5°C. Such details are included in experimental tables.

12. J. Shapiro, H. G. Weiss, M. Schmick, S. Skolnik, and G. B. L. Smith, J. Am. Chem. Soc., 74, 901 (1952).

13. D. R. Schultz, Ph.D. dissertation, Univ. of Mich., Ann Arbor, 1954.

b. Reaction of the Diammoniate of Diborane with Sodium Borohydride or Ammonium Bromide.

A mixture of the diammoniate of diborane and  $\text{NaBH}_4$  or  $\text{NH}_4\text{Br}$  was dissolved in liquid ammonia and held, with continuous stirring, at low temperatures ranging from  $-78.5^\circ$  to  $-33$ . Hydrogen evolution was negligible. Solvent ammonia was then sublimed off and the solid mixture was allowed to warm to room temperature. In one case the mixture was warmed to  $45^\circ\text{C}$ . Hydrogen was removed with a Toepler pump; the residue was redissolved in ammonia; after stirring, ammonia was again removed, the system warmed up, and  $\text{H}_2$  measured. This cycle was repeated 3 to 5 times.

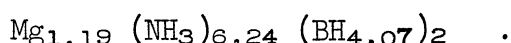
c. Reaction of the Diammoniate of Diborane with Sodium in Liquid Ammonia.

The reaction vessel was a 25-mm Pyrex tube with a 14/35  $\overline{\text{B}}$  joint sealed at right angles near the top of the tube. A side arm making about a  $60^\circ$  angle with the lower side of the tube had a 24/40  $\overline{\text{B}}$  inner-outer joint combination so materials could be placed in the side arm. A glass bulb (about 15 mm in diameter) containing about 230 mg Na was placed in the side arm together with a magnet in a heavy glass case. After evacuation and drying of the system, the diammoniate was prepared in the conventional fashion; ammonia was removed to check the stoichiometry; ammonia was returned to the system and frozen; then the reaction tube was tipped around the 14/35  $\overline{\text{B}}$  joint until the sodium bulb fell into the reaction vessel. The magnetic hammer, magnetically controlled from the outside, was held back, then was used to break the sodium bulb; the ammonia was allowed to melt and the reaction conducted at  $-78.5^\circ\text{C}$ .

The reaction between sodium and  $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{Br}$  was carried out in the same apparatus, using the same general technique.

d. The Reaction Between  $\text{B}_2\text{H}_6\text{-}2\text{NH}_3$  or  $\text{NaBH}_4$  and Magnesium Thiocyanate in Liquid Ammonia.

Attempts to scale-up the preparation of the "diammoniate" by increasing the amounts of reagents were generally unsuccessful. Accordingly, four batches of the compound were prepared ( $-78.5^\circ\text{C}$ ) and stored under dry nitrogen at  $-78.5^\circ\text{C}$  for from 4 to 48 hours. The combined sample (0.768 mmoles) was loaded in a dry box into one arm of an inverted Y-tube reactor; magnesium thiocyanate (2.5 mmoles) was placed in the other leg and the reactor was attached to a special vacuum-line filter assembly. Dry ammonia was then condensed in each leg and stirred; the solutions were mixed; then the precipitate was filtered off and washed eight times in the vacuum system with liquid ammonia. About .2 g of precipitate was obtained from the diammoniate. Analysis of the precipitate showed:



The slightly high value for Mg indicated that some of the  $\text{Mg}(\text{SCN})_2$  or some basic Mg (II) salt was contaminating the product, but the x-ray data left no doubt that the product was identical to the material obtained from  $\text{NaBH}_4$  and  $\text{Mg}(\text{SCN})_2$  which gave an analysis indicating:  $\text{Mg}(\text{NH}_3)_{5.7} \text{B}_{1.91} \text{H}_{3.0}$ . The pattern also

checked with a sample of  $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$  generously supplied by Callery Chemical Co.

e. Analytical Methods.

1. Magnesium was precipitated from ammoniacal solution using 8-hydroxyquinoline.<sup>14</sup>

2. Boron was converted to boric acid and titrated with NaOH in the presence of mannitol, using a Beckman pH meter.<sup>14</sup>

3. Nitrogen was determined, using a standard micro-Kjeldahl procedure.

4. Evolved hydrogen was always identified by gas density.

f. X-ray Methods.

A GE model XRD-1 instrument was used with a camera of 57-mm diameter. Cu-K $\alpha$  radiation was employed. Exposure times were one-half to one hour.

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14. W. F. Hillebrand, G. E. F. Lundell, W. A. Bright, and J. J. Hoffman. Applied Inorganic Analysis. New York: John Wiley and Sons, Inc., 1953.

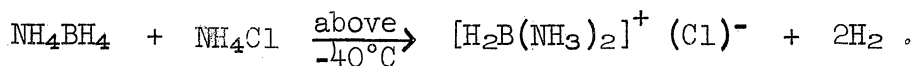
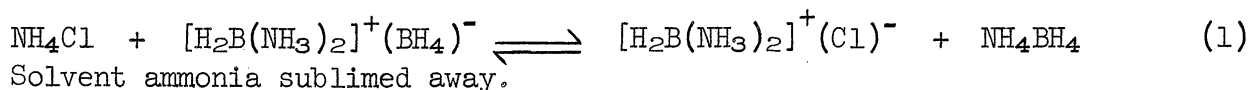


C. CHEMICAL EVIDENCE FOR THE STRUCTURE OF THE DIAMMONIATE OF DIBORANE (II). THE PREPARATION OF AMMONIA BORANE. (S. G. Shore and R. W. Parry)

Abstract

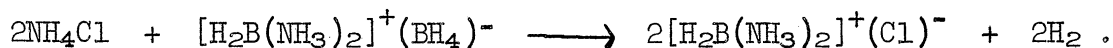
The monomeric compound  $H_3NBH_3$  has been prepared from the "diammoniate of diborane" and from lithium and sodium borohydrides. The reaction provides additional support for a borohydride formulation of the diammoniate,  $[H_2B(NH_3)_2]^+(BH_4)^-$ , and provides unequivocal evidence against all attempts to formulate the diammoniate as  $H_3NBH_3$ . The "diammoniate" and  $H_3NBH_3$  do not exist in labile equilibrium.

In a previous paper an alternative borohydride structure for the "diammoniate of diborane,"  $[H_2B(NH_3)_2]^+(BH_4)^-$ , was supported by chemical evidence. By making use of the fact that ammonium borohydride which has been prepared in liquid ammonia decomposes with evolution of hydrogen, Schultz and Parry<sup>1</sup> were able to prepare a bromide salt of the "diammoniate" cation. A chloride salt has been prepared in the same fashion. The reactions are:



Solvent added then removed again.

By repeating these two steps alternately, the following overall reaction was observed:



The successive treatments with solvent ammonia were essential in order to bring ammonium and borohydride ions into reaction range so that the interaction between a protonic hydrogen of the ammonium ion and a hydridic hydrogen of the borohydride ion could occur. The resulting chloride salt proved to be a definite crystalline substance.

As an alternative synthetic route to the chloride salt, the heterogeneous, room-temperature reaction between ammonium chloride and the "diammoniate of diborane" in a diethyl ether suspension seemed to offer interesting possibilities, especially since such a reaction would be less tedious to undertake than the ones cited above. The results were entirely unexpected, for the reaction in ether suspension led to the synthesis of the long-sought monomeric compound ammonia-borane,  $H_3NBH_3$ .

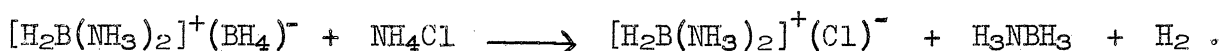
The Reaction Between the "Diammoniate of Diborane" and Ammonium Chloride in an Ether Slurry.—Under strictly anhydrous conditions and in the absence of all extraneous proton sources the reaction in an ether slurry at about room temperature between ammonium chloride and the "diammoniate of diborane" was negligible. It was found, however, that by altering the ether environment through the addition of a small quantity

1. D. R. Schultz and R. W. Parry, this Report, p.19.

of anhydrous ammonia, the rate of reaction increased markedly. The rate was followed by measuring hydrogen evolution as a function of time. Results for one run are indicated in Fig. 1. The dramatic break in the curve resulting after the addition of ammonia is proof of the efficacy of the catalyst. Data for several runs are summarized in Table I. It is significant that even a twofold excess of ammonium chloride in ether did not produce more than one mole of hydrogen per mole of the "diammoniate."

After an appropriate amount of hydrogen had been produced, solutions were filtered and ether was distilled from the filtrate. The crystalline ether soluble material isolated was analyzed and a correction was applied for the small amount of ammonia used to accelerate the reaction. The corrected analytical ratios were: hydridic hydrogen/boron = 3.0; nitrogen/boron = 1; Cl<sup>-</sup>/boron = 0.0. Yields of H<sub>3</sub>NBH<sub>3</sub> ranged up to 80% of theory.

An x-ray powder examination of the ether insoluble residues from typical ether runs indicated only a trace of the compound [H<sub>2</sub>B(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>(Cl)<sup>-</sup> which was expected from the equation



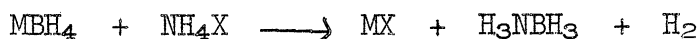
The principal crystalline material remaining in the ether insoluble residue was ammonium chloride. Since the reactants in the several experiments studied were in one-to-one stoichiometric quantity, the absence of significant amounts of chloride salt plus the presence of ammonium chloride in the reaction residues suggest that ammonium chloride was consumed and then regenerated, perhaps through the decomposition of the chloride salt.



The apparent instability of the chloride salt in the ether slurry is consistent with an earlier observation that the sample of chloride salt prepared by Schultz's<sup>1</sup> procedure displayed some evidence of decomposition also (presence of some ammonium chloride). The bromide salt prepared by Schultz, on the other hand, appeared to be more stable since no ammonium bromide was detected in the sample. Such observations are consistent with general acid-base theory (i.e., HCl, the weaker acid, forms a less stable salt than HBr). The increasing stability of the phosphonium halides illustrates this relationship:



The Reaction Between Lithium Borohydride and Ammonium Salts in an Ether Slurry.— The foregoing process for the synthesis of H<sub>3</sub>NBH<sub>3</sub> from the "diammoniate of diborane" was interpreted in terms of the reaction of a borohydride ion. Such an interpretation suggests that other borohydrides should react similarly with NH<sub>4</sub>Cl in ether slurry.



As a preliminary experiment, the reaction between sodium borohydride and ammonium

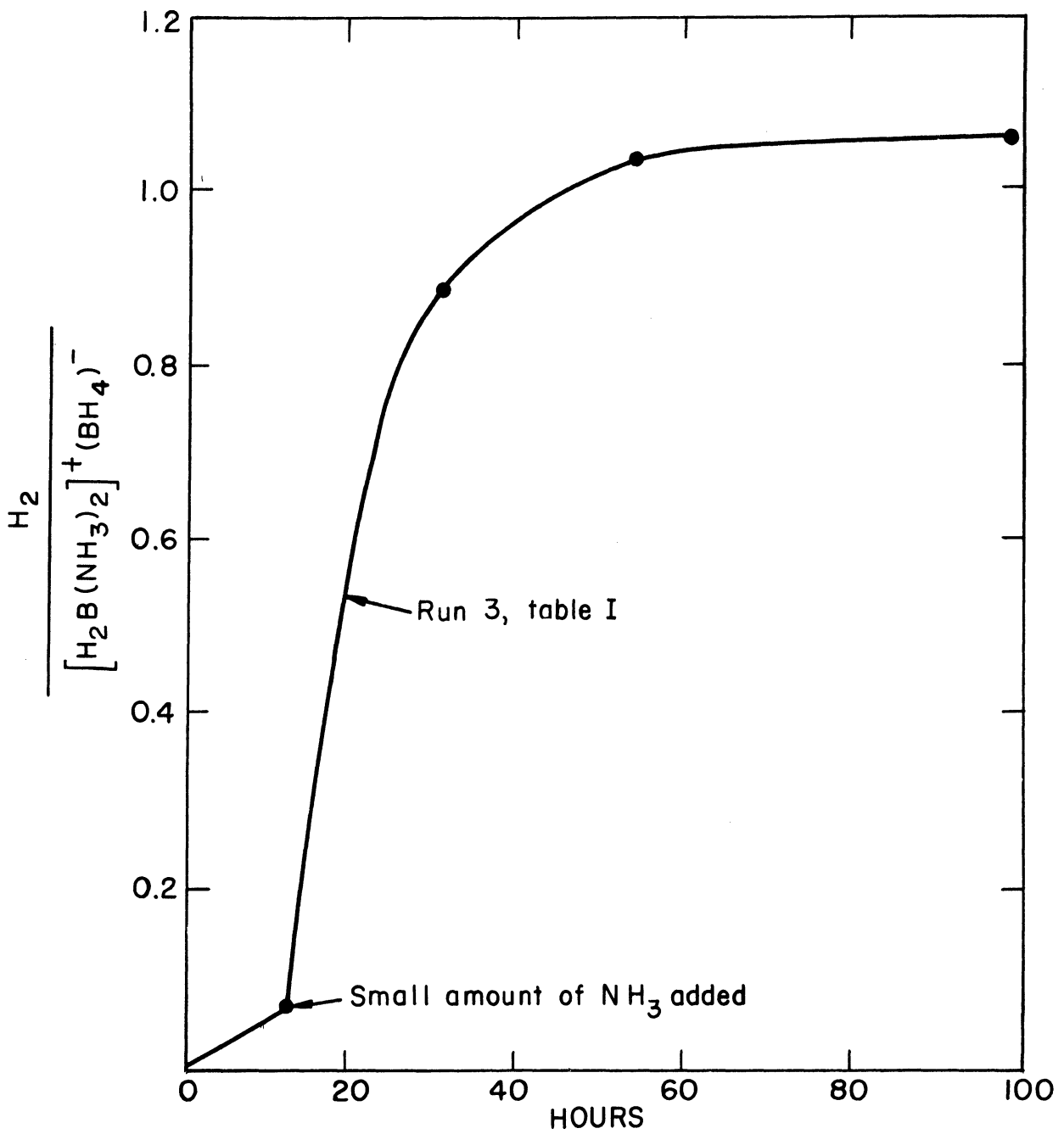


Fig. 1. The reaction between ammonium chloride and the "diammoniate of diborane" in an ether slurry.

TABLE I

THE REACTION BETWEEN THE "DIAMMONIATE OF DIBORANE"  
AND AMMONIUM CHLORIDE SLURRIED IN ETHER

Run	Mmoles [BH <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> (BH <sub>4</sub> ) <sup>-</sup>	$\frac{\text{NH}_4\text{Cl}}{[\text{BH}_2(\text{NH}_3)_2]^+(\text{BH}_4)^-}$	Ml Ether	Comments	Time-hr (cumulative)	$\frac{\text{H}_2(\text{cumulative})}{[\text{BH}_2(\text{NH}_3)_2]^+(\text{BH}_4)^-}$
1	2.02	1.86	5	0.3 mmole NH <sub>3</sub> added →	22 40	0.25 1.17
2	2.17	0.99	8	0.3 mmole NH <sub>3</sub> added →	12 32	0.55* 0.85
3	2.12	1.84	7	0.19 mmole NH <sub>3</sub> added →	12 32 54 99	0.07 0.89 1.04 1.06
4	1.93	0.97	10	0.15 mmole NH <sub>3</sub> added →	36 48	0.99* 1.02

\*Since the "diammoniate" was in excess, these values represent H<sub>2</sub>/NH<sub>4</sub>Cl.

chloride was studied in diethyl ether. Even when small amounts of ammonia were used to accelerate the gas evolution, the production of hydrogen was negligible. On the other hand E. A. Alton, Jr., of this laboratory was able to prepare  $\text{H}_3\text{NBH}_3$  in small yields through the reaction between  $\text{NH}_4\text{Br}$  and  $\text{NaBH}_4$  in Ansul 141 polyether. The polyether is a solvent for  $\text{NaBH}_4$ . It was also found that  $\text{LiBH}_4$ , which dissolves in diethyl ether, will react relatively rapidly with a diethyl ether slurry of ammonium chloride or sulfate at about room temperature to produce  $\text{H}_3\text{NBH}_3$ . The purest product is obtained from ammonium sulfate and  $\text{LiBH}_4$ . Schaeffer and Anderson<sup>2</sup> have used a similar type of reaction to prepare  $(\text{CH}_3)_3\text{NBH}_3$ . Results of several experiments are summarized in Table II. Although the theoretical yield of hydrogen was readily produced in each experiment with  $\text{LiBH}_4$ , the yield of ether soluble ammonia-borane did not ever exceed 50% of theory. The "diammoniate of diborane" is empirically  $\text{H}_3\text{NBH}_3$ , but ether insoluble, hence it is a possible alternative product. Its reaction with  $\text{NH}_4\text{Cl}$  is very slow in the ether containing no  $\text{NH}_3$ .

TABLE II

THE REACTION BETWEEN LITHIUM BOROHYDRIDE  
AND AN AMMONIUM SALT SLURRIED IN ETHER

Run	Mmoles $\text{LiBH}_4$	Meq. $\text{NH}_4^+$ Salt	Ml Ether	Time, hr	$\text{H}_2/\text{LiBH}_4$	% Yield Ether Soluble $\text{H}_3\text{NBH}_3$
1	2.08	2.10 $\text{NH}_4\text{Cl}$	15	2.5	0.99	33%
2	14.2	16.8 $(\text{NH}_4)_2\text{SO}_4$ (a)	50	6	(b)	40%
3	19.1	22.4 (a)	50	4.5	0.98	44%
4	23.0	26.0 (a)	50	7	(b)	47%

(a) Ammonium sulfate was used in preference to ammonium chloride in later experiments because the product lithium sulfate is even less ether soluble than lithium chloride.

(b) The extent of reaction was followed, qualitatively, by observing the rate of hydrogen evolution through a mercury bubbler.

Analytical ratios for ether soluble product from Runs 1 and 2.

N/B, 0.98, 0.98; H(hydridic)/B, 2.93, 2.98.

Analysis of ether soluble product from Run 3.

Calculated for  $\text{H}_3\text{NBH}_3$ : H(hydridic), 9.79; B, 35.0; N, 45.4.

Found: H(hydridic), 9.73; B, 35.1; N, 45.6.

The Properties of Ammonia-Borane.—Even though ammonia-borane and the "diammoniate of diborane" are both of empirical formula  $\text{H}_3\text{NBH}_3$ , their properties show striking con-

2. G. W. Schaeffer and E. R. Anderson, J. Am. Chem. Soc., 71, 2143 (1949).

trasts. Illustrative data are summarized in Table III. Molecular-weight determinations reported elsewhere<sup>3</sup> indicated a monomeric formula for the compound. This has since been confirmed for the solid state also by two independent evaluations of x-ray powder patterns.<sup>4</sup>

TABLE III

COMPARISON OF THE PROPERTIES OF AMMONIA-BORANE  
WITH THOSE OF THE "DIAMMONIATE OF DIBORANE"

$H_3NBH_3$	$[H_3NBH_2NH_3]^+(BH_4)^-$
1. Crystalline material which gives a definite x-ray powder pattern.	1. Apparently amorphous material which gives no x-ray powder pattern.
2. Soluble in ether.	2. Insoluble in ether.
3. Molecular weight in ether and dioxane corresponds to above formula.	3. Molecular weight in ammonia corresponds to above formula.
4. Not readily hydrolyzed by distilled water.	4. Readily hydrolyzed by distilled water.
5. Slowly splits out hydrogen at room temperature.	5. Stable to 80°. Splits out hydrogen very very slowly at room temperature.
6. Reacts with sodium in ammonia to produce $\frac{1/2 H_2}{H_3NBH_3}$	6. Reacts with sodium in ammonia to produce $\frac{1/2 H_2}{[H_3NBH_2NH_3]^+(BH_4)^-}$

Ammonia-borane has a negative temperature coefficient of solubility in diethyl ether from about -78° to 25°C. Clear, rigorously anhydrous ether solutions are stable at room temperature to the extent that only a small amount of precipitate appears after standing for several days. The precipitate is probably the "diammoniate of diborane" and some polymeric  $(H_2NBH_2)_n$ , since trace quantities of hydrogen were liberated. In the presence of trace quantities of moisture, the ether solution becomes very unstable and solid material is precipitated quite rapidly.

Ammonia-borane is soluble in and stable in anhydrous liquid ammonia. On the basis of x-ray powder pattern intensities there was no detectable conversion to the

3. S. G. Shore and R. W. Parry, J. Am. Chem. Soc., 77, 6084 (1955).

4. E. L. Lippert and W. N. Lipscomb, *ibid.*, 78, 503 (1956); E. W. Hughes, *ibid.*, p. 500

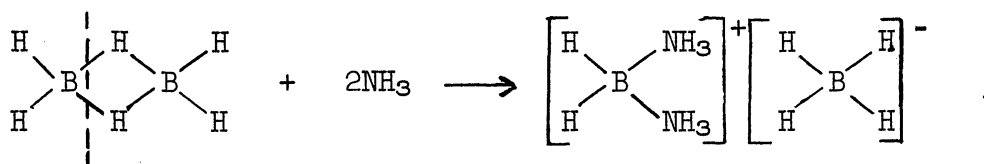
"diammoniate" when a sample stood for 30 hours at  $-78^{\circ}$  and an additional 18 hours at  $-45^{\circ}$  in liquid ammonia. Reaction of ammonia-borane with sodium in liquid ammonia liberated one equivalent of hydrogen per mole of ammonia-borane. The stoichiometry of the process suggests the reaction



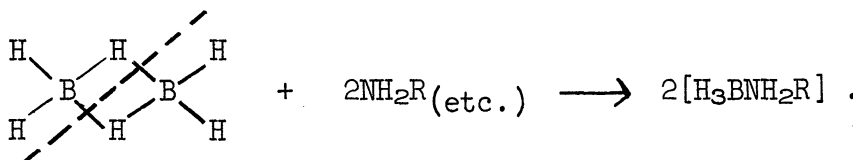
The sodium amidotrihydrido borate (III) has not been isolated in pure form.

Solid ammonia-borane appears to undergo slow conversion to the "diammoniate of diborane" at room temperature. Very slow loss of hydrogen at room temperature occurs also. A sample which stands at  $25^{\circ}\text{C}$  in a dry atmosphere for a period of even five minutes will not redissolve completely in ether; the diammoniate and  $(\text{H}_2\text{NBH}_2)_n$  are the most probable components of the precipitate. Solid ammonia-borane sublimes with difficulty under high vacuum at room temperature; the purity of the sublimate was not determined. The density of the solid, determined from x-ray powder data,<sup>4</sup> is  $0.74 \text{ g/cm}^3$ .

Discussion.—Data summarized in this and other papers<sup>1</sup> support the borohydride formulation for the product produced in the reaction between ammonia and diborane,  $[\text{H}_2\text{B}(\text{NH}_3)_2]^+(\text{BH}_4)^-$ . This reaction of diborane with ammonia differs from reactions with mono-, di-, and trimethyl amines in that the former process appears to involve nonsymmetrical cleavage of the hydrogen bridges in diborane,



whereas the latter reactions involve symmetrical cleavage of the bridge to give monomeric products,<sup>5</sup>



The conversion of the classical "diammoniate" to  $\text{H}_3\text{BNH}_3$  through its reaction with  $\text{NH}_4\text{Cl}$  makes untenable all earlier arguments<sup>6</sup> which supported the hypothesis that the "diammoniate" has the structure  $\text{H}_3\text{NBH}_3$ , but shows abnormally high molecular weights in liquid ammonia as a result of dipole association. Comparative properties of  $\text{H}_3\text{NBH}_3$  and the "diammoniate" demonstrate unequivocally that two separate compounds are being considered. The formation of  $\text{H}_3\text{NBH}_3$  from  $\text{LiBH}_4$  and from the "diammoniate" by comparable reactions adds strong support for a structure containing

5. R. W. Parry, G. Kodama, and D. R. Schultz, this Report, p. 82.

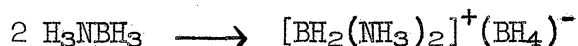
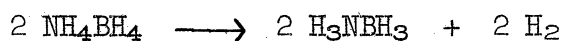
6. E. Wiberg, A. Bolz, P. Buchkeit, Z. anorg. Chem., 256, footnote 5, p. 287, and footnote 41, p. 301 (1948); Gmelin's Handbuch der anorganischen Chemie, 8. Auflage. System 13, 1954, pp. 100, 235.

the borohydride ion in the solid state. Ammonia-borane, on the other hand, shows properties which are consistent with those of the methyl substituted amine-boranes.

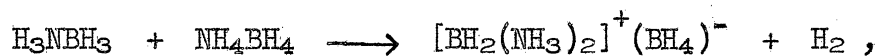
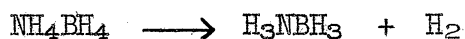
It now becomes of interest to examine the experimental procedures of this investigation and compare them with earlier procedures which have invariably led to the "diammoniate of diborane."

Work of Schultz and Parry<sup>1</sup> and of Taylor, Schultz, and Emery<sup>7</sup> indicated that the product obtained by the solid-phase decomposition of ammonium borohydride was the "diammoniate of diborane," rather than ammonia-borane, (H<sub>3</sub>NBH<sub>3</sub>). In an earlier study Schlesinger and Burg<sup>8</sup> added ammonia to solid (CH<sub>3</sub>)<sub>2</sub>OBH<sub>3</sub> in an attempt to form H<sub>3</sub>NBH<sub>3</sub>, but the "diammoniate" was produced instead. In the normal procedure for preparing the "diammoniate," solid ammonia picks up diborane. All the foregoing processes which produce the "diammoniate" have the reaction of a solid phase in the absence of solvent as a common factor. The principal feature which differentiates the process for preparing ammonia-borane is the presence of ether during the reaction between an ammonium salt and a borohydride salt. The role of a solvent in moderating or altering the course of the reaction is not unusual. The reaction of hydrazine and diborane<sup>9</sup> and the reaction PCl<sub>3</sub> and LiAlH<sub>4</sub><sup>10</sup> are both strongly dependent on the presence of ether as a solvent. Although reaction takes place in the absence of solvent, products differ from those obtained in ether.

The role of ether in the present process is reasonably certain, but its mode of action is still unknown. The facts can be interpreted in terms of the following hypothesis. If the decomposition of ammonium borohydride to the "diammoniate of diborane" can be considered to take place through either of the following reaction schemes,



or



then the role of ether in an ether slurry of an ammonium salt and a borohydride salt might be twofold. The ether might serve as a heat transfer medium preventing localized heating at reaction sites by dissipating the heat of the initial exothermic re-

7. R. C. Taylor, D. R. Schultz, and A. R. Emery, this Report, p. 92.

8. H. I. Schlesinger and A. B. Burg, J. Am. Chem. Soc., 60, 290 (1938).

9. H. I. Schlesinger and M. J. Steindler, *ibid.*, 75, 756 (1953).

10. J. T. Yoke III, G. Kodama, and R. W. Parry, this Report, p. 162.



action between protonic and hydridic hydrogen. Therefore, the possibility of ammonia-borane possessing the energy of activation required for conversion to the "diammoniate of diborane" is diminished. Secondly, ether is a solvent for ammonia-borane. Therefore, ammonia-borane is removed from the reaction sites as soon as it is formed and the possibility of participating in conversion to the "diammoniate" is diminished due to dilution. These reasons are consistent with the observation that the reaction of ammonium and borohydride salts in an ether slurry produces ammonia-borane, while the decomposition of solid ammonium borohydride produces the "diammoniate of diborane" exclusively.

### Experimental.—

#### a. Materials.

1. Ammonia—commercial tank  $\text{NH}_3$  was dried and stored over sodium metal in the vacuum system.
2. Ammonium chloride and ammonium sulfate—reagent grade  $\text{NH}_4\text{Cl}$  and  $(\text{NH}_4)_2\text{SO}_4$  were dried at  $80^\circ$  for two hours prior to their introduction into the vacuum system.
3. Diethyl ether—reagent grade  $(\text{C}_2\text{H}_5)_2\text{O}$  was dried and stored over lithium aluminum hydride in the vacuum system.
4. Lithium borohydride and sodium borohydride— $\text{LiBH}_4$  and  $\text{NaBH}_4$  (supplied by Metal Hydrides, Inc.) were purified by extraction with liquid ammonia at  $-65^\circ$  to  $-75^\circ$ . The extractor was similar to the vacuum-line filter of Schultz and Parry<sup>1</sup> and was operated in the same manner. The bulk of the solvent ammonia was removed by sublimation as the system was slowly warmed from  $-78^\circ$  to  $-40^\circ$ . Remaining traces of ammonia were pumped away at room temperature.

#### b. The Reaction Between the Diammoniate of Diborane and Ammonium Chloride in an Ether Slurry.

The apparatus in which this work was carried out is depicted in Fig. 2. It was similar in appearance and operation to that described earlier,<sup>1</sup> except that the vacuum-line filtering device contained a drip-tip and the magnetically actuated stirrer was of spiral construction in order to insure efficient stirring. All the stopcocks and joints in the system which had to be rotated were greased with Dow-Corning High Vacuum Grease. All the joints which did not have to be rotated were sealed with DeKhotinsky cement.

In a typical run,<sup>11</sup> "diammoniate of diborane"<sup>12</sup> was prepared and isolated in the reaction tube of the apparatus. The system was then filled with dry nitrogen and the tube was removed from the line; it was charged with a known

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11. See Table I for the actual amounts of materials used in the individual runs.

12. S. G. Shore and R. W. Parry, this Report, p. 54.

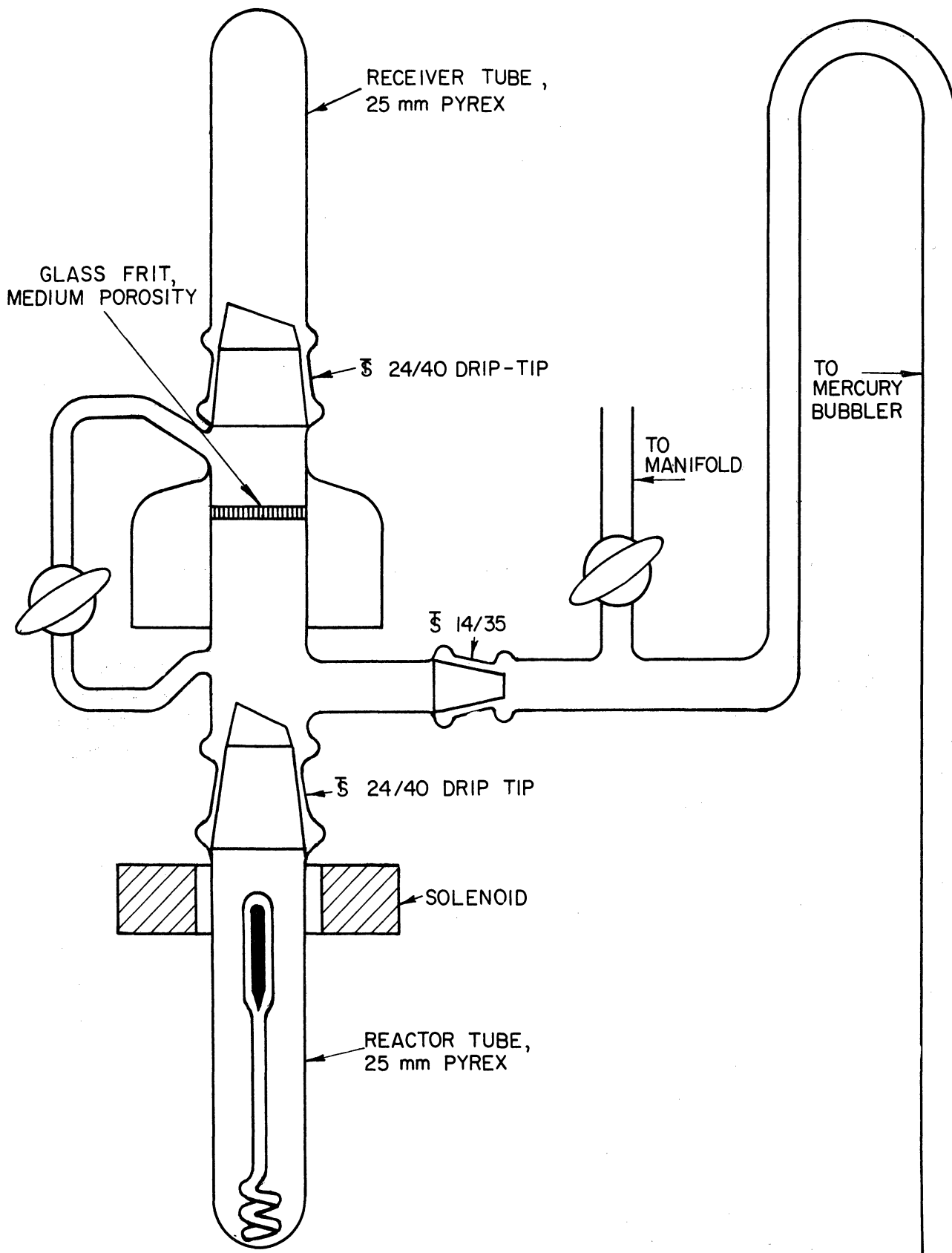


Fig. 2. Apparatus for the reaction between ammonium chloride and the "diammoniate of diborane" in an ether slurry.

amount of ammonium chloride and returned to its original position as rapidly as possible. The vacuum system was evacuated and ether was distilled into the reaction tube. A small quantity of anhydrous ammonia was distilled in also. Hydrogen evolution was initiated by maintaining the reaction tube at about room temperature and stirring its contents vigorously. In order to prevent the condensation of ether in other parts of the system, the temperature of the reactor tube was actually maintained at just below room temperature by immersing it in a beaker of water.<sup>13</sup> The extent of reaction was determined at various intervals by quenching the reaction tube in liquid nitrogen and measuring volumetrically the quantity of hydrogen produced. Upon completion of the reaction the contents of the reactor tube were filtered and extracted with ether. The filtration and extraction were carried out at about  $-75^{\circ}$  in order to take advantage of the negative temperature coefficient of solubility of ammonia-borane. Crystalline ammonia-borane was obtained from the filtrate by distilling away the ether as the receiver tube was warmed from  $-70^{\circ}$  to  $-20^{\circ}$ .

c. The Reaction Between Lithium Borohydride and Ammonium Salts in an Ether Slurry.

The reaction with ammonium chloride was carried out in the apparatus mentioned above. The reaction with ammonium sulfate was carried out on a tenfold larger scale and it was therefore necessary to modify the apparatus slightly. In this case the reactor consisted of a 100-ml, round-bottom flask which was fitted with a standard taper 24/40 drip-tip. This reactor flask was charged with a magnetic stirring bar and weighed quantities of lithium borohydride and ammonium sulfate<sup>14</sup> in the protective atmosphere of the "dry box." The flask was then transferred to the vacuum system as rapidly as possible. After thoroughly evacuating the system, anhydrous ether was distilled into the flask. Hydrogen evolution was initiated by maintaining the flask at about room temperature and stirring its contents vigorously. The extent of reaction was followed either by measuring, at various intervals, the quantity of hydrogen produced or by qualitatively observing the rate of hydrogen evolution through a mercury bubbler. After the theoretical amount of hydrogen had been produced, or after the rate of hydrogen evolution had decreased appreciably, the contents of the flask were filtered and extracted with ether at  $-75^{\circ}$ . Crystalline ammonia-borane was isolated by distilling the bulk of the ether from the filtrate as it was slowly warmed from  $-70^{\circ}$  to  $-40^{\circ}$ . The remaining traces of ether were pumped from the solid as it was slowly warmed from  $-40^{\circ}$  to  $-20^{\circ}$ . For further purification, samples of solid ammonia-borane were placed on the frit of the vacuum-line filter and re-extracted with ether at  $-75^{\circ}$ .

d. The Reaction Between Ammonia-Borane and Sodium in Liquid Ammonia.

Through the use of standard techniques,<sup>12</sup> a 0.96-mmole sample of ammonia-borane was allowed to react with a large excess of sodium in about 5 ml of li-

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13. All the reactions in this investigation which are described as carried out at room temperature were actually carried out at slightly below room temperature through this technique.

14. See Table II for the actual amounts of materials used in the individual runs.

quid ammonia at  $-78^{\circ}$ . The reaction produced 0.96 H/H<sub>3</sub>NBH<sub>3</sub> in 16 hours. Just a trace quantity of hydrogen was produced within the next 10 hours at  $-78^{\circ}$ .

e. Analytical.

1. X-ray powder analyses--Crystalline products were identified by means of x-ray powder techniques which used nickel filtered copper K $\alpha$  radiation. Specimens were sealed into thin-walled glass capillaries of 0.3-mm diameter (supplied by the Cain Specialties Co. of Chicago). A 5.7-cm Debye-Scherrer camera was used for routine analyses. Exposures were of the order of 1-2 hours at 30 kv and 15 ma. For the characterization of ammonia-borane and the examination of complex patterns produced by reaction mixtures, a high-resolution, 11.4-cm Debye-Scherrer camera was used. Exposures with this camera were of the order of 5-7 hours at 30 kv and 15 ma.

2. Chemical analyses--Boron was determined by titrating boric acid with sodium hydroxide in the presence of mannitol. Hydridic hydrogen was determined through the sealed-tube hydrolysis of the sample at  $100^{\circ}$  followed by the volumetric determination of the hydrogen produced. Nitrogen was determined by the Kjeldahl method. The procedures for these analytical methods are discussed by Bissot.<sup>15</sup>

3. Molecular-weight determinations--The determination of the molecular weight of ammonia-borane in dioxane, by freezing-point depression, was carried out in a Beckmann-type freezing-point apparatus. The molecular-weight determination of ammonia-borane in ether, by vapor-pressure depression, was carried out in equipment similar to that described by Parry, Kodama, and Schultz,<sup>5</sup> except that a mercury-filled differential manometer was used. The molecular-weight cells were thermostated at  $26^{\circ}$  and the temperature was held constant within  $\pm 0.05^{\circ}$ .

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15. D. H. Campbell, T. C. Bissot, and R. W. Parry, this Report, p. 145.

D. CHEMICAL EVIDENCE FOR THE STRUCTURE OF THE DIAMMONIATE OF DIBORANE (III).  
THE REACTIONS OF BOROHYDRIDE SALTS WITH LITHIUM HALIDES AND ALUMINUM CHLORIDE  
(S. G. Shore and R. W. Parry)

Abstract

It is shown that LiBr, LiCl, and LiBH<sub>4</sub> bring about slow evolution of H<sub>2</sub> from a diethylether suspension of B<sub>2</sub>H<sub>6</sub>·2NH<sub>3</sub>. Results are interpreted in terms of polarization of the borohydride by the Li (I). A diethyl ether solution of AlCl<sub>3</sub> will react with an ether suspension of B<sub>2</sub>H<sub>6</sub>·2NH<sub>3</sub> to give hydride-halide interchange. B<sub>2</sub>H<sub>6</sub>·2NH<sub>3</sub> will dissolve slowly in an ether solution of AlCl<sub>3</sub>.

One of the important pieces of evidence pertinent to the structure of the "diammoniate of diborane," B<sub>2</sub>H<sub>6</sub>·2NH<sub>3</sub>, is the instability of ammonium borohydride. Such instability justifies the reaction between the "diammoniate" and ammonium salts if a borohydride ion is assumed in the formula. By the same token, the previously reported lack of reaction between the "diammoniate" and sodium borohydride argues against the presence of an ammonium ion in the "diammoniate."<sup>1</sup> In connection with reactions of the latter type, an observation of Schaeffer<sup>2</sup> to the effect that LiBH<sub>4</sub> in ether reacted slowly with an ether slurry of "diammoniate" to give off hydrogen seemed to merit additional study.

The Decomposition of the Diammoniate of Diborane in the Presence of Lithium Salts.—One of the interesting features of the "diammoniate of diborane" is the fact that it is relatively stable to 80°, even though its most likely structure is [H<sub>2</sub>B(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>(BH<sub>4</sub>)<sup>-</sup>. In the past, before Schultz and co-workers demonstrated that the "diammoniate" contains a borohydride ion,<sup>3</sup> it was argued that "such a structure is unreasonable on the grounds that the strong proton-donor character of the quaternary nitrogen atoms should render the proton-sensitive BH<sub>4</sub><sup>-</sup> incapable of existence."<sup>4</sup> Actually, in view of newly available evidence, the stability of such a structure can be justified, for hexamminechromium (III) borohydride, [Cr(NH<sub>3</sub>)<sub>6</sub>](BH<sub>4</sub>)<sub>3</sub>, is stable up to 60°.<sup>1</sup> Since such a compound is stable, the existence of [H<sub>2</sub>B(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>(BH<sub>4</sub>)<sup>-</sup> cannot be denied on the grounds cited above. Both the chromium salt and the "diammoniate" are stable because the cations Cr(NH<sub>3</sub>)<sub>6</sub><sup>+++</sup> and H<sub>2</sub>B(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> are relatively large. They therefore have low charge densities and are of low-polarizing character.

It is well known that the proton sensitivity of the borohydride ion increases

1. D. R. Schultz and R. W. Parry, this Report, p. 19.

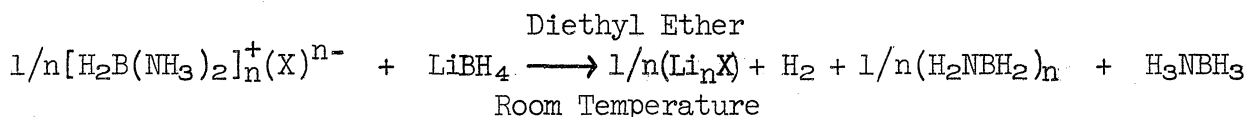
2. G. W. Schaeffer, private communication.

3. D. R. Schultz and R. W. Parry, this Report, p. 19; R. C. Taylor, D. R. Schultz, and A. R. Emery, *ibid.*, p. 92.

4. A. B. Burg, *J. Am. Chem. Soc.*, 69, 747 (1947).

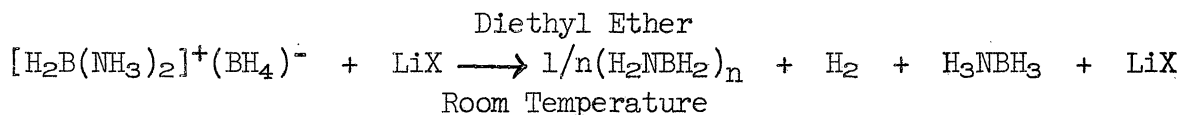
with the polarizing character of its associated cation. Thus, for example, potassium borohydride can be crystallized from the protonic solvent water; but lithium borohydride reacts vigorously with the protons of water; and aluminum borohydride reacts explosively with water.

From arguments of this type one might rationalize hydrogen evolution from the ether slurry of the "diammoniate" and lithium borohydride on the basis of a reaction between the proton-sensitive borohydride ion in lithium borohydride and the weakly protonic hydrogens attached to the nitrogens in the dihydrido-diammine boron (III) cation. In other words, the lithium (I) influenced the borohydride to such an extent that its hydridic hydrogens reacted with the protons of the cation, e.g.,



$\text{X}^{n-}$  = any anion.

If the foregoing arguments are valid, the "diammoniate of diborane" should evolve hydrogen in the presence of any lithium salt, since the presence of the Li (I) would increase the proton sensitivity of the "diammoniate's" borohydride ion.



An experimental study proved to be in accord with this supposition. It was found that the addition of a lithium halide to an ether slurry of the "diammoniate of diborane" caused the decomposition of the "diammoniate." Of the several experiments carried out, the most significant were those in which it was first established that a particular sample of the "diammoniate" is only slightly decomposed upon slurring in ether at room temperature, but that upon addition of a lithium halide to the slurry, the rate of decomposition, evidenced by hydrogen evolution, is increased very markedly. The results of such experiments are summarized in Fig. 1.

To avoid complications in the preceding study, it was important to exclude, rigorously, protonic substances such as water or ammonia. Extreme precautions were taken in the drying and handling of the lithium salts. That such precautions were successful in avoiding contamination is supported by the following facts:

1. Hydrogen evolution was slow compared to normal protolysis due to traces of water or ammonia.
2. Ammonia-borane and hydrogen were produced in almost a one-to-one ratio as demanded by the equation above. If traces of water had been present, the ether soluble ammonia-borane would have formed an ether insoluble precipitate, thereby giving a much smaller yield of ammonia-borane.<sup>5</sup>

5. S. G. Shore and R. W. Parry, this Report, p. 31.

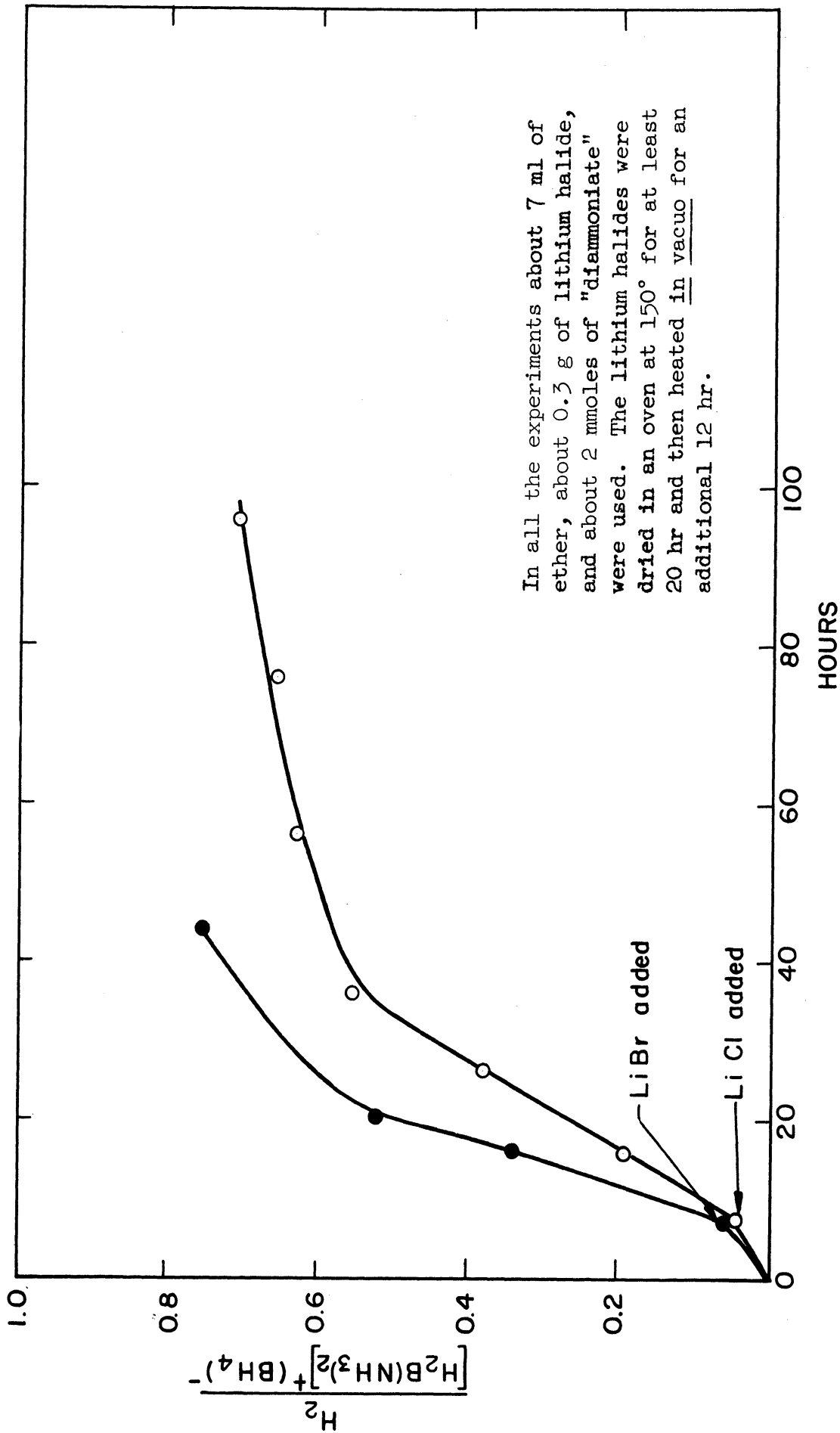


Fig. 1. The decomposition of the "diammoniate of diborane" in the presence of a lithium halide.

Since the +diammoniate+ is quite insoluble in ether, and since the lithium salts used are only slightly soluble in ether, the rate of decomposition of the "diammoniate" is probably dependent in part on the surface areas of the salts used. It seems probable, however, that the somewhat greater catalytic activity of lithium bromide as compared to lithium chloride is related to the greater solubility in ether of the former compound.

The Reactions of Borohydrides with Anhydrous Aluminum Chloride in Diethyl Ether.— On the basis of the foregoing arguments and results it was thought that the strongly polarizing aluminum (III) ion of aluminum chloride would be more effective than the lithium (I) of a lithium halide in accelerating hydrogen evolution from  $[H_2B(NH_3)_2] (BH_4)^-$ . However, contrary to the original expectation, the production of hydrogen was negligible when traces of water were scrupulously avoided. Results of two representative runs are summarized in Table I.

TABLE I

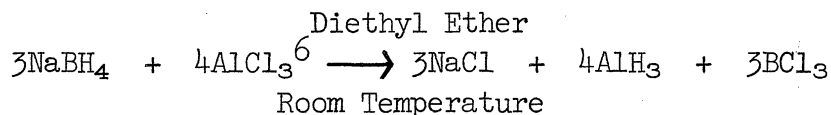
THE REACTION BETWEEN THE "DIAMMONIATE OF DIBORANE"  
AND ALUMINUM CHLORIDE IN ETHER

Run	Mmoles $[H_2B(NH_3)_2]^+(BH_4)^-$	ML Ether	Mmoles AlCl <sub>3</sub>	Time, hr	$\frac{H_2}{[H_2B(NH_3)_2]^+(BH_4)^-}$
1	1.93	10	ca. 6	0.3 12	0.09 0.11
2	2.88	5	ca. 10	0.3 36	0.01 0.05

In each run reaction took place as soon as the aluminum chloride was added to the ether slurry and within 20 minutes all the ether insoluble "diammoniate" had been converted into ether soluble compounds. The resulting clear solution proved to be unstable, for within eight hours the presence of a fine gelatinous precipitate became noticeable. The precipitate which was isolated by filtration proved to be amorphous (determined by x-ray powder techniques); it was polymerized aluminum hydride etherate. An x-ray powder examination of the solid obtained by removal of ether from the filtrate revealed the absence of familiar materials such as ammonium chloride, dihydrido-diammine boron (III) chloride  $[H_2B(NH_3)_2]^+(Cl)^-$ , and ammonia-borane. It was possible, however, to sublime with difficulty from the residue a small amount of solid boron trichloride etherate.

The experimental facts strongly suggest that the borohydride ion of the "diammoniate of diborane" was destroyed through hydride-chloride interchange. If this were the case, a simpler borohydride such as sodium borohydride might act similarly under comparable conditions.

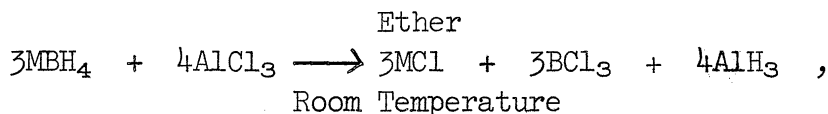




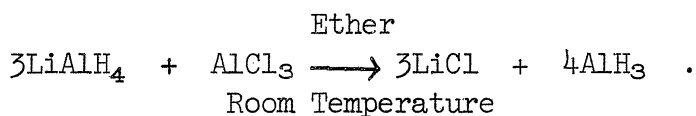
Schlesinger and co-workers<sup>7</sup> have already established that the high-temperature reaction between solid sodium borohydride and dry aluminum chloride produces aluminum borohydride, but the experimental conditions of the present study were completely different. The more significant differences were (1) the use of an ether slurry, (2) reaction was carried out at room temperature, and (3) the rigorous exclusion of all traces of moisture from the starting materials and the reaction system.

In a typical experimental test a five-to-one molar excess of aluminum chloride was added to an ether slurry of sodium borohydride at room temperature. The reaction mixture was stirred for about 38 hours to insure complete reaction; only a trace of hydrogen was evolved during this period. The precipitate from the reaction mixture contained sodium chloride and polymerized aluminum hydride etherate. The residue obtained by evaporating ether from the filtrate contained boron trichloride etherate, which was removed for identification by vacuum sublimation at room temperature. The results strongly favor the equation shown above.

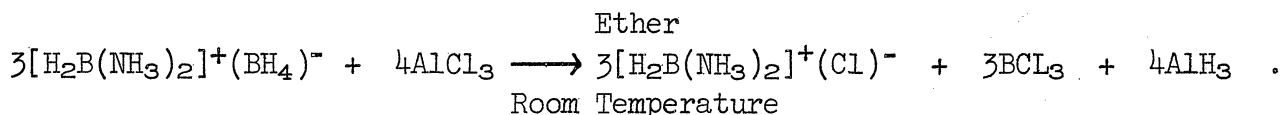
Discussion.—Although the lithium halides followed the reaction pattern which was expected from theoretical arguments, the reaction of aluminum chloride was anomalous in the sense that little hydrogen was produced; hydride-chloride exchange took place instead. The strong solvation of aluminum chloride probably plays an important role in determining the ultimate course of the reaction:



which simply parallels the well-known reaction between lithium aluminum hydride and aluminum chloride:<sup>8</sup>



Thus for the reaction involving the "diammoniate of diborane" one would expect



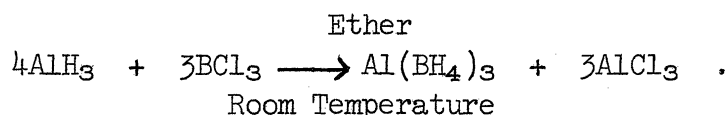
6.  $\text{AlH}_3$ ,  $\text{AlCl}_3$ , and  $\text{BCl}_3$  are actually etherates, but for the sake of simplicity the ether is omitted from the formulas.

7. H. I. Schlesinger, H. C. Brown, and E. K. Hyde, J. Am. Chem. Soc., 75, 209 (1953).

8. A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *ibid.*, 69, 1199 (1947).

However, there was no evidence for dihydrido-diammine boron (III) chloride or its decomposition product ammonium chloride. Apparently the  $[H_2B(NH_3)]^+$  cation underwent exchange also. One might expect such exchange to produce  $H_3NBCl_3$ , which is unstable and undergoes decomposition to form boron amide,  $B(NH_2)_3$ ,<sup>9</sup> and ammonium chloride. But the absence of ammonium chloride from the reaction mixtures negates this possibility. Therefore, the exchange reaction involving the cation of the "diammoniate" most likely involves the formation of boron trichloride etherate, as in the case of the borohydride ion.

Finholt and co-workers<sup>8</sup> have shown that



What apparently happened in this investigation was a reversal of this reaction due to the use of excess aluminum chloride. The destruction of both the cation and anion of the "diammoniate of diborane" by hydride-chloride exchange to produce products which contained hydrogens of a less active nature accounts for the small amounts of hydrogen gas produced.

#### Experimental.—

##### a. Materials.

1. Diethyl ether and sodium borohydride—the purification of these substances is described in the preceding paper.<sup>5</sup>

2. Aluminum chloride— $AlCl_3$  is extremely hygroscopic and readily hydrolyzed. It was therefore purified and prepared for reaction in the following manner. Reagent-grade aluminum chloride was placed in the apparatus depicted in Fig. 2, which was then sealed off and evacuated. By pumping on the system continuously and applying a soft flame to the apparatus, pure aluminum chloride was sublimed past the thin glass-wool plugs and through the constriction into the u-trap, which was immersed in ice water. Then about 8 ml of anhydrous ether was vacuum distilled into the u-trap, which was now cooled to about  $-78^\circ$ . The stopcock was closed and the apparatus was removed from the vacuum system. The u-trap was slowly warmed to room temperature and through appropriate tipping of the apparatus the ether was allowed to dissolve small portions of aluminum chloride at a time. Care was taken to prevent the vigorous solution of aluminum chloride since this can result in ether cleavage. After the aluminum chloride was completely dissolved, the apparatus was tilted so that a portion of the solution was poured into one of the bulbs. The solution in the bulb and the solution remaining in the u-trap were then frozen and the bulb was sealed off. In the same manner the remaining bulbs were filled and sealed off, one at a time. The amount of aluminum chloride in each of the bulbs was determined, approximately, by analyzing the contents of one of the bulbs.

9. A. Joannis, *Compt. rend.*, 135, 1106 (1902).

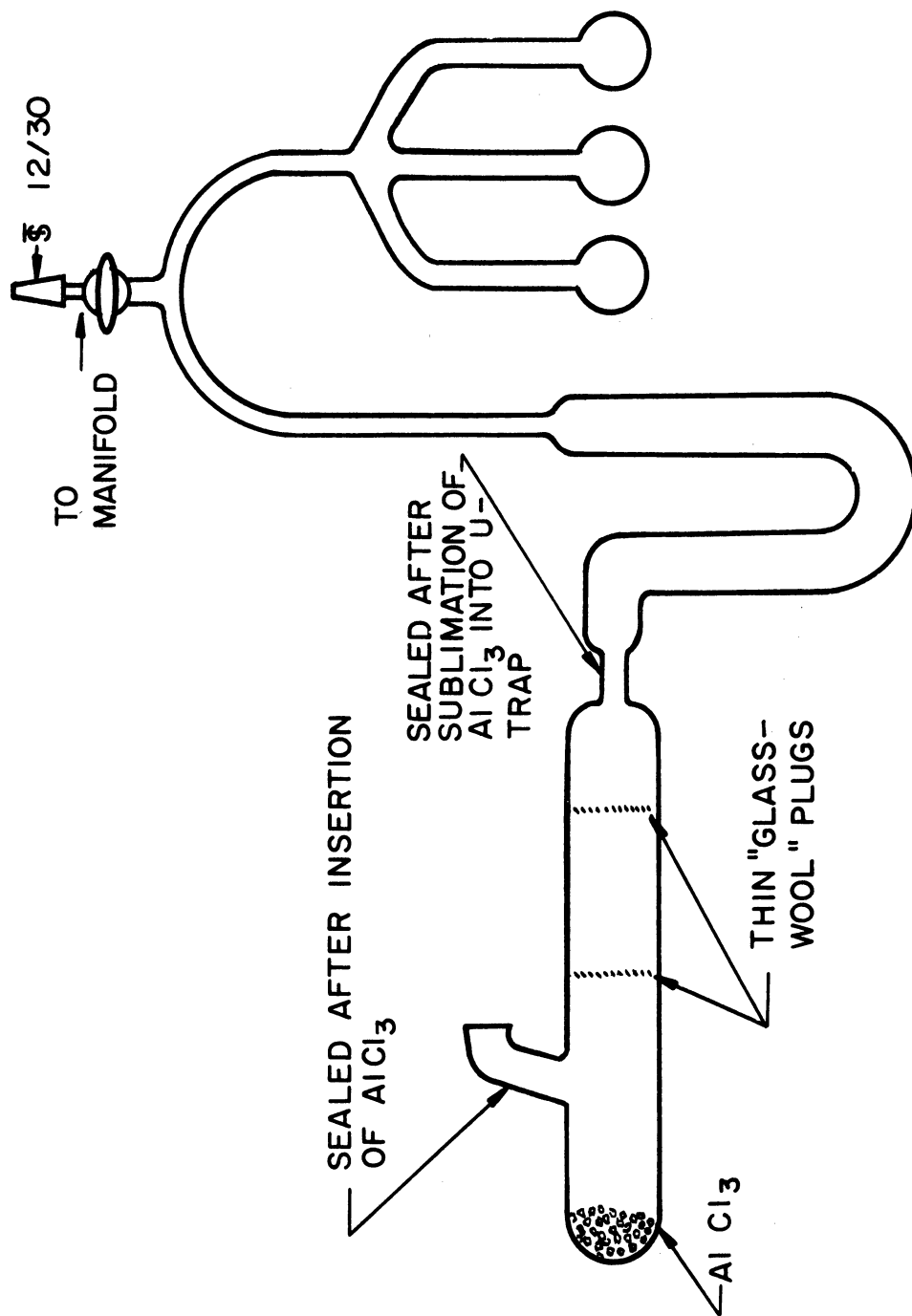


Fig. 2. Apparatus for the preparation of solutions of aluminum chloride in ether.

3. Lithium chloride and lithium bromide--LiCl and LiBr are very hygroscopic materials. They were therefore treated in the manner described in Fig. 1 in order to insure the complete removal of all traces of water.

b. The Decomposition of the Diammoniate of Diborane in the Presence of a Lithium Halide.

The apparatus in which these experiments were carried out is depicted in Fig. 3. All the stopcocks and joints which had to be rotated were greased with Dow-Corning High Vacuum Grease. All the joints which did not have to be rotated were sealed with DeKhotinsky Cement. Initially, the side arm containing the lithium halide<sup>10</sup> was placed in an oven and a standard taper cap was put in its place on the apparatus. The system was thoroughly evacuated and the "diammoniate of diborane" was prepared and isolated in the reactor tube, according to the standard procedure.<sup>11</sup> Since the purpose of these experiments was to cause interaction between the protonic and hydridic hydrogens of the "diammoniate," great care was taken to remove all traces of excess ammonia from the system. After the apparent removal of all of the ammonia, the solid "diammoniate" was pumped on for an additional 12 hours at room temperature. Then dry nitrogen gas was flushed through the system at atmospheric pressure and the tube containing the lithium halide was transferred, while it was still warm, from the oven to its position on the apparatus. The system was then re-evacuated and the halide was dried at 100° under vacuum for 12 hours; anhydrous ether was then vacuum distilled into the reactor tube. Through appropriate manipulation of the apparatus, the lithium halide was dropped upon the "diammoniate"-ether slurry. The decomposition was carried out under vigorous stirring at about room temperature.<sup>12</sup> The rate of decomposition was followed by measuring the amount of hydrogen given off. After appreciable decomposition had taken place, the solution was filtered at -75°. Ether soluble ammonia-borane was isolated by vacuum distilling ether from the filtrate.

c. The Reactions of Borohydrides with Aluminum Chloride in Diethyl Ether.

The apparatus in which these experiments were carried out is depicted in Fig. 4. "Diammoniate" of diborane was prepared and isolated in the reactor tube.<sup>13</sup> After the apparent removal of all the ammonia, the "solid diammoniate" was pumped on for an additional 12 hours at room temperature. Then anhydrous ether was vacuum distilled into the reactor. Sublimed aluminum chloride in ether solution was contained in the bulb suspended above the ether slurry. By rotating the arm of the bulb crusher, the bulb was crushed and its contents dripped into the ether slurry which was maintained at about room temperature. Immediate reaction ensued and with vigorous stirring all the solid "diammoniate" disappeared within 20 minutes. Within eight hours of continuous stirring at

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10. See Table I for the actual amounts of material used in the individual runs.

11. S. G. Shore and R. W. Parry, this Report, p. 54.

12. See the preceding paper for experimental conditions.

13. See Table I for the actual amounts of material used in the individual runs.

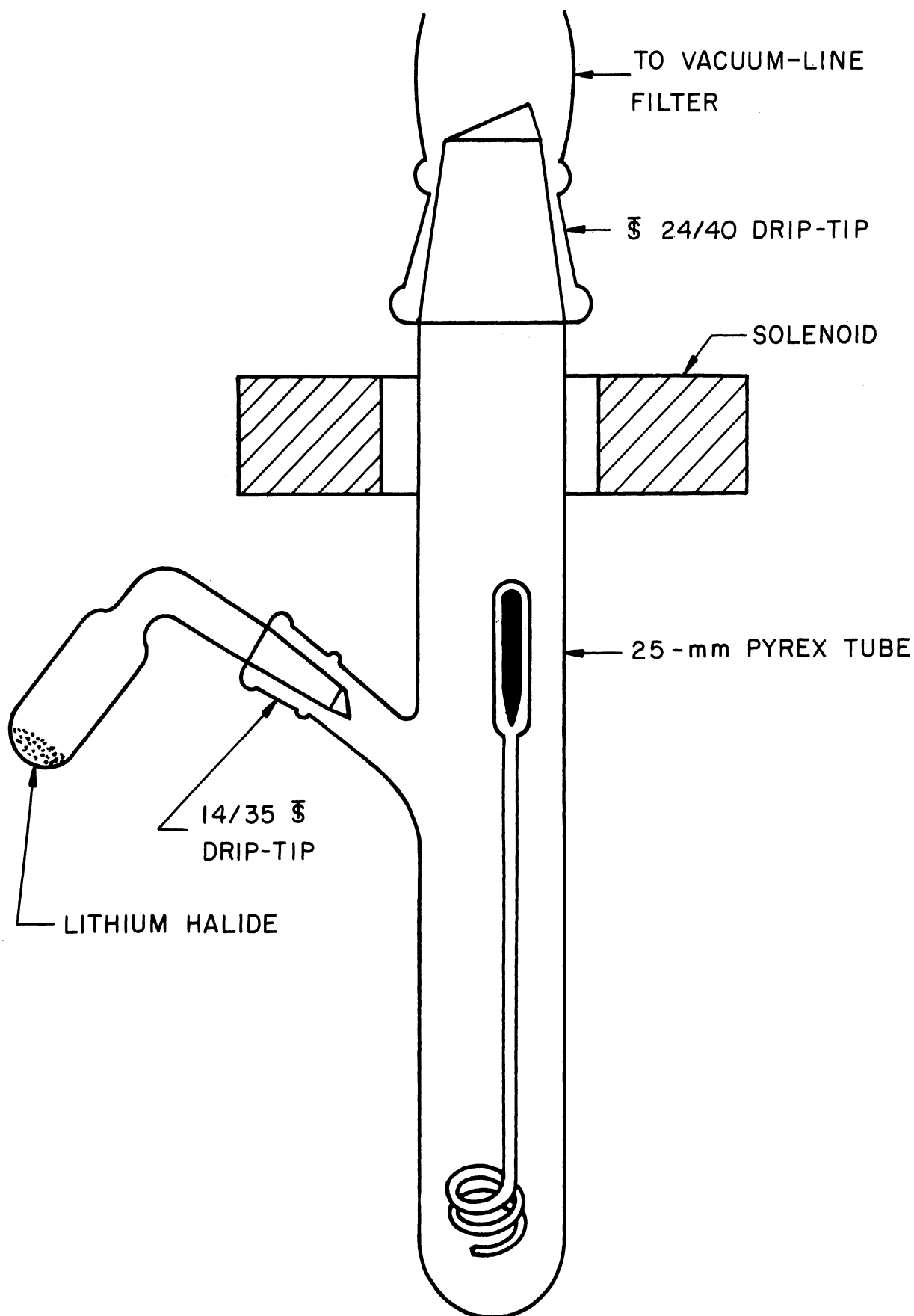


Fig. 3. Reactor tube for the decomposition of the "diammoniate of diborane" in the presence of a lithium halide.

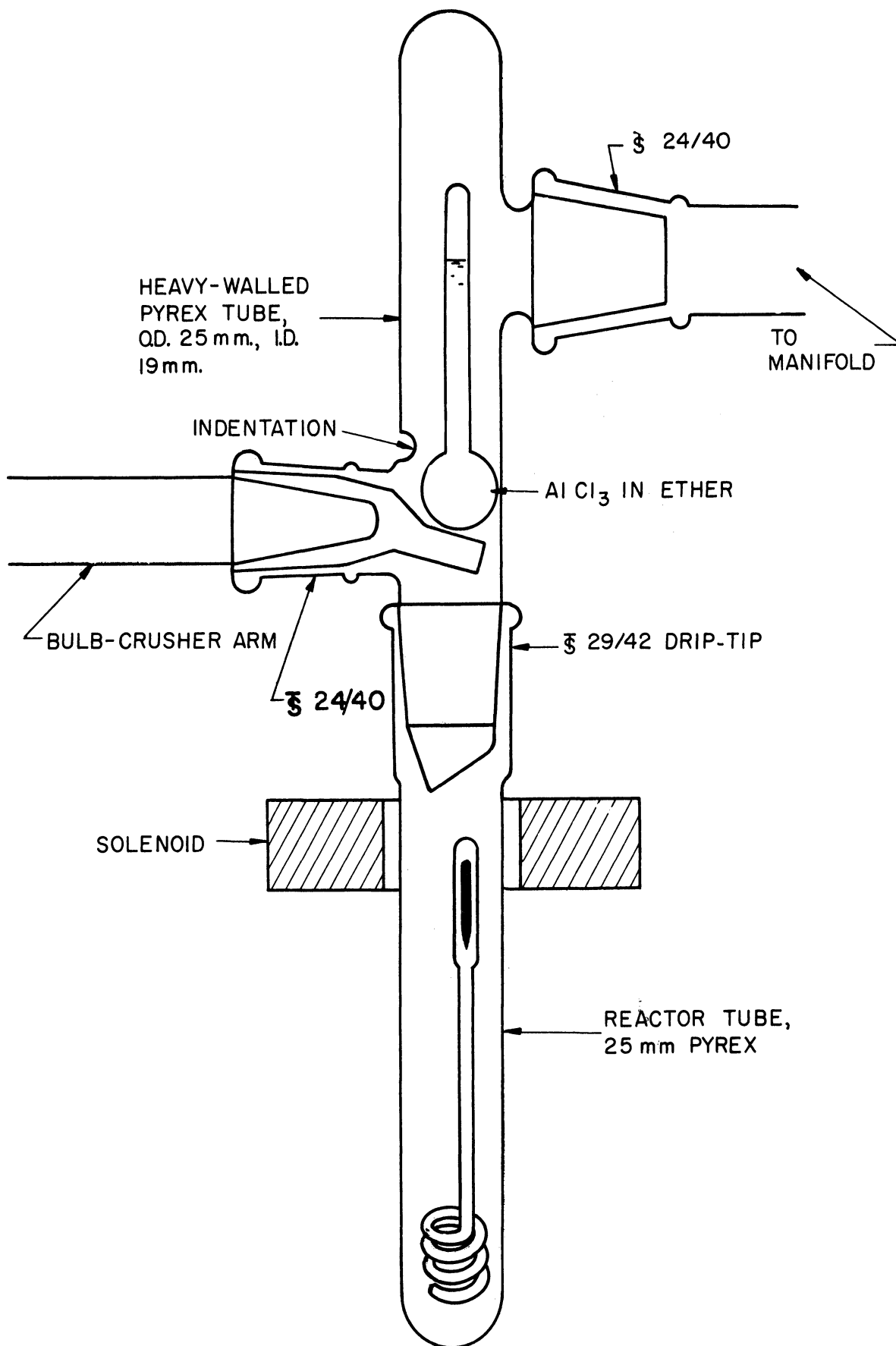


Fig. 4. Apparatus for the reaction between the "diammoniate of diborane" and aluminum chloride in ether.

room temperature, a fine gelatinous precipitate, polymerized aluminum hydride etherate, appeared. The reactor tube was cooled to about  $-70^{\circ}$  and the bulk of the ether was distilled away as the reactor was slowly warmed from  $-70^{\circ}$  to  $-40^{\circ}$ . The remaining traces of ether were pumped away as the system was warmed to room temperature. It was possible to sublime, with difficulty, small quantities of boron trichloride etherate in vacuo at room temperature into a receiver tube for identification. The system was then flushed with dry nitrogen, and the reactor tube containing the remaining residue after distillation and sublimation was transferred as rapidly as possible to a vacuum filter such as the one depicted in Fig. 2. The system was re-evacuated and 5 ml of anhydrous ether was vacuum distilled in upon the residue, most of which dissolved at room temperature. The slurry was filtered and the precipitate of polymerized aluminum hydride etherate was extracted with ether at room temperature and removed from the system for identification.

The same procedure was employed for the reaction between sodium borohydride and aluminum chloride in ether, except that the sodium borohydride was added to the reactor tube in the protective atmosphere of the "dry box." The tube was then transferred to the vacuum system as rapidly as possible.

#### d. Analytical.

1. X-ray powder analyses—Reaction products were examined for the presence or absence of known crystalline materials such as ammonia-borane, ammonium chloride, dihydrido-diammine boron (III) chloride, and sodium chloride. The equipment and techniques are described elsewhere (p. 42).

2. Chemical analyses—The products aluminum hydride etherate and boron trichloride etherate which were produced in the reactions involving aluminum chloride did not lend themselves to physical analysis and, because only small quantities of material could be isolated from the complex reaction mixtures, could not be identified by direct quantitative chemical analysis. It was necessary to rely on observations of the characteristic properties of these compounds.

In this investigation it was shown that the fine gelatinous material which precipitated slowly from ether solution was amorphous. Qualitative analysis showed that it contained only aluminum and hydridic hydrogen. It is known that aluminum hydride etherate in ether solution slowly precipitates, forming a material of indefinite composition.<sup>8</sup>

The product which was sublimed in vacuo from the aluminum chloride reaction mixtures slowly split out ethyl chloride and melted at about  $55^{\circ}$ . Qualitative analysis showed that it contained boron and chlorine. It is known that boron trichloride etherate can be sublimed in vacuo at room temperature and that it slowly splits out ethyl chloride. It has a melting point of  $56^{\circ}$ .<sup>14</sup>

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14. E. Wiberg and W. Sutterlin, Z. anorg. Chem., 202, 22 (1931).

E. CHEMICAL EVIDENCE FOR THE STRUCTURE OF THE DIAMMONIATE OF DIBORANE (IV). THE REACTION OF SODIUM WITH LEWIS ACIDS IN LIQUID AMMONIA (R. W. Parry and S. G. Shore)

Abstract

The reactions between sodium and four Lewis acids in liquid ammonia have been studied. HCN, H<sub>3</sub>BO<sub>3</sub>, CO<sub>2</sub>, and B<sub>2</sub>H<sub>6</sub> have been considered. The complexity of the system increases in the order given. The sensitivity of the B<sub>2</sub>H<sub>6</sub>-NH<sub>3</sub> system to experimental details is interpreted by an extension of Werner's coordination theory. The ion [HB(NH<sub>3</sub>)<sub>3</sub>]<sup>++</sup> is postulated to explain observed facts.

Introduction.—Past investigations have demonstrated that the stoichiometry of the reaction of the "diammoniate of diborane" with sodium in liquid ammonia is very sensitive to the conditions imposed. Only "diammoniate" which has been carefully prepared under a specific set of conditions will react with sodium in liquid ammonia to produce one equivalent of hydrogen per mole of diborane in a short period of time. A slow secondary process yields small quantities of additional hydrogen as a function of time.<sup>1</sup> However, if the "diammoniate" has been mistreated, either through the rapid addition of diborane to ammonia or by maintaining carefully prepared "diammoniate" at the relatively high temperature of -40°, then the resulting material has been shown to react with sodium to produce up to 1.3-1.4 equivalents of hydrogen per mole of diborane in short period of time.<sup>1,2</sup> In contrast to such observations, an early investigation in this laboratory,<sup>3</sup> which seemingly followed the same careful procedure of Schlesinger and Burg,<sup>1</sup> could not obtain much more than one-half an equivalent of hydrogen per mole of diborane. Furthermore, it was observed that sodium was used up without further hydrogen evolution taking place.

From these observations it is obvious that the ammonia-diborane-sodium system is very complex. In order to obtain a better understanding of the system, it was thought that a study of the generalized reaction between sodium and Lewis acids in liquid ammonia was in order, starting with a simple reaction and working up to the complicated case involving diborane. The acids chosen in addition to diborane were hydrogen cyanide, boric acid, and carbon dioxide.

Hydrogen Cyanide in Liquid Ammonia.—Hydrogen cyanide reacts with ammonia to form ammonium cyanide. A previous investigation<sup>4</sup> has shown that ammonium cyanide reacts with an active metal in liquid ammonia to produce one equivalent of hydrogen per mole of cyanide. This simple reaction was confirmed. It was found that ammonium cyanide

1. H. I. Schlesinger and A. B. Burg, J. Am. Chem. Soc., 60, 290 (1938).

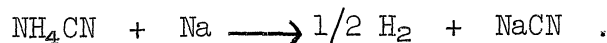
2. W. L. Jolly, Univ. of Calif. Radiation Laboratory, Livermore Site, Livermore, Calif., Contract No. W-7405-eng-48, UCRL-4504.

3. R. W. Parry, P. R. Girardot, et al., Final Report, Chemistry of Boron Hydrides and Related Hydrides, Univ. of Mich., Eng. Res. Inst., Project M966, U. S. Air Force, Contract AF 33(616)-8, E.O.R.-464 Br-1, 1952.

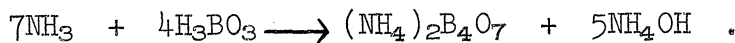
4. H. H. Frank and C. Freitag, Z. angew. Chem., 39, 1430 (1926).



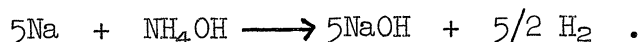
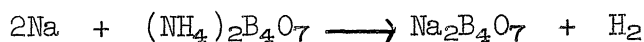
and sodium in ammonia at  $-78^{\circ}$  produce hydrogen gas according to the equation



Boric Acid in Liquid Ammonia.—It was shown that the reaction between boric acid and liquid ammonia forms a tetraborate and in terms of acid hydrogens can be represented as



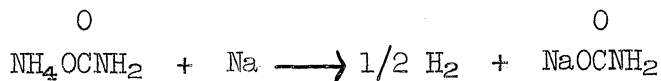
In the light of the simple ammonium cyanide case and other well-known reactions of ammonium salts,<sup>5</sup> it was expected that the ammonium tetraborate and ammonium hydroxide would react with sodium in liquid ammonia according to the following equations:



Thus the total hydrogen evolved was expected to be in the ratio of 1.75 equivalents of hydrogen per mole of boric acid used ( $7\text{H}/4\text{H}_3\text{BO}_3$ ). The actual results, which are given below, were in good agreement with this value and offer strong support for the reaction scheme.

Ammonia (ca. 5 ml) was condensed upon a sample of boric acid (1.61 mmoles) and the system was maintained at  $-52^{\circ}$  for two hours. Reaction with a large excess of sodium at  $-52^{\circ}$  produced 1.81 equivalents of hydrogen per mole of boric acid in 10 hours. A negligible quantity of hydrogen gas was produced within the next 10 hours at  $-52^{\circ}$ . In order to avoid the possibility of secondary reactions, another experiment was carried out at a lower temperature. Ammonia (ca. 5 ml) was condensed upon boric acid (1.87 mmoles) and the system was maintained at  $-64^{\circ}$  for half an hour. Reaction with a large excess of sodium at  $-64^{\circ}$  produced 1.74 equivalents of hydrogen per mole of boric acid in 18 hours. Further hydrogen evolution was negligible.

Carbon Dioxide in Liquid Ammonia.—Carbon dioxide reacts with ammonia to form ammonium carbamate, which has been shown to react with sodium in liquid ammonia to give off one equivalent of hydrogen per mole of carbon dioxide.<sup>6</sup>



It was possible to reproduce this observation, but the system appears to be more complicated than was previously indicated. Therefore, the results are tabulated in Table I and are discussed further.

In Run 1 ammonia in excess was added to solid carbon dioxide and allowed to melt. Then the excess ammonia was sublimed away at  $-78^{\circ}$ , leaving behind solid ammonium car-

5. G. W. Watt, Chem. Revs., 46, 317 (1950).

6. E. Rengade, Bull. Soc. Chim., Paris, 31, 565 (1904).

TABLE I

## THE REACTION OF AMMONIUM CARBAMATE WITH SODIUM IN LIQUID AMMONIA

Run (a)	Comments	CO <sub>2</sub> mmoles	Na CO <sub>2</sub>	Reaction Temp. °C	Reaction Time (cumulative) hr	H Evolved (cumulative) CO <sub>2</sub>
1	Excess NH <sub>3</sub> was sublimed away to isolate NH <sub>4</sub> CO <sub>2</sub> NH <sub>2</sub> . Then the NH <sub>3</sub> was returned.	2.57	10-15	-78	3	1.06
				-64	6	1.06
2	Excess NH <sub>3</sub> was never removed.	1.03	10-15	-78	1	0.19
				-78	3	0.48
				-78	7	0.53
				-78	17	0.58
				-78	39	0.71
				-78	51	0.86
3	Excess NH <sub>3</sub> was never removed.	24.2	1.01	-78	24	0.35
				-78	48	0.60
				-78	72	0.78
				-78	96	0.88
				-78	120	0.89
				-64	126	0.92
				-64	132	0.95
				-64	144	1.00

(a) All reactions were carried out in about 5 ml of solution.

bamate. Upon returning the ammonia to the solid and introducing sodium metal, the reaction at -78° was in accordance with the equation above. One equivalent of hydrogen per mole of carbon dioxide was evolved in less than three hours. Little evidence for further reaction was noted.

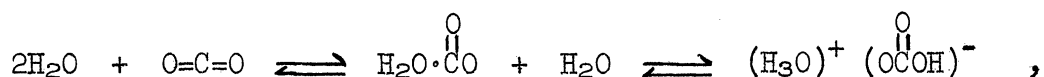
In Run 2 ammonia in excess was added to frozen carbon dioxide and in Run 3 carbon dioxide was added to frozen ammonia in excess. In both cases the excess ammonia was never removed, so the solid carbamate was never really isolated and identified. In both cases abnormally long reaction times were required to produce one equivalent of hydrogen per mole of carbon dioxide.

Although ammonia and carbon dioxide are known to react readily with each other to form ammonium carbamate, Hughes and Soddy<sup>7</sup> found that if the two substances

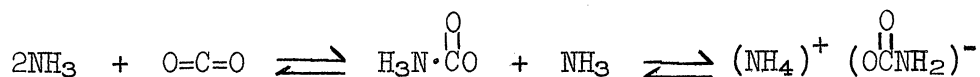
7. R. E. Hughes and F. Soddy, Chem. News, 69, 138 (1894).

are thoroughly dried, not the faintest sign of interaction occurs, even after the gases have been in contact with each other for 24 hours at room temperature. Since the experiments were carried out under strictly anhydrous conditions, the very slow hydrogen evolution of Runs 2 and 3 suggests that little ammonium carbamate was present at the time that sodium was added to the ammonia solutions. Rengade,<sup>6</sup> who first studied this system, also noted the very slow evolution of hydrogen from a sodium ammonia solution into which he introduced carbon dioxide under anhydrous conditions. He assumed that ammonium carbamate had formed but did not react since it is only slightly soluble in ammonia. However, his explanation seems to be unlikely since once the carbamate is isolated as the solid (Run 1), it reacts relatively rapidly with sodium in ammonia.

Although the nature of carbon dioxide in ammonia is unknown, it probably is analogous to carbon dioxide in water. It has been reported that for the most part carbon dioxide is simply dissolved in water. According to Mills and Urey,<sup>8</sup> only about 1% is hydrated. Furthermore, it is well known that the reaction between water and carbon dioxide is not instantaneous. The rate of hydration is dependent on catalysts which affect the pH of the solution. From available information,<sup>8</sup> one may represent the formation of carbonic acid as



in which the slow step is considered to be hydration. Similarly then, in the absence of catalysts, carbon dioxide may be simply dissolved in liquid ammonia, with conversion to ammonium carbamate taking place very slowly.



The experimental observation that removal of excess ammonia from the carbon dioxide—ammonia system seems to facilitate ammonium carbamate formation (Run 1) might be attributed to the concentration of trace quantities of catalytic material such as water. Rengade<sup>6</sup> also found it necessary to remove excess ammonia to be certain that the reaction with sodium would take place.

Diborane in Ammonia.—In Table II typical experimental results of Schlesinger and Burg<sup>1</sup> are compared with results from this laboratory<sup>3</sup> for the study of the reaction between sodium and carefully prepared diammoniate of diborane in liquid ammonia. Careful examination of the experimental procedures revealed a subtle difference similar to that described for carbon dioxide in ammonia. This difference is believed to account for the difference in observations.

Schlesinger and Burg<sup>1</sup> prepared and isolated the diammoniate through the slow low-temperature addition of diborane to ammonia, followed by the removal of excess ammonia by sublimation. The remaining solid was the diammoniate; it was shown to contain ammonia and diborane in a two-to-one mole ratio. Then the diammoniate was

8. G. A. Mills and H. C. Urey, J. Am. Chem. Soc., 62, 1019 (1940).

TABLE II

A COMPARISON OF THE RESULTS OF SCHLESINGER AND BURG  
WITH THOSE FROM THIS LABORATORY

Run	B <sub>2</sub> H <sub>6</sub> mmoles	$\frac{\text{Na}}{\text{B}_2\text{H}_6}$	Reaction Temp. °C	Reaction Time hr	$\frac{\text{H Evolved}}{\text{B}_2\text{H}_6}$
1 (S + B)	0.930	1.07	-77	0.5	0.98
2 (S + B)	0.872	1.05	-77	0.5	0.99
1	2.3	1.0	-81	1.8	0.57
2	0.511	1.02	-80 to -50	2.7	0.64

redissolved and its reaction with sodium in ammonia produced one equivalent of hydrogen per mole of diborane.

In the other investigation<sup>3</sup> diborane was added to ammonia under the conditions prescribed by Schlesinger and Burg. However, since the diborane was readily taken up by the ammonia, it was assumed that the diammoniate had been formed; therefore, the excess ammonia was not removed to confirm the formation of the diammoniate, but sodium was simply added to the solution. In this case only about one-half an equivalent of hydrogen per mole of diborane was produced, but nevertheless one equivalent of sodium was used up. The blue color of sodium in ammonia was discharged without further evolution of hydrogen.

A detailed study confirmed that the difference in procedure is responsible for the difference in results.

Dependence of Results on Experimental Procedure.—Whereas the ultimate product of the carbon dioxide--ammonia interaction is ammonium carbamate, the diborane-ammonia reaction seems to be more complicated. Many details of preparation must be closely observed. Therefore, before the results of this section can be considered, it is first necessary to describe the simple, but rather specific, procedure for preparing pure diammoniate of diborane.

A thin film of ammonia is condensed along the walls and bottom of a cylindrical reactor tube. A band of diborane is then condensed from one to several inches above the ammonia and the entire reactor is slowly warmed from -140° to about -80° in a period of about eight hours. During this time the diborane melts (-165.5°) and adds, usually in the gas phase at a temperature near -120°, to the surface of the solid ammonia. Addition is evidenced by a marked decrease in the pressure of the system. Since the addition depends on the surface available, the ammonia is in excess by at least a four-to-one mole ratio. When excess ammonia is removed by sublimation at -78°, the solid, nonvolatile diammoniate remains.

As a preliminary experiment, diammoniate, prepared and isolated in the foregoing fashion, was redissolved in liquid ammonia (ca. 5 ml) and allowed to react with sodium ( $\text{Na}/\text{B}_2\text{H}_6 = 2$ ) at  $-78^\circ$ . In less than one hour one equivalent of hydrogen per mole of diborane had been produced. In a second study diborane was added to ammonia, but the excess ammonia was never removed to isolate the diammoniate. At the end of one hour upon reaction of the ammonia solution (ca. 5 ml) with sodium ( $\text{Na}/\text{B}_2\text{H}_6 = 1.7$ ), only 0.58 of an equivalent of hydrogen per mole of diborane had been produced. The total amount of hydrogen which had been given off by the end of the second hour was 0.72 of an equivalent per mole of diborane. Thus both sets of observations reported in Table II were repeated.

In order to follow the evolution of hydrogen more carefully, the reactions were slowed down by using a 10-15-fold excess of sodium.<sup>9,10</sup> The new results are presented in Tables III and IV. Table III presents results equivalent to those of Schlesinger and Burg.<sup>1</sup> Diammoniate was prepared and isolated; then it was redissolved in ammonia and allowed to react with a large excess of sodium at  $-78^\circ$ . One equivalent of hydrogen per mole of diborane was given off in about three hours. Table IV represents successful attempts to reproduce the earlier work in this laboratory.<sup>3</sup> Diborane was added to ammonia in the above fashion, but the excess ammonia was never removed from the system. The reaction of such a system with sodium at  $-78^\circ$  produced less than one equivalent of hydrogen per mole of diborane in the normal reaction time of about three hours. A much longer period of time was required to produce one equivalent of hydrogen per mole of diborane. Professor G. W. Schaeffer of St. Louis University was informed of these observations and was able to repeat them by using the same procedure.<sup>11</sup>

In addition to the fact that ammonia was never removed from the systems of Table IV, it was necessary to condense the diborane ring at least three inches above the ammonia in the preparative procedure and to age the system at  $-78^\circ$  for several hours after the diborane had been taken up by the ammonia. If all three conditions were not carefully imposed, the results were inconsistent, giving the stoichiometry of Schlesinger and Burg in some cases, and the slow evolution of this laboratory in others.

All the above conditions which appear to be conducive to consistent results are designed to avoid localized heating effects. The effect of sudden warming was demonstrated in one particular experiment in which diborane had been apparently taken up by ammonia, but the temperature of the system had not been above  $-100^\circ$ ; upon suddenly thermostating this system at  $-78^\circ$ , a vigorous reaction occurred during

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9. The stability of a sodium-ammonia solution increases with increasing concentration of alkali metal,<sup>10</sup> which indicates a decrease in the reducing rate of the dissolved metal. The slowing of the reaction by using a large excess of sodium is probably due to the properties of the concentrated solution and to a slightly different experimental procedure which the concentrated solution makes possible.
  10. C. A. Kraus, J. Am. Chem. Soc., 43, 749 (1921); W. C. Johnson and A. W. Meyer, *ibid.*, 54, 3624 (1932).
  11. Private communication.

TABLE III

THE REACTION OF THE DIAMMONIATE OF DIBORANE WITH SODIUM IN LIQUID AMMONIA

Run (a)	Comments	B <sub>2</sub> H <sub>6</sub> mmoles	Reaction Time (cumulative) hr	H Evolved (cumulative) B <sub>2</sub> H <sub>6</sub>
1	In all cases NH <sub>3</sub> was removed to identify [H <sub>2</sub> B(NH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> (BH <sub>4</sub> ) <sup>-</sup> . The NH <sub>3</sub> was then re-turned.	1.69	1	0.73
			2	0.89
			3	0.99
			16	1.00
2		1.90	3	0.97

(a) In all cases Na and B<sub>2</sub>H<sub>6</sub> were used in a 10-15 mole ratio in about 5 ml of solution at -78°.

TABLE IV

THE REACTION OF SODIUM WITH DIBORANE-AMMONIA SYSTEMS FROM WHICH AMMONIA WAS NEVER REMOVED

Run (a)	Height of B <sub>2</sub> H <sub>6</sub> Above NH <sub>3</sub> in.	Time System Was Aged at -78° After B <sub>2</sub> H <sub>6</sub> Had Been Taken Up by NH <sub>3</sub>	B <sub>2</sub> H <sub>6</sub> mmoles	Reaction Time (cumulative) hr	H Evolved (cumulative) B <sub>2</sub> H <sub>6</sub>
1	3	8	2.02	1	0.43
				2	0.51
				12	0.63
				21	0.71
				33	0.72
2	3	8	2.02	1	0.66
				3	0.76
				7	0.82
				17	0.90
				41	0.96
3	6	6	1.21	1	0.71
				3	0.82
				7	0.87
				20	0.93
				44	0.99
4	5	8	1.40	1	0.72
				3	0.80
				7	0.87
				16	0.92

(a) In all cases Na and B<sub>2</sub>H<sub>6</sub> were used in a 10-15 mole ratio in about 5 ml of solution at -78°.

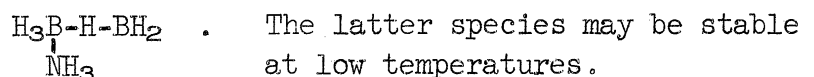
which solid products were scattered throughout the reactor. This observation plus the slow evolution of hydrogen in the reaction with sodium suggests that the mere taking up of diborane by ammonia, if heating effects are carefully avoided, does not necessarily result in the formation of the diammoniate of diborane.

The condition that diborane be condensed several inches above the ammonia facilitates gas-phase addition of diborane and avoids or lessens the possibility of liquid diborane coming in contact with ammonia to cause localized heating. The aging process at  $-78^{\circ}$ , once the diborane has been added to ammonia, maintains the system at just below its freezing point ( $-77.7^{\circ}$ ), where ammonia has a vapor pressure of about 45 mm. Under such circumstances the slow solvation or solution of adsorbed diborane can take place with the heat evolved being properly dissipated so that the possibility of bond rupture to form the diammoniate is diminished. Once the system is properly aged in this manner, it can apparently become liquid without conversion to the diammoniate taking place. However, if the system is not aged, inconsistent results in the reaction with sodium are obtained.

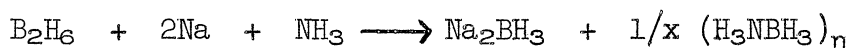
Discussion.—It is evident that the addition of diborane to ammonia through various procedures does not result in the formation of a unique substance. By considering the possible substances formed as coordination compounds in which ammonia is coordinated to boron (III), all available information can be correlated and interpreted in a reasonable fashion.

In those studies which repeated Girardot's original observations, it is believed that the slow, low-temperature addition of diborane to ammonia resulted in the adsorption of diborane on the surface of the solid ammonia without cleavage of the hydrogen-bridged bonds. Evidence for this is offered in the observations of Schaeffer and co-workers,<sup>12</sup> who report that upon the addition of diborane to ammonia, if the system is warmed from  $-140^{\circ}$  to  $-80^{\circ}$  in four hours instead of eight hours as in this investigation, it is then necessary to age the system at  $-78^{\circ}$  for at least an additional two hours. Otherwise it is possible to distill small quantities of diborane from the system. Further evidence is offered in the previously described experiment, from this investigation, in which after the initial low-temperature addition of diborane to ammonia the sudden raising of the temperature to  $-78^{\circ}$  caused a violent reaction to take place.

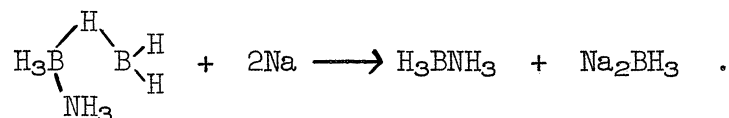
After the diborane was taken up by the ammonia, it is believed that the aging process at  $-78^{\circ}$  permitted slow solvation or solution to occur without the rupture of both of the hydrogen-bridged bonds. The nature of diborane in ammonia is unknown (henceforth it will be referred to as a solution of diborane in ammonia), but it may be simply dissolved in the ammonia, or one hydrogen-bridged bond may be ruptured and it may exist as



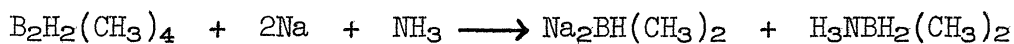
The following reaction probably took place upon the addition of sodium to the solution of diborane in ammonia:



12. G. W. Schaeffer, M. D. Adams, and F. J. Koenig, J. Am. Chem. Soc., 78, 725 (1956).

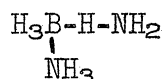


The latter equation would suggest a one-to-one molar ratio for the products. The actual separation and identification of these products was not attempted because of the complexity of the reaction mixtures due to secondary reactions. However, this proposed reaction is analogous to the observation of Burg and Campbell<sup>13</sup> that tetramethyl diborane,  $\text{B}_2\text{H}_2(\text{CH}_3)_4$ , is split symmetrically upon contact with sodium in liquid ammonia.



This system is less prone to secondary reactions; it was possible for them to identify the products unequivocally. When the theoretical amount of sodium was used, its characteristic blue color was completely discharged. The formation of disodium-borane,  $\text{Na}_2\text{BH}_3$ , accounts for a similar observation in this laboratory.<sup>3</sup> In analogy to B-dimethyl ammonia-borane,  $\text{H}_3\text{NBH}(\text{CH}_3)_2$ , the material which is designated  $(\text{H}_3\text{NBH}_3)_n$  should be monomeric  $\text{H}_3\text{NBH}_3$ , ammonia-borane. Although such a compound exists,<sup>14</sup> the possibility of the formation of some diammoniate, empirically  $(\text{H}_3\text{NBH}_3)_2$ , must be considered also. The presence of either material accounts for the slow evolution of one equivalent of hydrogen per mole of diborane, which was noted in this investigation. If the diammoniate were formed according to the equation above, then its reaction with additional hydrogen would produce only one-half an equivalent of hydrogen per mole of diborane. An additional hydrogen would come from slow secondary processes. If ammonia-borane were formed according to the equation above, its reaction with sodium would produce one equivalent of hydrogen per mole of diborane; this reaction has been shown to be slower than the reaction between the diammoniate and sodium.<sup>14</sup>

When excess ammonia is removed from a solution of diborane in ammonia, it can be said, very definitely, that the remaining solid will be the diammoniate of diborane. It appears as though removal of ammonia actually causes the conversion to the diammoniate. Of course, in preparing a solution of diborane in ammonia it is virtually impossible to avoid the formation of some diammoniate also, but upon removal of ammonia the diammoniate is present in quantitative or near quantitative yield relative to the amount of diborane used. This was determined throughout the course of this investigation, in which the diammoniate was prepared many times by the slow, low-temperature addition of diborane to ammonia, followed by the removal of excess ammonia. One might postulate that a solution of diborane in ammonia is actually



in ammonia and that the removal of ammonia could cause conversion to the diammoniate.

13. A. B. Burg and G. W. Campbell, Jr., J. Am. Chem. Soc., 74, 3744 (1952).

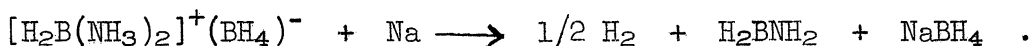
14. S. G. Shore and R. W. Parry, this Report p. 31.



The existence of such a species would be consistent with the fact that Burg and Campbell<sup>13</sup> were able to obtain disodium-borane and B-dimethyl ammonia-borane in equimolar quantities from tetramethyl diborane.

On the other hand, the role of solvent removal in the formation of ammonium carbamate from ammonia and carbon dioxide has already been noted and tentatively attributed to the concentration of trace quantities of a catalyst; water or hydrolysis products are possibilities. A similar explanation might be invoked in the present situation, especially since traces of water, or hydrolysis products, cause ammonia-borane to precipitate from ether solution as  $(H_3NBH_3)_n$ .<sup>15</sup> It should be emphasized, however, that if such substances are truly responsible for the conversion, then only a very minute quantity is sufficient for catalysis, because the experiments with carbon dioxide and diborane were carried out under anhydrous conditions.

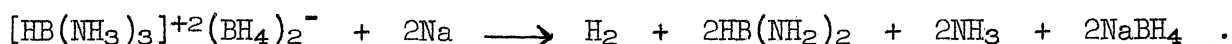
For reasons previously cited,<sup>15</sup> the diammoniate of diborane is considered to be the coordination compound  $[H_2B(NH_3)_2]^+(BH_4)^-$ . This formulation applies only to material which has been prepared through the slow, low-temperature addition of diborane to ammonia, followed by the removal of excess ammonia. Its primary reaction with sodium in ammonia is represented as



The slow secondary reaction<sup>1</sup> in which additional hydrogen is given off was confirmed as a matter of course in this investigation. The source of the secondary hydrogen is the material of empirical composition  $H_2NBH_2$ . It probably consists of various substances, any one of which would react slowly with sodium.

It is apparent that the handling of diammoniate under relatively severe conditions causes its conversion to another substance. Schlesinger and Burg<sup>1</sup> found that by maintaining the diammoniate at  $-40^\circ$  for 20 hours the final product had about the same empirical composition as the diammoniate, but that its properties were different. It retained ammonia more strongly than ordinary diammoniate; the solid split out hydrogen more readily than the diammoniate; and its reaction with sodium in liquid ammonia at  $-78^\circ$  produced around 1.3 equivalents of hydrogen per mole of diborane in a short period of time. Jolly<sup>2</sup> noted similar results from a material he obtained by allowing liquid diborane to react with ammonia at  $-78^\circ$ .

An explanation of these observations can be given by assuming that under such relatively severe treatment ammonia replaces a third hydridic hydrogen to form the coordination compound  $[HB(NH_3)_3]^{+2}(BH_4)_2^-$  in which three ammonia molecules are coordinated to boron (III). Such a compound should retain ammonia more strongly than the diammoniate because the hydrogens of its ammonias are more acidic than those of the diammoniate. For the same reason it should split out hydrogen more readily than the diammoniate. The reaction of such a compound with sodium in ammonia can be represented as



15. See the preceding papers in this report.

The hydrogen produced is equal to 1.33 equivalents per mole of diborane. Thus the expected properties are consistent with the experimental observations.

### Experimental.—

#### a. Materials.

1. Ammonia—commercial tank  $\text{NH}_3$  was dried and stored over sodium metal in the vacuum system.

2. Boric acid—reagent-grade  $\text{H}_3\text{BO}_3$  was dried by pumping on it for several hours in vacuo at room temperature.

3. Carbon dioxide— $\text{CO}_2$  gas was obtained from Dry Ice. It was dried by passing it several times through a trap which was immersed in a  $\text{CS}_2$  slush bath ( $-111.9^\circ$ ).

4. Diborane— $\text{B}_2\text{H}_6$  was prepared by the reaction between  $\text{LiAlH}_4$  and excess  $\text{BF}_3$  etherate in ether solution.<sup>16</sup> It was purified at low-temperature trap-to-trap distillation at  $-145^\circ$  until its vapor pressure was 225 mm at  $-111.6^\circ$ .

5. Sodium—sealed, evacuated, thin-walled glass bulbs 1.5-2 cm in diameter and containing 0.5-0.75 g of sodium metal were prepared by standard techniques.<sup>17</sup>

#### b. Procedures.

All the reactions were carried out in a bulb crusher such as the one depicted in Fig. 1. In a typical study a thin-walled, evacuated, glass bulb containing sodium metal was placed in the crusher, which was then put in place on the vacuum line and evacuated. The materials to be studied were then prepared in the reaction tube of the bulb crusher as follows:

1. Carbon dioxide in ammonia—A known amount of carbon dioxide was condensed an inch or so above an excess of frozen ammonia which was at the bottom of the tube, and the system was warmed from about  $-140^\circ$  to  $-80^\circ$  in a period of about eight hours. In other experiments the positions of the ammonia and carbon dioxide were reversed. The excess ammonia was sublimed away at  $-78^\circ$  when the formation of ammonium carbamate was desired. See Table I for the actual amounts of reactants which were used in the individual runs.

2. Boric acid in ammonia—A known amount of finely divided boric acid was placed in a glass bucket which was lowered on a thread into the bulb crusher. When the bucket was on the bottom of the reactor tube of the bulb crusher, it was tipped by pulling a second string which was fastened to its bottom. The boric acid was spilled onto the bottom of the reactor tube and the bucket was

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16. I. Shapiro, H. G. Weiss, M. Schmick, S. Skolnik, and G. E. L. Smith, J. Am. Chem. Soc., 74, 901 (1952).

17. R. S. Sanderson. Vacuum Manipulation of Volatile Compounds. New York: John Wiley and Sons, Inc., 1948, p. 72.

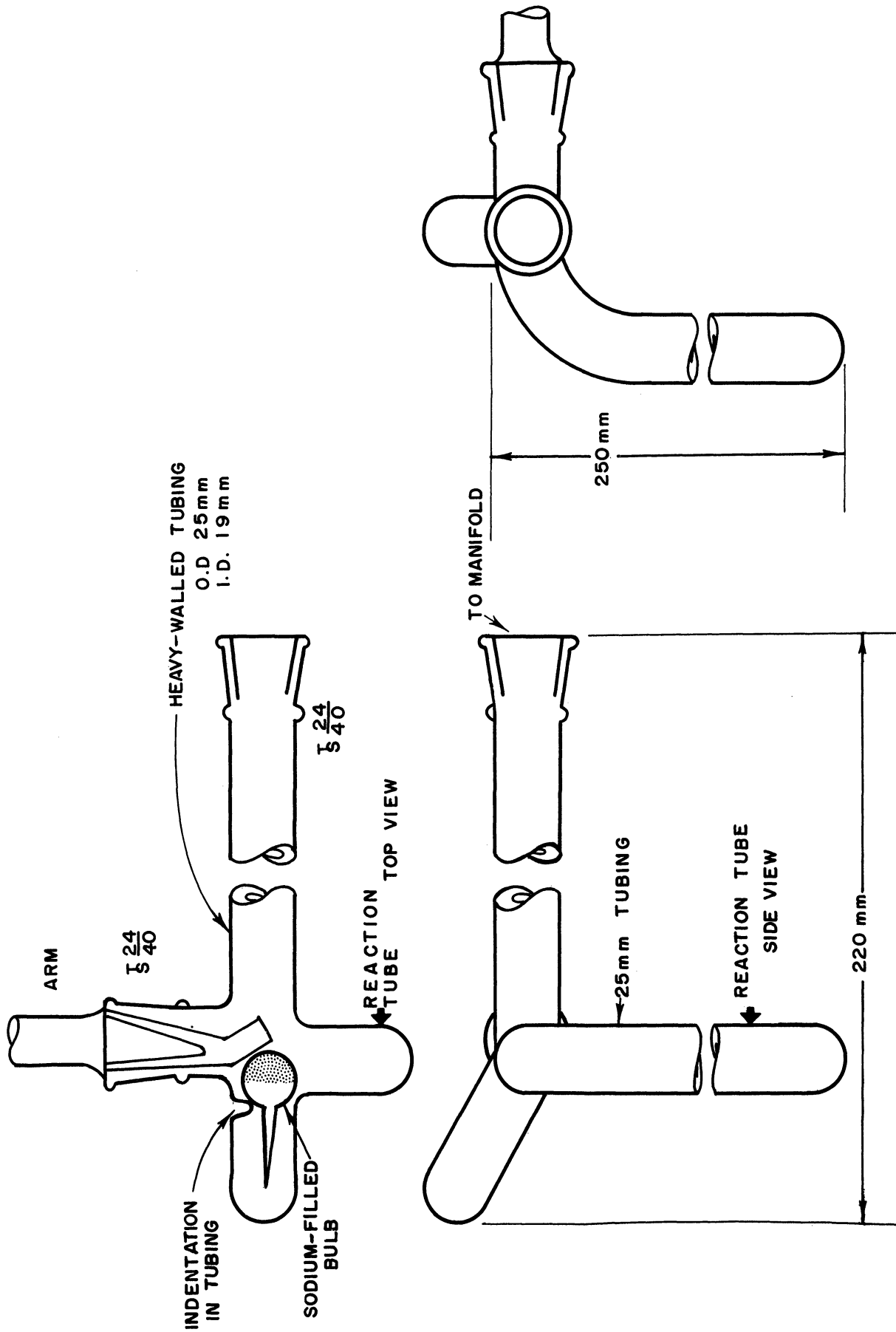


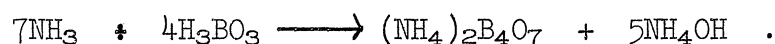
Fig. 1. Bulb crusher for reactions with sodium in liquid ammonia.

withdrawn. Then the bulb crusher was loaded with a sodium-containing bulb and was transferred to the vacuum system and evacuated. Ammonia was then condensed upon the boric acid. See page 55 for the conditions of the individual runs.

It was shown that the action of ammonia on boric acid produces a tetraborate. Liquid ammonia was condensed upon a small quantity of finely divided boric acid. Then the excess ammonia was sublimed away at  $-78^{\circ}$ . Final traces of volatile material were removed by pumping on the remaining solid for about an hour at room temperature. The nonvolatile solid was analyzed and the percentage composition of nitrogen and boron indicated that the final residue was  $\text{NH}_4\text{HB}_4\text{O}_7 \cdot 5/2 \text{H}_2\text{O}$

Anal. Calcd. for  $\text{NH}_4\text{HB}_4\text{O}_7 \cdot 5/2 \text{H}_2\text{O}$ : N, 6.39; B, 19.73.  
Found: N, 6.40; B, 19.6.

In terms of acid hydrogens, the reaction between boric acid and ammonia can be represented as



3. Diborane in ammonia—A thin film of ammonia, about two inches high, was condensed along the walls and bottom of the reactor tube of the bulb crusher. Diborane was then condensed in a solid ring at least two inches above the ammonia, which was in excess by more than a four-to-one mole ratio. The reactor was then immersed in a Dewar flask containing Phillips commercial methyl pentanes which had been previously cooled to  $-140^{\circ}$ . The bath was allowed to warm at the rate of about  $5^{\circ}$  per hour. During this period of warming, the vapor pressure of the diborane in the system rose and then fell off sharply at some point in the temperature range from  $-125^{\circ}$  to  $-115^{\circ}$ , indicating that the diborane had been taken up by the ammonia. When the temperature of the system had reached  $-80^{\circ}$ , the ammonia was allowed to melt and run down the walls to the bottom of the reactor tube. The reactor tube was then thermostated in a Dry Ice—*isopropanol* slush at  $-78^{\circ}$  and all the excess ammonia was sublimed away, leaving behind solid diammoniate of diborane. In most cases the exact amount of ammonia which was put in and removed from the reactor tube was known. In each such case it was found that ammonia and diborane had reacted in a two-to-one mole ratio. The ammonia was then returned to the system by condensing ammonia, in rings, along the wall of the reactor tube and then allowing it to melt, thus washing any solid diammoniate on the walls down to the bottom of the tube.

The preparation of a solution of diborane in ammonia was carried out in essentially the same manner, except that the diborane was condensed at least three inches above the ammonia, and after the addition of diborane to ammonia the system was aged at  $-78^{\circ}$  for an additional 5-8 hours. The excess ammonia was never removed from the system. See Tables III and IV for the actual amounts of reactants which were used in the individual runs.

After the material to be studied was prepared in the reactor tube and a sufficient quantity of ammonia was present, the ammonia solution was frozen and

the sodium-containing bulb was crushed by rotating the arm of the bulb crusher. The crushed bulb was dropped onto the frozen solution by rotating the crusher around its axis. Sufficient ammonia was then condensed upon the crushed bulb so that the total volume of solution when the ammonia melted would be about 5 ml.

When a large excess of sodium was used, the reaction was initiated by warming the system to a point where a portion of the ammonia melted and dissolved the sodium. The system was then thermostated in a Dry Ice--isopropanol slush at  $-78^{\circ}$ .<sup>18</sup> The sodium-ammonia solution melted the remaining frozen ammonia and thus it was possible to bring about solution without raising the temperature of the system significantly above  $-78^{\circ}$  for any appreciable period of time. When a small amount of sodium (stoichiometric quantity or small excess) was used, it was generally necessary to obtain complete solution before thermostating the system at  $-78^{\circ}$ ; otherwise the remaining frozen ammonia would not melt because the quantity of sodium in the system was insufficient to cause an appreciable freezing point depression for the ammonia. This difference in procedure may account in part for the observation that when a large excess of sodium is used (p. 59) the reaction time is greater than when an equivalent amount of sodium is used, since in the latter case the system has been subjected to somewhat higher temperatures and localized heating effects. At any rate, a consistent set of results is obtained from either procedure.

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18. This does not apply to the reactions with boric acid in ammonia which were carried out at a higher temperature (p. 55).

Abstract

A tracer study of the reaction between sodium and the "diammoniate of diborane" in liquid ammonia, using deuterium as the labeling element showed that in the low-temperature reactions with sodium only nitrogen-hydrogen bonds were broken; no boron-hydrogen bonds were ruptured. In the high-temperature ammolysis reaction involving the residues of the sodium reaction, a boron-hydrogen and a nitrogen-hydrogen bond were broken. A rather high separation factor for the isotopes of hydrogen is suggested by the data.

Introduction.—It appears that the so-called "diammoniate of diborane,"  $[\text{H}_2\text{B}(\text{NH}_3)_2]^+(\text{BH}_4)^-$  is one of several possible coordination compounds of boron (III) in which the hydride ion and the ammonia molecule act as coordinated ligands. The existence of ammonia-borane,  $\text{H}_3\text{NBH}_3$ , is well established.<sup>1</sup> Furthermore, evidence has been presented<sup>2</sup> that the addition of diborane of ammonia through various procedures does not result in the formation of a unique substance. It has been pointed out<sup>2</sup> that the formation of the "diammoniate" is guaranteed only by a very specific preparative method. Under slightly different conditions it appears to be possible to prepare a solution of diborane in ammonia. Under more vigorous conditions there is evidence for the formation of  $[\text{HB}(\text{NH}_3)_3]^{+2}(\text{BH}_4)^{-2}$ .

In an exchange study of the "diammoniate" in ammonia, using deuterium as a tracer, Burg<sup>3</sup> demonstrated that H-D exchange between the solute and solvent occurs only between those hydrogens which were originally bound to nitrogen. His results indicate that the hydrogens which are bound to boron in the "diammoniate" are not sufficiently acidic to form an ammonium salt, since it is known<sup>4</sup> that rapid proton exchange takes place between an ammonium ion and ammonia, even at  $-60^\circ$ . Burg's work refutes the early diammonium formulation,  $(\text{NH}_4)_2\text{B}_2\text{H}_4$ , of Stock.<sup>5</sup>

Insofar as exchange experiments can be accepted as a criterion for acidic character, Burg's evidence is convincing; however, his reaction conditions were mild. A more severe test for acidic character would be to determine whether boron-hydrogen bonds, nitrogen-hydrogen bonds, or bonds of both types are ruptured in the reaction

1. S. G. Shore and R. W. Parry, this Report, p. 31; E. W. Hughes, J. Am. Chem. Soc., 78, 502 (1956); E. L. Lippert and W. N. Lipscomb, *ibid.*, 503 (1956).
2. R. W. Parry and S. G. Shore, this Report, p. 54.
3. A. B. Burg, J. Am. Chem. Soc., 69, 747 (1947).
4. C. J. Nyman, Si-Chang Fung, and H. W. Dodgen, *ibid.*, 78, 725 (1956).
5. A. Stock. Hydrides of Boron and Silicon. Ithaca: Cornell Univ. Press, 1933.

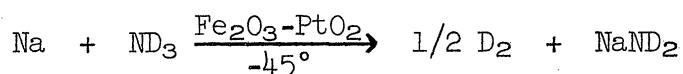
of the "diammoniate" with sodium in liquid ammonia. Since a knowledge of the acidic character of the hydrogens in the "diammoniate of diborane" and its related substances is of importance in testing proposed models of their structures, tracer studies of their reactions with sodium in liquid ammonia were undertaken.

A Tracer Study of the Reaction of the "Diammoniate of Diborane" with Sodium in Liquid Ammonia.—Since Burg<sup>3</sup> has demonstrated that hydrogen which is bound to boron does not exchange with hydrogen which is attached to nitrogen, the following species of the "diammoniate" may be regarded as being stable in liquid ammonia-h<sub>3</sub> or liquid ammonia-d<sub>3</sub>: B<sub>2</sub>D<sub>6</sub>·2NH<sub>3</sub>, B<sub>2</sub>D<sub>6</sub>·2ND<sub>3</sub>, and B<sub>2</sub>H<sub>6</sub>·2ND<sub>3</sub>.<sup>6</sup>

When the classical "diammoniate of diborane" has been prepared under carefully prescribed conditions, and when it has been always maintained below -70°, it will react with sodium in liquid ammonia to produce one equivalent of hydrogen per mole of "diammoniate."<sup>2</sup> The species which are listed above were allowed to react with sodium in liquid ammonia; the results are summarized in Table I.

The complete absence of deuterium<sup>7</sup> in the gas evolved from the reaction between sodium and B<sub>2</sub>D<sub>6</sub>·2NH<sub>3</sub> in ammonia-h<sub>3</sub> (Run 2) confirms Burg's contention that the hydrogens which are bound to boron in the "diammoniate" have no acidic character. Even under the comparatively vigorous conditions of this reaction, no boron-hydrogen bonds were broken. However, the reaction between B<sub>2</sub>H<sub>6</sub>·2ND<sub>3</sub> and sodium in ammonia-d<sub>3</sub> (Run 3) produced gas which was only 77% deuterated. This result could not have arisen from contamination of the system because of the elaborate experimental procedures which were employed.<sup>8</sup> Therefore, the possibility of B-H bond rupture in this particular reaction was considered. If the protium which was given off in this reaction did come about through the rupture of B-H bonds, then one would expect B<sub>2</sub>D<sub>6</sub>·2ND<sub>3</sub> to give off gas which is much richer in deuterium. However, the gas which was produced in the reaction between B<sub>2</sub>D<sub>6</sub>·2ND<sub>3</sub> and sodium in ammonia-d<sub>3</sub> was about 78% deuterated (average of Runs 4 and 5). Since the diborane-d<sub>6</sub> which was used in this latter case was about 96% deuterated, and since the hydrogen which is bound to boron does not exchange with hydrogen which is bound to nitrogen,<sup>3</sup> there was insufficient protium in the form of B-H bonds to account for the composition of the gas. There-

6. For the sake of simplicity, isotopically substituted "diammoniate" will be represented by its empirical formula.
7. In discussing the tracer studies, the term hydrogen will refer to the elements of atomic number one. Protium and deuterium will refer to its isotopes of mass one and two, respectively.
8. In order to be certain that any protium enrichment in the evolved gas did not arise from the contamination of the system, control experiments were carried out concurrently with the regular tracer studies under identical conditions of handling and analysis. The control experiments consisted of a tracer study of the reaction of sodium with ammonia-d<sub>3</sub> in the presence of a catalyst.



There was little, if any isotopic fractionation. The vapor pressure of the ammonia-d<sub>3</sub> indicated that it was about 97% deuterated, and the samples of gas which were obtained from two separate control experiments were 95.9 and 95.1% deuterated.

TABLE I

A TRACER STUDY OF THE REACTION OF THE  
"DIAMMONIATE OF DIBORANE" WITH SODIUM IN LIQUID AMMONIA

Run	Solvent	Solute	Diborane, mmoles	Reaction Time, (cumulative) hr	Hydrogen Equivalents Evolved (cumulative) diammoniate, mmoles	Isotopic Analysis, Total % D
1	NH <sub>3</sub>	B <sub>2</sub> H <sub>6</sub> · 2NH <sub>3</sub>	1.69	1	0.73	0.0
				2	0.89	0.0
				3	0.99	0.0
2	NH <sub>3</sub>	B <sub>2</sub> D <sub>6</sub> · 2NH <sub>3</sub>	1.87	1	0.70	0.0
				2	0.77	0.0
				6	1.00	0.0
3	ND <sub>3</sub>	B <sub>2</sub> H <sub>6</sub> · 2ND <sub>3</sub>	1.92	2	0.77	74.3
				4	0.91	77.1
				8	1.00	
				14	1.02	
4	ND <sub>3</sub>	B <sub>2</sub> D <sub>6</sub> · 2ND <sub>3</sub>	1.95	1	0.51	72.5
				2	0.56	73.4
				4	0.62	75.7
				20	0.86	80.3
				44	0.98	81
5	ND <sub>3</sub>	B <sub>2</sub> D <sub>6</sub> · 2ND <sub>3</sub>	2.07	2	0.51	69.6
				5	0.57	72.3
				27	0.79	74.9
				33	0.83	75.1
				56	0.92	75.7
6	ND <sub>3</sub>	B <sub>2</sub> D <sub>6</sub> · 2ND <sub>3</sub>	1.91	1	0.62	
				2	0.71	
				4	0.75	
				16	0.88	
				36	1.00	

## Notes:

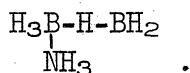
- (a) In all cases sodium and diborane were used in a 10-15 mole ratio in about 5 ml of solution at -78°. The concentration of the "diammoniate" was about 0.01 M.
- (b) In an attempt to decrease the reaction time, solid B<sub>2</sub>D<sub>6</sub> · 2ND<sub>3</sub> was aged for 22 hr at -78°.
- (c) The diborane-d<sub>6</sub> was about 98% deuterated and the ammonia-d<sub>3</sub> was about 96% deuterated.



fore, the most reasonable interpretation of these observations is that the "diammoniate of borane" reacts with sodium through the rupture of nitrogen-hydrogen bonds only. Since the ammonia-d<sub>3</sub> was about 96% deuterated, it contained N-H as well as N-D bonds. The fact that the evolved gas from B<sub>2</sub>H<sub>6</sub>·2ND<sub>3</sub> and B<sub>2</sub>D<sub>6</sub>·2ND<sub>3</sub> was greatly enriched in protium is attributed to an isotope effect in which the N-H bond was preferentially ruptured.

In view of the foregoing discussion one might expect "diammoniate" which contains ammonia-d<sub>3</sub> to react more slowly with sodium than "diammoniate" which contains ammonia-h<sub>3</sub>. The results are roughly consistent with this expectation. In fact, the reactions of B<sub>2</sub>D<sub>6</sub>·2ND<sub>3</sub> with sodium were much slower than any of the other reactions, even when a deliberate attempt was made to increase the rate of hydrogen evolution (Footnote b, Table I). The reason for the much slower rate is not immediately obvious since differences are greater than expected from theory, but the observations appear to be real.

A Tracer Study of the Reaction of Sodium with Solutions of Diborane in Ammonia.— It has been pointed out<sup>2</sup> that under certain conditions it appears to be possible to prepare a solution of diborane in ammonia, which may be diborane simply dissolved in ammonia, or may be



This solution produces hydrogen upon reaction with sodium, but much more slowly than the "diammoniate." Tracer studies of the reaction with sodium were carried out and the results are presented in Table II.

It was found that the reaction between sodium and a solution of diborane-d<sub>6</sub> in ammonia-h<sub>3</sub> produced essentially pure protium (Run 3), but the reaction between sodium and diborane-h<sub>6</sub> in ammonia-h<sub>3</sub> produced hydrogen gas which was about 74% deuterated (average of Runs 4, 5, and 6). These observations, with respect to the isotopic composition of the gas evolved, are in complete accord with the tracer studies of comparably deuterated "diammoniate of diborane," and indicate that the rupture of nitrogen-hydrogen bonds is the only source of hydrogen in the reaction. These results then are consistent with the previously stated belief<sup>2</sup> that the source of hydrogen in the reaction is either the "diammoniate" or ammonia-borane, both of which are similar in that they contain coordinated ammonia.

A Tracer Study of the Reaction of "Mistreated Diammoniate of Diborane" with Sodium in Liquid Ammonia.—"Mistreated diammoniate of diborane" is a substance which has the same empirical composition as the "diammoniate of diborane" but is prepared either through the rapid addition of diborane to ammonia or by maintaining carefully prepared "diammoniate of diborane" at temperatures above -70° for several hours or more.<sup>2</sup> The resulting product is believed to be [HB(NH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>2(BH<sub>4</sub>)<sub>2</sub><sup>-</sup>, since it reacts with sodium in liquid ammonia to produce around 1.3 equivalents of hydrogen per mole of diborane used in its preparation. This model suggests that only nitrogen-hydrogen bonds should be broken in the reaction with sodium, and the hydrogen which is given off in excess of one equivalent per mole of diborane should not come from the interaction of protonic and hydridic hydrogen, but rather from the direct sodium-cation interaction.

TABLE II

## A TRACER STUDY OF THE REACTION OF SODIUM WITH SOLUTIONS OF DIBORANE IN AMMONIA

Run	Solvent (a)	Solute	Diborane, mmoles	Sodium Diborane	Reaction Time, hr	Reaction Temp., °C	Hydrogen Equivalents		Isotopic Analysis, total % D
							Evolved	diborane, mmoles	
1	NH <sub>3</sub>	B <sub>2</sub> H <sub>6</sub>	0.51	1.0	1.8	-81	0.57		0.0
2	NH <sub>3</sub>	B <sub>2</sub> H <sub>6</sub>	2.3	1.02	2.7	-80 to -50	0.64		0.0
3	NH <sub>3</sub>	B <sub>2</sub> D <sub>6</sub> (b)	1.55	1.00	0.83	-81	0.59		0.25
4	ND <sub>3</sub> (b)	B <sub>2</sub> H <sub>6</sub>	0.97	1.01	1.7	-79	0.50		70.0
5	ND <sub>3</sub>	B <sub>2</sub> H <sub>6</sub>	1.57	0.92	0.67	-79	0.59		76.3
6	ND <sub>3</sub>	B <sub>2</sub> H <sub>6</sub>	1.96	10-15	4 4.5 weeks (c)	-78 -78	0.55 1.04 (d)		74.6 75.3 (d)

(a) About 5 ml of solution was used in all the reactions.

(b) The ammonia-d<sub>3</sub> was about 96% deuterated and the diborane-d<sub>6</sub> was about 98% deuterated.

(c) An interval somewhere between 1 and 4-1/2 weeks may be adequate; 4-1/2 weeks was simply a matter of experimental convenience.

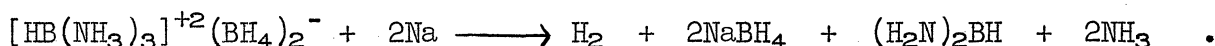
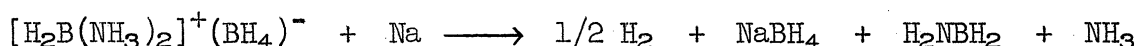
(d) These values represent the total amount of gas given off and the deuterium content of that gas.

The results of this investigation plus the more recent observations of Jolly<sup>9</sup> are summarized in Table III. In agreement with the model which is proposed for the "mistreated diammoniate," the results show that all the hydrogen which is given off in the reaction with sodium, even that which is in excess of one equivalent per mole of diborane, arises from the rupture of nitrogen-hydrogen bonds.

Ammonolysis Reactions.—Schaeffer, Adams, and Koenig<sup>10</sup> report that the non-volatile products from the reaction of the "diammoniate of diborane" with sodium in liquid ammonia are sodium borohydride and polymeric aminoborane,  $(H_2NBH_2)_n$ . They observed that this residue reacts with ammonia at temperature above  $-78^\circ$ ; hydrogen gas is produced. This reaction was noted also in this laboratory. After the reaction with sodium had taken place, all the solvent ammonia was sublimed away at  $-78^\circ$  and the reactor was warmed to room temperature. Only small quantities of hydrogen were split out from the solid residue; however, when gaseous ammonia was introduced above this solid, hydrogen evolution at room temperature was rapid. The maximum amount of hydrogen which was obtained from the reaction with ammonia was 3.10 equivalents per mole of diborane, or a total of 4.10 equivalents including the quantity of gas which was given off in the reaction with sodium.

A tracer study of the reaction between ammonia and the residue from the "diammoniate"-sodium reaction demonstrated, unequivocally, that hydrogen is produced through the interaction of acidic hydrogen which is bound to nitrogen and hydridic hydrogen which is bound to boron. The results are summarized in Table IV. It should be noted in Run 1 that D from N-D bonds reacted with H from B-H bonds to form HD which was identified through the use of a mass spectrometer. Furthermore, it is of interest to point out that the residue from the "mistreated diammoniate"-sodium reaction undergoes ammonolysis also. The hydrogen which was given off in Run 3 was 50% deuterated,<sup>11</sup> presumably HD.

Discussion.—The results of this investigation are in accord with the models which have been proposed for the "diammoniate of diborane" and "mistreated diammoniate of diborane." The reactions with sodium in liquid ammonia take place through the rupture of nitrogen-hydrogen bonds only, and may be represented as<sup>2</sup>



The production of hydrogen in the reaction of sodium with a solution of diborane in ammonia comes from the rupture of nitrogen-hydrogen bonds, the sources of which are believed to be the diammoniate and/or ammonia-borane.<sup>2</sup>

9. W. L. Jolly, Univ. of Calif. Radiation Laboratory, Livermore Site, Livermore, Calif., Contract No. W-7405-eng-48, UCRL-4504.

10. G. W. Schaeffer, M. D. Adams, and F. J. Koenig, J. Am. Chem. Soc., 78, 725 (1956)

11. This sample was analyzed by a thermal conductivity technique which gives the total % D.

TABLE III  
 A TRACER STUDY OF THE REACTION OF "MISTREATED DIAMMONIATE  
 OF DIBORANE"(a) WITH SODIUM IN LIQUID AMMONIA

Source	NH <sub>3</sub> , ml	B <sub>2</sub> D <sub>6</sub> , mmoles	$\frac{\text{Na}}{\text{B}_2\text{D}_6}$	Reaction Time, (cumulative) hr	Reaction Temp., °C	Hydrogen Equivalents Evolved (cumulative) diborane, mmoles	Isotopic Analysis, total % D
This investigation	5	2.06	10-15	0.75	-78	0.65	0.0
				3	-78	0.94	0.0
				21	-78	1.13	0.0
Jolly	15	1.42	4.3	0.33	-64	1.28	0.0

(a) In this investigation diborane was added to ammonia in the usual fashion for preparing the diammoniate but the excess ammonia was removed at -45° and the solid was stored at -45° for five hours.

(a) Jolly prepared mistreated diammoniate through the rapid addition of diborane to ammonia above -78°.

TABLE IV

## AMMONOLYSIS REACTIONS

Run	Residue From:	Ammonia	Isotopic Composition of Gas Produced, total % D	
1	B <sub>2</sub> H <sub>6</sub> · 2ND <sub>3</sub>	ND <sub>3</sub>	49.4	88.2% HD
2	B <sub>2</sub> D <sub>6</sub> · 2ND <sub>3</sub>	ND <sub>3</sub>	97	
3	Mistreated B <sub>2</sub> D <sub>6</sub> · 2NH <sub>3</sub>	NH <sub>3</sub>	47	

The isotope effect which occurred when ammonia-d<sub>3</sub> was the coordinated ligand (e.g., B<sub>2</sub>D<sub>6</sub>·2ND<sub>3</sub>) arose from the fact that since the ammonia-d<sub>3</sub> was not completely deuterated, it contained N-H bonds which were ruptured preferentially over the N-D bonds. Since all the nitrogen deuterium bonds in the system, including solvent ammonia-d<sub>3</sub>, were not ruptured in the reaction with sodium, the evolved gas was enriched in protium. The calculation of an instantaneous separation factor,<sup>12</sup>  $\alpha_0$ , seemed to be attractive, but the complexity of the system and the large errors in  $\alpha_0$  which are introduced by the comparatively small errors in hydrogen analysis have made its value very uncertain. The best estimate places it in the range of 7 to 15. Details concerning its estimation and the complexity of the system are summarized elsewhere.<sup>13</sup>

The presence of the isotope effect implies that the rate-determining step in the process is the rupture of the nitrogen-hydrogen bond. In contrast to the regular tracer studies, the control reaction (Footnote 8) in which sodium reacted with ammonia in the presence of a catalyst showed little evidence of an isotope effect, which implies that the slow step of the reaction is not the rupture of the nitrogen-hydrogen bond.

Schaeffer, Adams, and Koenig<sup>10</sup> report that ammonia attacks polymeric aminoborane in the ammonolysis reaction of the nonvolatile residue from the sodium-diammoniate reaction. They represent the reaction, empirically, as



This representation is in accord with the tracer study. Although they make no mention of it, their results indicate that the ammonia which reacts with the aminoborane is coordinated to metal cation of the metal borohydride which is also formed in the metal-diammoniate reaction. The effect of coordination is to increase the acidic character of hydrogen which is bound to nitrogen in the ammonia, thereby facilitating the attack on hydridic hydrogen by acidic hydrogen.

12.  $\alpha_0 = \frac{\text{H/D hydrogen evolved}}{\text{H/D ammonia-d}_3}$  at zero extent of reaction.

13. S. G. Shore, doctoral dissertation, Univ. of Mich., Ann Arbor, 1956.

## Experimental.—

### a. Materials.

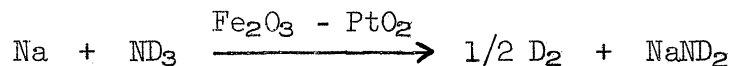
1. Ammonia—Commercial tank  $\text{NH}_3$  was dried and stored over sodium metal in the vacuum system. The  $\text{ND}_3$  which was used in the tracer studies was prepared through the hydrolysis of  $\text{Mg}_3\text{N}_2$  by  $\text{D}_2\text{O}$ .

$\text{Mg}_3\text{N}_2$  was prepared by passing pure, dried nitrogen gas for 12 hours over 20 g of highest purity Dow magnesium metal which was heated to  $650^\circ$  in a stainless steel tubular furnace. The  $\text{Mg}_3\text{N}_2$  was then transferred as rapidly as possible to a 125-ml round-bottom flask which was connected to the vacuum system. About a milliliter of  $\text{D}_2\text{O}^{14}$  (ca. 99% deuterated) was distilled onto the  $\text{Mg}_3\text{N}_2$  which was maintained at  $-78^\circ$ . Vigorous reaction occurred upon warming the flask to room temperature, but the volume of the system was large enough to accommodate all the  $\text{ND}_3$  which was produced without having the final pressure exceed one atmosphere. The  $\text{ND}_3$  was sublimed from the system at  $-78^\circ$ . The process of adding milliliter quantities of  $\text{D}_2\text{O}$  was repeated until all the  $\text{Mg}_3\text{N}_2$  was used up. The  $\text{ND}_3$  was purified by further sublimation at  $-78^\circ$  and by drying it over distilled sodium metal. Its vapor pressure indicates that it was about 97% deuterated.

Observed vapor pressure (corrected): 110.2 mm at  $-63.5^\circ$ ; 354.2 mm at  $-45.2^\circ$ .

Reported<sup>15</sup> vapor pressure (corrected)  
for  $\text{ND}_3$ , 98% deuterated; 109.7 mm at  $-63.5^\circ$ ; 353.8 mm at  $-45.2^\circ$ .

The hydrogen which was obtained from the control reactions



was between 96 and 95% deuterated. The latter value probably represents a lower limit on the purity of the  $\text{ND}_3$ .

2. Diborane— $\text{B}_2\text{H}_6$  was prepared through the well-known<sup>16</sup> procedure of adding  $(\text{C}_2\text{H}_5)_2\text{OBF}_3$ , in excess, to an ether slurry of  $\text{LiAlH}_4$ .  $\text{B}_2\text{D}_6$  was prepared in a different manner.

About 4 g of  $\text{AlCl}_3$  (obtained from a freshly opened bottle) was dissolved in 30 ml of anhydrous ether in a dropping funnel. The dropping funnel was connected to a standard diborane generating apparatus,<sup>17</sup> and the solution was allowed to

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14. Supplied on allocation by permission of the Atomic Energy Commission.

15. I. Kirschenbaum and H. C. Urey, *J. Chem. Phys.*, 10, 706 (1942).

16. I. Shapiro, H. G. Weiss, M. Schmick, S. Skolnik, and G. B. L. Smith, *J. Am. Chem. Soc.*, 74, 901 (1952).

17. P. R. Girardot, doctoral dissertaion, Univ. of Mich., Ann Arbor, 1952.

drip slowly into a continuously stirred slurry containing 50 ml of anhydrous ether, 1 g of 200-mesh LiD, and a trace quantity of LiAlD<sub>4</sub>,<sup>18</sup> which served as a catalyst. The system was flushed continuously with dry nitrogen. After one and one-half hours of continuous stirring, 10 ml of distilled (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>OBF<sub>3</sub> [prepared by passing BF<sub>3</sub> into anhydrous (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O] was added slowly, by means of the dropping funnel, to the ether slurry. The slurry was stirred for an additional three hours. The B<sub>2</sub>D<sub>6</sub> which was produced was purified in the vacuum system by trap-to-trap distillation at -145° until it displayed a constant vapor pressure. The yield was about 80% of theory. Its vapor pressure was in excellent agreement with the only reported value for B<sub>2</sub>D<sub>6</sub>.<sup>19</sup>

Observed vapor pressure (corrected): 238.3 mm at -111.9°.

Reported vapor pressure (corrected)  
for B<sub>2</sub>D<sub>6</sub>, 98% deuterated: 238.3 mm at -111.9°.

Further evidence for the purity of the B<sub>2</sub>D<sub>6</sub> was given through its quantitative hydrolysis.



The gas obtained was 48.5% D.

3. Sodium—All the sodium which was used in the tracer studies was distilled. The still is depicted in Fig. 1. Metallic sodium was scraped free of its oxide coating and was placed in the side arm of the still. The system was evacuated by gently heating the side arm; the sodium melted and ran into the still pot. The constriction in the side arm was sealed off and after placing a tubular furnace around the pot, the sodium was refluxed in vacuo, with continuous pumping on the system, at 300° for several hours. Then the column of the still was heated and the metal was vacuum distilled at about 480°. Sodium collected above the constrictions leading to the small glass bulbs (1.5-2 cm in diameter). With gentle heating and tapping, the metal melted and ran through the constrictions into the bulbs. The bulbs were then sealed off in vacuo.

4. Catalytic mixed oxides for the control reaction between sodium and ammonia-d<sub>3</sub>—Reagent-grade Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O was decomposed, thermally, at 300°. The resultant Fe<sub>2</sub>O<sub>3</sub> was heated at 700° for two days in order to remove traces of water. The mass was then pulverized. About 10% by weight of PtO<sub>2</sub> was thoroughly mixed with the Fe<sub>2</sub>O<sub>3</sub> and the mixture was heated for another day at 700°. About 0.2 g of the hot catalyst was transferred to the bulb crusher—reactor<sup>20</sup>

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18. Both the LiD and LiAlD<sub>4</sub> were obtained from Metal Hydrides, Inc., Beverly, Mass.

19. A. B. Burg, J. Am. Chem. Soc., 74, 1340 (1952).

20. The mode of transfer of catalyst and the bulb crusher—reactor used were identical with those of boric acid, described elsewhere in this report (p. 64).

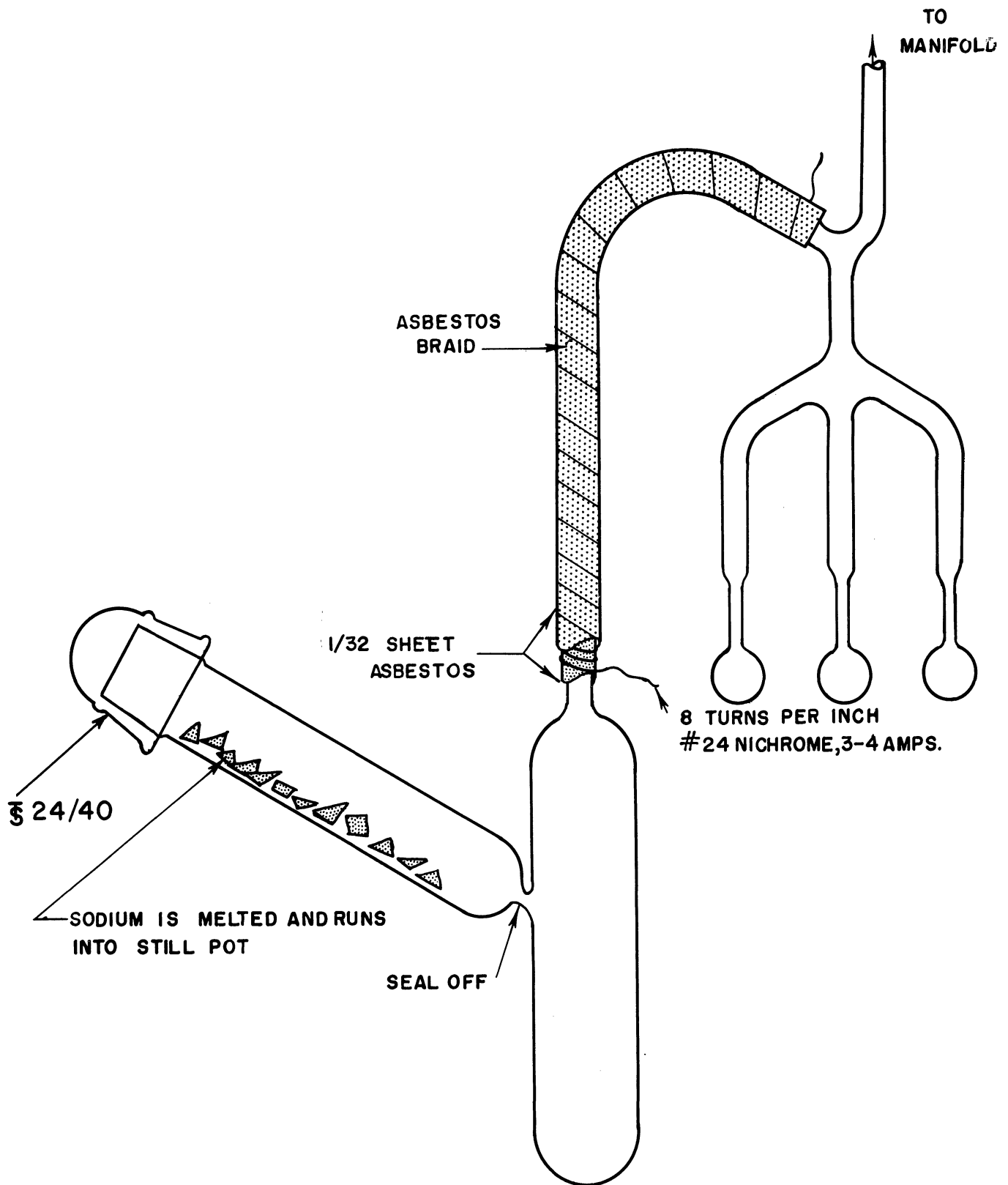


Fig. 1. Sodium still.



on the vacuum system. The catalyst was heated in vacuo at 300°-400° (at least 24 hours) until it was used.

b. Procedures.

A schematic diagram of the system in which the tracer studies were carried out is given in Fig. 2. All the stopcocks and joints which had to be rotated were greased with Apiezon N; all the stationary joints were sealed with Apiezon W. The system was provided with space for two bulb-crusher reactors so that a tracer study and a control experiment could be carried out simultaneously.

The procedures which were used in the tracer studies were essentially the same as those which have been used previously,<sup>21</sup> except that great care was taken to prevent contamination of ammonia-d<sub>3</sub> by H-D interchange which can arise from the presence of impurities containing active protons. In order to minimize errors due to this source, the system was conditioned as described below.

The vacuum system, with the bulb crushers in place, was out-gassed for one day under high vacuum; then a small amount of D<sub>2</sub>O, in the vapor phase, was admitted to the system and allowed to equilibrate, for one day, with the active hydrogen of the residual impurities. Following equilibration the system was again out-gassed under high vacuum for a minimum of three days. This procedure guaranteed that any traces of impurities would be rich in deuterium and thus would not seriously contaminate the highly deuterated ammonia. Once the system was conditioned it was never opened until a given run was completed.

In a typical tracer run a control experiment was set up in one bulb-crusher reactor. This amounted to maintaining a sodium-ammonia-d<sub>3</sub> solution in the presence of the mixed-oxides catalyst at -45°. The regular tracer experiment was set up in the second reactor. After the control had produced a significant quantity of hydrogen, it was quenched by immersing the reactor in liquid nitrogen. The hydrogen was freed of traces of ammonia-d<sub>3</sub> by passing it through the u-trap which (Fig. 2) was packed with glass helices and immersed in liquid nitrogen. Then the gas was passed into one of the sample bulbs and into the previously calibrated thermal conductivity cell for H-D analysis. After the gas was analyzed, the stopcock on the sample bulb was closed and the system was evacuated. The sample bulb was then sealed off at the constriction. The gas in the sample bulb was submitted to mass-spectrometer analysis in order to cross-check the thermal conductivity method.

The same procedure was followed in the regular tracer experiment. At various intervals the reaction was quenched, the hydrogen was freed of traces of ammonia, and the gas was passed into a sample bulb and the thermal conductivity cell for H-D analysis. Since the volume of the system was known, the amount of hydrogen gas which was produced in the reaction could be determined from PVT measurements.

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21. The use of the bulb crusher, the preparation of the "diammoniate" and solutions of diborane in ammonia, and the carrying out of reactions with sodium in liquid ammonia are all described in the experimental section of the preceding paper (p. 54).

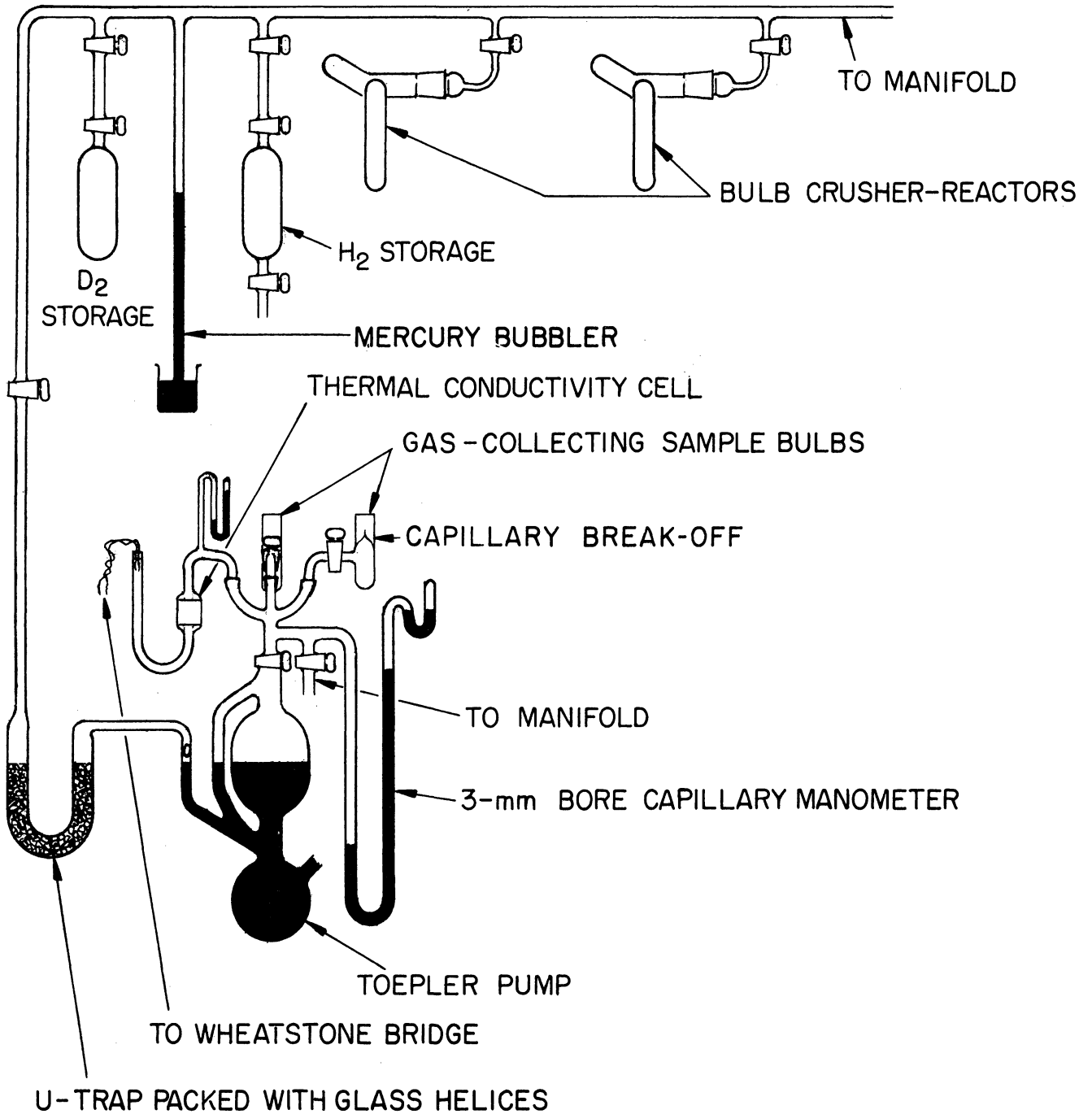


Fig. 2. Schematic diagram of system for tracer studies.

c. Analytical.

The magnitude of the isotope effect observed made it possible to use a relatively simple thermal conductivity technique for analyzing the H-D gas mixtures. The particular procedure which was used was patterned after that of Peri and Daniels,<sup>22</sup> with a few modifications.<sup>23</sup> Several of the analyses were cross-checked by mass spectrometer analyses; the agreement was very good. The precision of individual measurements, for the most part, was within 1% D. Considering the good agreement between analyses which were obtained by both mass analysis and thermal conductivity techniques, and considering the general consistency of the results, it is believed that the accuracy of the thermal conductivity technique was well within 3% D in the range 50-100% D.

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22. J. B. Peri and F. Daniels, J. Am. Chem. Soc., 72, 424 (1950).

23. A detailed description of the thermal conductivity method is given in the doctoral dissertation of S. G. Shore, Univ. of Mich., Ann Arbor, 1956.

G. MOLECULAR-WEIGHT MEASUREMENTS IN LIQUID AMMONIA. THE MOLECULAR WEIGHTS OF THE METHYLAMINE BORANES, THE DIAMMONIATE OF DIBORANE, AND AMMONIA BORON TRIFLUORIDE (R. W. Parry, G. Kodama, and D. R. Schultz)

Abstract

Molecular-weight measurements in liquid ammonia by vapor-pressure depression show that  $H_3NBF_3$ ,  $MeH_2NBH_3$ ,  $Me_2HNBH_3$ , and  $Me_3NBH_3$  are all monomeric in liquid ammonia under conditions comparable to those used for studying the "diammoniate of diborane." The conventional dimeric formula is confirmed for the diammoniate prepared at  $-78.5^\circ C$  but a higher value above 80 is indicated for the diammoniate prepared at  $-45^\circ C$ . The conversion of  $H_3NBF_3$  to  $NH_4BF_4$  in water solution is noted.

The original problem associated with the formulation of the ammonia-diborane addition compound arose from the early observation of Stock and Pohland<sup>1</sup> showing that the product corresponded to the formula  $B_2H_6 \cdot 2NH_3$  in liquid ammonia. Rathjens and Pitzer<sup>2</sup> reported that freezing-point depression measurements confirmed the observations of Stock and Pohland,<sup>1</sup> but their points showed wide scatter and the same disturbing rise in molecular weight with dilution was noted which had been found in the earlier study. Even more disturbing at the present time is the fact that it is now known that the technique which Rathjens and Pitzer used does not produce the so-called classical diammoniate in liquid ammonia.<sup>3</sup>

Although the "diammoniate of diborane" has long been considered to be unique among the boron hydride addition compounds, no molecular-weight measurements on  $H_2MeNBH_3$ ,  $HMe_2NBH_3$ ,  $Me_3NBH_3$ , or  $H_3NBF_3$  have been carried out under conditions comparable to those used in the study of the diammoniate, hence the generality of the "diammoniate" structure under low-temperature conditions remains undetermined.

A study of molecular weights in liquid ammonia was undertaken:

1. to check the validity of Stock's observations as to the molecular weight of an authentic sample of the "diammoniate";
2. to check the molecular weights of other better-known ionic solids in liquid ammonia in order to provide a frame of reference for interpretation; and
3. to check the molecular weights in liquid ammonia of methylamine borane, dimethylamine borane, trimethylamine borane, and ammonia-boron trifluoride.

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1. A. Stock and E. Pohland, Ber., 58, 657 (1925).

2. G. W. Rathjens, Jr., and K. S. Pitzer, J. Am. Chem. Soc., 71, 2783 (1949).

3. S. G. Shore and R. W. Parry, this Report, p. 54.

These compounds had not been measured under conditions comparable to those used in studying the "diammoniate," hence a real question existed as to their nature in relation to the "diammoniate."

### Experimental.

#### a. Reagents.

The "diammoniate of diborane," methylamine borane, dimethylamine borane, and trimethylamine borane were prepared from carefully purified reagents using standard procedures.<sup>4</sup>

Commercial amines (Eastman Kodak Co.) were distilled through a low-temperature fractionating column at 400-mm pressure and dried over sodium metal before use.

Commercial  $\text{NaBH}_4$  (Metal Hydrides) was placed on the sintered glass frit of a vacuum-line extraction apparatus and extracted directly into the molecular-weight apparatus with liquid ammonia.

$\text{NH}_4\text{Br}$ , reagent grade, was dried at  $80^\circ\text{C}$  for three hours then stored over  $\text{Mg}(\text{ClO}_4)_2$  before use.

Ammonia-boron trifluoride was prepared by the interaction of dry  $\text{NH}_3$  and commercial tank  $\text{BF}_3$  which had been passed through a  $\text{B}_2\text{O}_3\text{-H}_2\text{SO}_4$  mixture. A one-liter, three-necked flask cooled in ice water served as the reaction vessel. The solid product was placed on a sintered glass frit and leached into the molecular-weight vessel with liquid ammonia. Ammonia analysis on the product gave 20.01% as compared to 20.05% theoretical for  $\text{H}_3\text{NBF}_3$ . An x-ray powder pattern of the solid checked the pattern reported by Koenig<sup>5</sup> and by Keenan<sup>5</sup> but not the pattern reported by Laubengayer and Condike.<sup>6</sup> It was also found, contrary to earlier reports, that  $\text{H}_3\text{NBF}_3$  was converted almost quantitatively to  $\text{NH}_4\text{BF}_4$  under conditions of this experiment by slow crystallization from water at room temperature. Isolation of crystalline  $\text{NH}_4\text{BF}_4$  from the solution and precipitation of  $\text{AsO}_4\text{BF}_4$  from the water solution indicated the change.

An x-ray powder pattern of the sample taken before and after the molecular-weight measurement in liquid ammonia showed that the sample had not changed on standing in liquid ammonia at  $-40^\circ\text{C}$ . No lines for  $\text{NH}_4\text{BF}_4$  were found in the product.

#### b. Apparatus and Experimental Procedure.

Details of apparatus design were extremely important since very small tem-

4. The authors wish to thank Dr. Thomas C. Bissot who prepared the  $\text{R}_3\text{NBH}_3$ .

5. Rev. F. J. Koenig, S. J., Summary Report XVI, Mathieson Chemical Corp. Project, Subcontract M-3181-14, Dept. of Chem., St. Louis Univ., St. Louis, Mo.

6. A. W. Laubengayer and G. F. Condike, J. Am. Chem. Soc., 70, 2275 (1948).

perature differences throughout the system caused serious vapor-pressure differences. The apparatus is shown in Fig. 1. The system could be effectively tested for temperature differences by putting solvent in both tubes. No pressure differential could be detected on the manometer when the system was operating properly. The stirrer could be removed from one of the dried tubes, then the tube capped and weighed. It could then be attached directly to a vacuum-line extractor, and moisture or air-sensitive solutes could be extracted directly into the tube with liquid ammonia. After ammonia was removed, the tube was filled with dry nitrogen, capped, and reweighed. The dry stirrer was then inserted and the tube was sealed to the molecular-weight apparatus, using Apiezon W wax on the 14/35  $\text{F}$  joint. Ammonia was added from a flask containing a solution of lithium nitrate in ammonia. By weighing the lithium flask before and after addition of ammonia, the weight of solvent added to the system could be accurately determined. Pressure differences were read using a precision cathetometer. Stopcocks were lubricated with silicon grease.

c. Calibration of Apparatus.

To check the reliability of the procedure on a well-behaved solute, the molecular weight of urea was determined. Values obtained by three different observers using various modifications of the apparatus are tabulated below in Table I.

TABLE I  
MOLECULAR WEIGHTS OF UREA

Observer	Molal Conc. of Soln.	Observed Mol Wt
A	0.267	$60.8 \pm 0.3$
B	0.202	$60.0 \pm 0.3$
	0.382	$60.2 \pm 0.3$
C	0.20	$60 \pm 1$
	0.30	$60 \pm 1$
	0.60	$60 \pm 1$
	1.2	$62 \pm 1$
	1.6	$64 \pm 1$

Results and Discussion.

a. The Molecular Weights of Well-Known Ionic Solids in Liquid Ammonia.

Molecular-weight determinations on  $\text{NH}_4\text{Br}$ ,  $\text{NH}_4\text{BF}_4$ , and  $\text{NaBH}_4$  were made. Results are presented in Table II. In the concentration range studied  $\text{NH}_4\text{Br}$

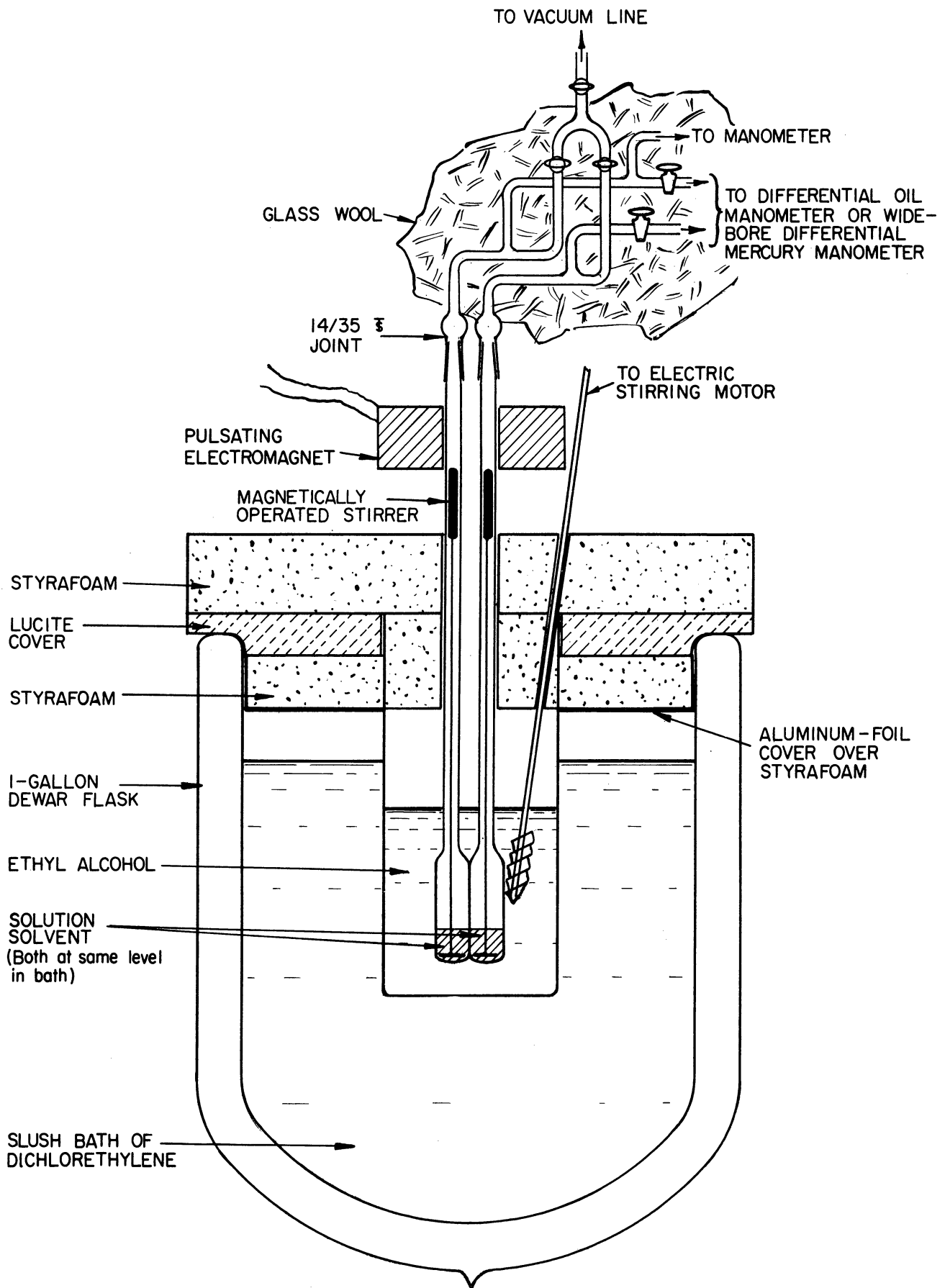


Fig. 1. Molecular-weight apparatus.

TABLE II

MOLECULAR WEIGHTS OF  $\text{NH}_4\text{Br}$ ,  $\text{NH}_4\text{BF}_4$ , AND  $\text{NaBH}_4$  IN LIQUID AMMONIA

Salt	Molal Conc. of Soln.	Observed Mol Wt
$\text{NaBH}_4$	1.90	28.6
Theor. Mol Wt	1.04	33.9
= 37.8	0.71	35.2
	0.56	35.4
	0.45	33.0
	0.41	34.7
$\text{NH}_4\text{Br}$	1.52	97.5
Theor. Mol Wt	0.75	98.0
= 97.9	0.50	98.0
	0.30	98.5
$\text{NH}_4\text{BF}_4$	1.58	92.0
Theor. Mol Wt	0.80	96.0
= 104.8	0.52	93.0
	0.30	85.0
	0.20	75.0

} dissociation

and  $\text{NaBH}_4$  exist in ammonia solution as nondissociated ion pairs. The data indicate that  $\text{NH}_4\text{BF}_4$  was undergoing some dissociation in the more dilute solutions. Data on potassium iodide were somewhat erratic and showed an increase in molecular weight with dilution. The results of a number of measurements could be extrapolated to give a value of about 166 at zero concentration, but the precision of measurements in the potassium iodide study was in general low. Further study is needed for this solute.

b. The Molecular Weight of Ammonia Boron Trifluoride in Liquid Ammonia.

The only previous molecular-weight measurements on  $\text{NH}_3\text{BF}_3$  were made in water solution.<sup>6</sup> Since at least under some conditions  $\text{H}_3\text{NBF}_3$  may undergo conversion to  $\text{NH}_4\text{BF}_4$  in water solution, additional molecular-weight data seemed desirable. The possible existence of a species in liquid ammonia,  $[\text{F}_2\text{B}(\text{NH}_3)_2](\text{BF}_4)$ , analogous to  $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ , seemed to be worthy of investigation at low temperatures. Data for liquid ammonia solutions are summarized in Fig. 2. It was found that solutions with a molal concentration above 0.65 reached equilibrium in less than half an hour and held constant within  $\pm 2$  molecular-weight units for at least four hours; longer observations were not made. A linear extrapolation of these points to zero concentration gives a molecular weight of 93 as opposed to a theoretical value of 85 expected for the monomer. These data indicate that  $\text{H}_3\text{NBF}_3$  is indeed monomeric in liquid ammonia solution and a structure comparable to



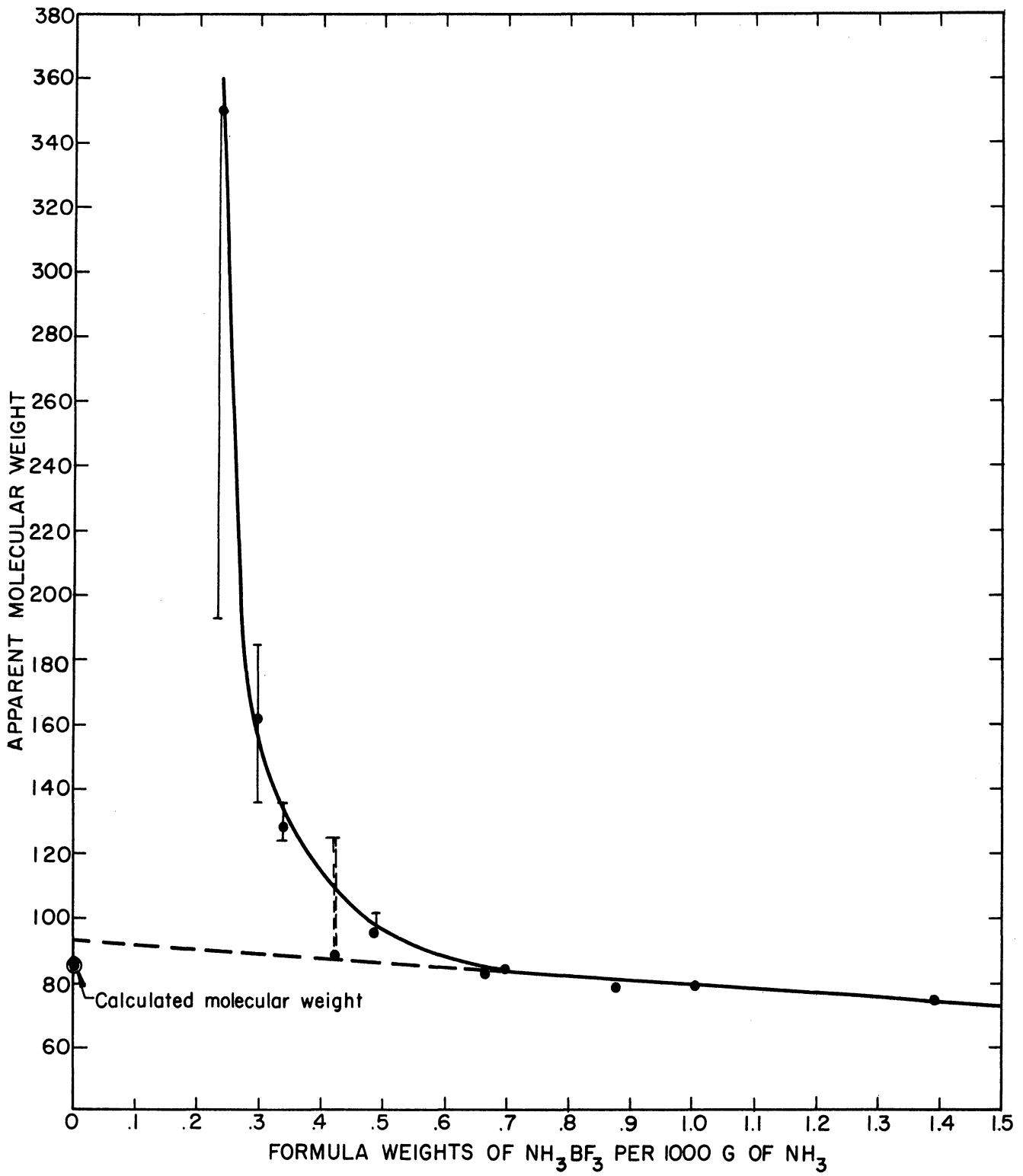


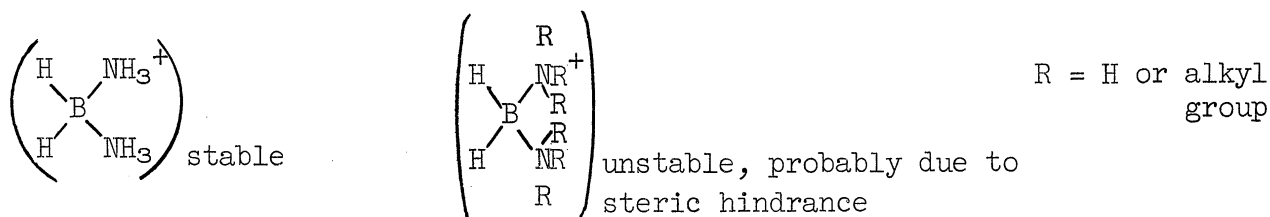
Fig. 2. Determination of the molecular weight of  $\text{NH}_3\text{BF}_3$  in liquid ammonia.

$B_2H_6 \cdot 2NH_3$  is eliminated. An unexplained characteristic of the measurement is clearly revealed, however, by the available data. For solutions in the concentration range 0.30 to 0.56, values were well above the extrapolated curve; the system was slow (two to nine hours) in reaching equilibrium and an uncertainty of about  $\pm$  five molecular-weight units was observed. The uncertainty and time required to reach a steady state both increased with dilution. In solutions more dilute than 0.3 molal, results were completely erratic; in the most dilute solutions no equilibrium value was apparent after more than nine hours. The results were similar to those observed with KI in dilute solution. Although the exact cause of this behavior is unknown, it is apparently associated with the solute and not with the apparatus proper. Table I shows that a well-behaved solute such as urea gives consistent and reproducible values in the concentration range .2 to .4 molal; hence, systematic errors due to pressure measurement, etc., are not the primary cause of such behavior.

c. The Molecular Weights of the Methylamine Boranes in Liquid Ammonia.

The variation of apparent molecular weight with concentration for the three methylamine boranes is shown in Fig. 3. Again, if uncertainties of dilute solutions are neglected, an extrapolation of the data to zero concentration gives 51 for  $CH_3NH_2BH_3$  as opposed to a value of 45 expected for the monomer, a value of about 61 for  $(CH_3)_2NHBH_3$  as opposed to a value of 59 expected for the monomer, and a value of 79 for  $(CH_3)_3NBH_3$  as opposed to a value of 73 expected for the monomer. The data offer convincing proof that the methylamine adducts of diborane, prepared and measured under conditions comparable to those used in studying the "diammoniate of diborane," are not dimerized but are instead normal addition compounds of the borane group.<sup>7</sup>

Such observations have a precedent in the study of the metal coordination compounds. Cobalt (II) chloride will pick up ammonia to give the very stable compounds  $CoCl_2 \cdot 2NH_3$ ,  $CoCl_2 \cdot 4NH_3$ , and  $CoCl_2 \cdot 6NH_3$ , yet Yoke and Parry<sup>8</sup> found that only one trimethylamine or triethylamine will coordinate with  $CoCl_2$ . It would appear that the extra energy needed to expand the lattice of  $CoCl_2$  in order to get more than one molecule of tertiary amine coordinated to the cobalt (II) is greater than the energy released in the coordination to the cation of the second molecule of the amine. In a similar manner it appears that the steric strains associated with the coordination of two methylamine molecules to the small boron (III) cation are greater than or comparable to the energy released in the coordination process for the second amine molecule. At the present time the data seem to be explained most easily by the concept of F-strain:



7. These data do not preclude the possibility of forming a dimeric species  $(R_3NBH_3)_2$  by other techniques.

8. J. T. Yoke III and R. W. Parry, to be published.

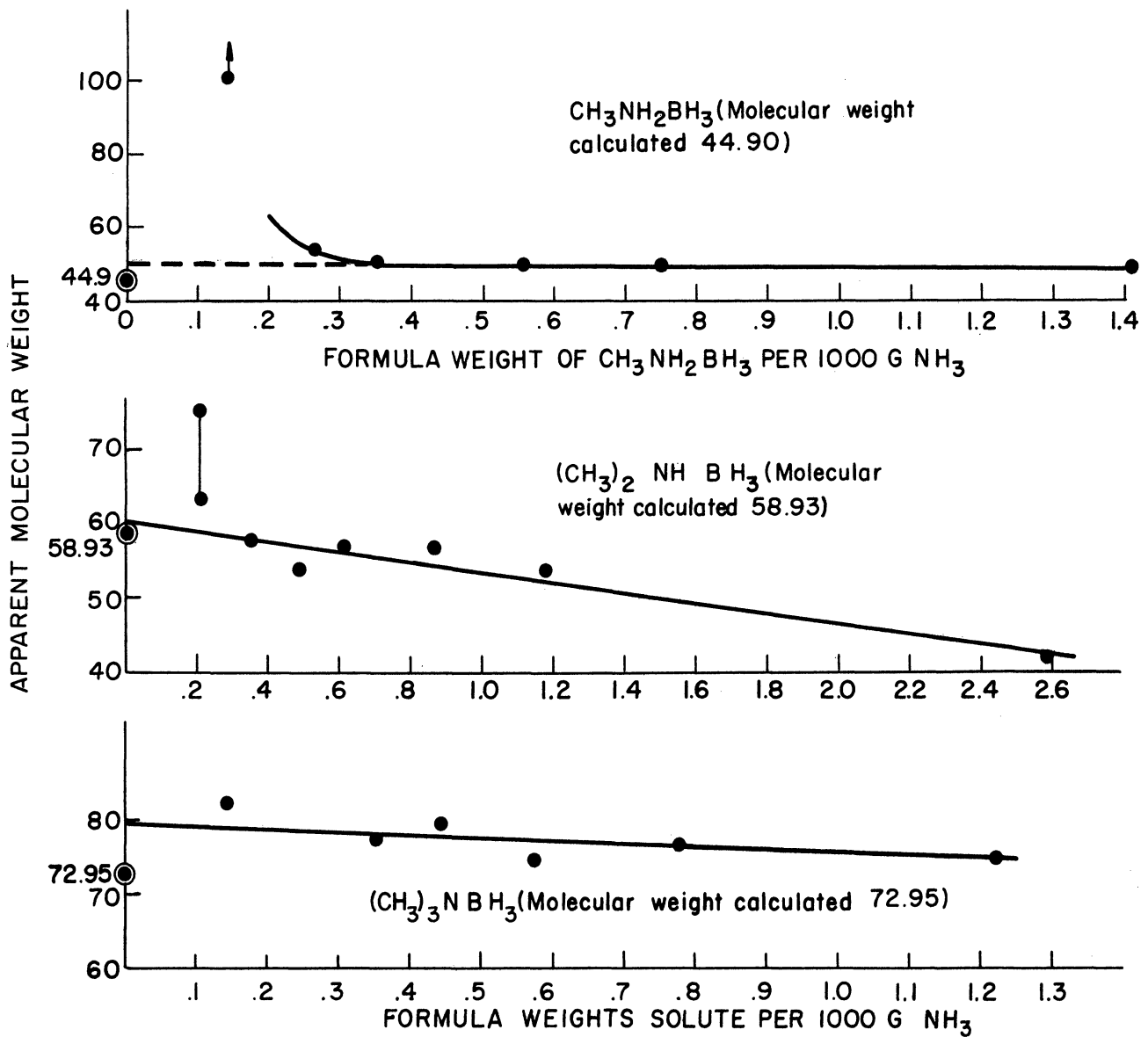
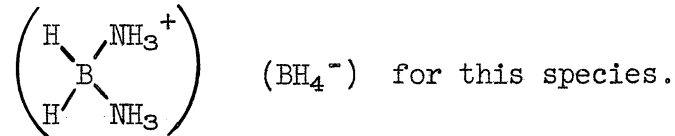


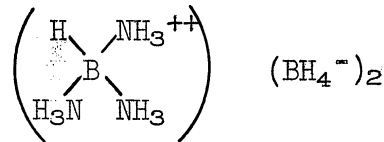
Fig. 3. Molecular weights of the methylamine boranes in liquid ammonia.

d. The Molecular Weights of the "Diammoniate of Diborane" in Liquid Ammonia.

The extreme sensitivity to experimental conditions of the ammonia-diborane reaction has already been noted.<sup>3</sup> In Fig. 4 data are presented for molecular weights of two samples of the diammoniate. In one case ammonia was removed at  $-78.5^{\circ}\text{C}$  to give the so-called classical diammoniate of Schlesinger and Burg.<sup>9</sup> Although the values show uncertainty characteristic of this solute, they check fairly well with the earlier measurements of Stock and Pohland<sup>1</sup> and justify the simple dimeric formulation and are consistent with the structure



When the ammonia is removed at the higher temperature of  $-45^{\circ}\text{C}$ , the sodium reaction indicates that a new species is formed. The formula



has been tentatively assigned to this compound to account for the stoichiometry of hydrogen liberation.<sup>3</sup> Molecular-weight measurements on a sample from which ammonia was removed at  $-45^{\circ}$  showed a higher value than the  $-78.5^{\circ}$  product. An extrapolation of data for the  $-45^{\circ}$  case shows a molecular weight of about 82 as compared to a value of 92 expected for the formula written above. Within the limits of accuracy of the evidence, the molecular-weight data support the postulates made to explain the data on the stoichiometry of the sodium reaction. It is recognized that somewhat more precise measurements would be desirable. An effort is currently being made to obtain such additional data on the  $\text{B}_2\text{H}_6\text{-NH}_3$  system.

9. H. I. Schlesinger and A. B. Burg, J. Am. Chem. Soc., 60, 290 (1938).

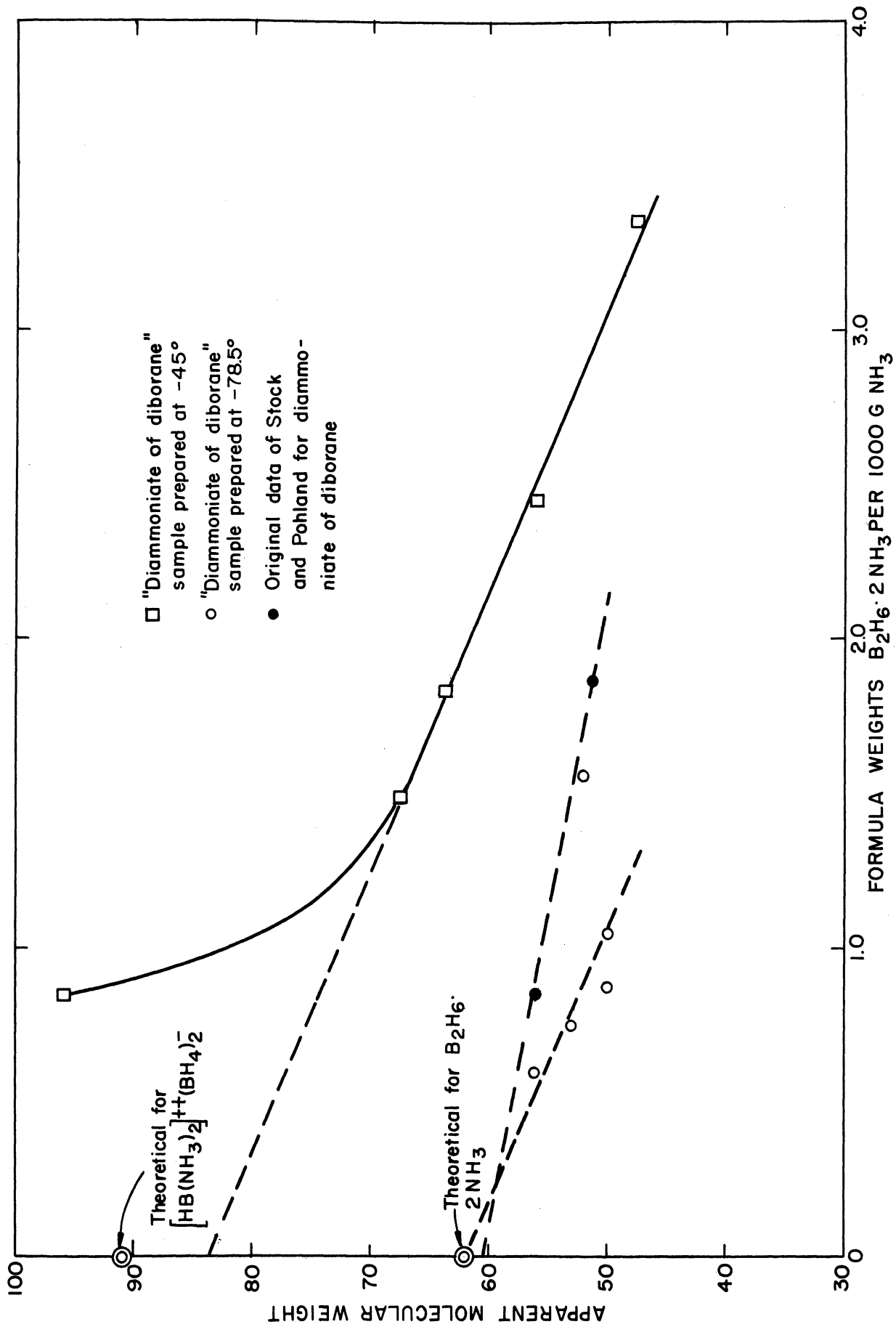


Fig. 4. Molecular-weight measurements on the "diammoniate of diborane."

H. THE RAMAN SPECTRUM OF THE BOROHYDRIDE ION AND EVIDENCE FOR THE CONSTITUTION OF THE DIAMMONIATE OF DIBORANE (R. C. Taylor, D. R. Shultz, and A. R. Emery)

Abstract

The spectroscopic work presented on the borohydride ion appears adequate to establish satisfactorily the fundamental frequencies of this ion in liquid ammonia solution although precise values of two of the fundamentals have not been determined. Additional work using isotopically pure boron and perhaps  $\text{ND}_3$  as a solvent appears desirable in this connection.

The results on the diammoniate of diborane give strong evidence for the presence of a borohydride ion in solutions of this substance in liquid ammonia and agree with the formulation which has been proposed in this laboratory for the cation, although they are not conclusive. The evidence from the B-H stretching region however is not in agreement with what one would expect from the presently accepted formulation of Schlesinger and Burg.

Data on the decomposition product of ammonium borohydride and the product of the reaction of the diammoniate with ammonium bromide confirm the conclusions based on the chemical work.

The usefulness and advantages of liquid ammonia as a solvent and reaction medium have been amply demonstrated by many workers ever since the early work of Franklin and Kraus before the turn of the century. Experimental difficulties encountered in obtaining vibrational spectra of substances dissolved in this solvent, however, have handicapped workers in their attempts to study the nature of the solute species present. Solvent absorption presents an almost insurmountable barrier to the use of liquid  $\text{NH}_3$  in the case of infrared, but the situation is quite favorable for Raman spectroscopy, the chief difficulties being experimental in nature and involving the development of satisfactory methods for preparing, clarifying, and transferring solutions below the boiling point of the solvent ( $-33^\circ\text{C}$ ). Very few papers have appeared on the Raman spectra of liquid ammonia solutions, and those which have appeared have dealt exclusively with substances forming solutions having less than an atmosphere vapor pressure at room temperature.

The present paper deals with the vibrational spectra of the borohydride and borodeuteride ions and, in addition, presents the results of a spectroscopic study of the diammoniate of diborane, the decomposition product of ammonium borohydride, and the product of the reaction between the diammoniate of diborane and ammonium bromide. All spectra were obtained in liquid ammonia solution at temperatures below  $-33^\circ$ . The Raman spectra of none of these substances have been published previously, although the infrared spectrum of the borohydride ion in the solid state has appeared. The nature of the diammoniate of diborane has long been the subject of discussion and the present results supply, as far as it is known, the first piece of purely physical evidence as to its structure.

## Experimental.---

### a. Materials.

Sodium and lithium borohydrides were obtained from Metal Hydrides, Inc., and purified by removing all ammonia insoluble material before use. As a check on the purity, all borohydrides were analyzed after purification. Potassium borohydride was prepared by the method published recently<sup>1</sup> and purified as above, while the ammonium borohydride was prepared in solution as described elsewhere (this Report, p. 4). Lithium borodeuteride was prepared by the reaction of LiD and B<sub>2</sub>D<sub>6</sub>, while the potassium salt was obtained by the reaction of KB(OCH<sub>3</sub>)<sub>4</sub> and B<sub>2</sub>D<sub>6</sub>. Both salts were purified and analyzed before use. The method of preparation of the diammoniate of diborane and the other compounds studied has been described elsewhere.<sup>2</sup> The ammonia used was the standard Matheson product, which was dried before use by storing over metallic sodium in a small steel cylinder.

### b. Preparation of Samples.

The volumes of the samples examined varied from about 3 to 12 ml and the concentrations from about 1 to 5 molar, according to the amount of substance available. No significant effects of concentration on band shapes or positions were noted. The solution to be examined usually was prepared by condensing ammonia on the dry solid in a small graduated tube and having a medium-porosity glass frit in the bottom. Ammonia gas, admitted up through the frit, served both to keep the solution in the bulb and to stir it; if solution took place slowly dry nitrogen could be substituted for the ammonia to prevent excessive dilution. When solution was complete and the volume adjusted to the desired value, the sample was filtered through the frit by nitrogen pressure on the upper surface and transferred to a second bulb having a 30-mm ultrafine, bacteriological-type, sintered glass disc in the bottom. Any fine suspended particles remaining were removed here as the solution dripped through by gravity. The sample finally was transferred to the Raman tube by nitrogen pressure. Those samples suspected of being contaminated by traces of stopcock grease, which fluoresced badly, were allowed to flow through about a two-cm column of Norite prior to the ultrafine filter. The Raman tubes were approximately 15 cm long with a diameter appropriate to the volume of solution. The system was completely closed to the air during the preparation of the sample and was opened only for a second at the end when the Raman tube was removed and capped. The design was such that the filtering apparatus could be completely immersed in a 100 x 400-mm clear Dewar flask filled with isopropyl alcohol at -35° or below during all operations. A diagram of the apparatus is seen in Fig. 1. Transfer of the Raman tube from the filling system to the light source could be accomplished sufficiently rapidly so that negligible warming of the sample occurred. Suitable precautions were taken to eliminate the frosting of the sample tube during transfer.

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1. M. D. Banus, R. W. Bragdon, and A. A. Hinckley, J. Am. Chem. Soc., 76, 3848 (1954).

2. R. W. Parry and S. G. Shore, this Report, p. 54.

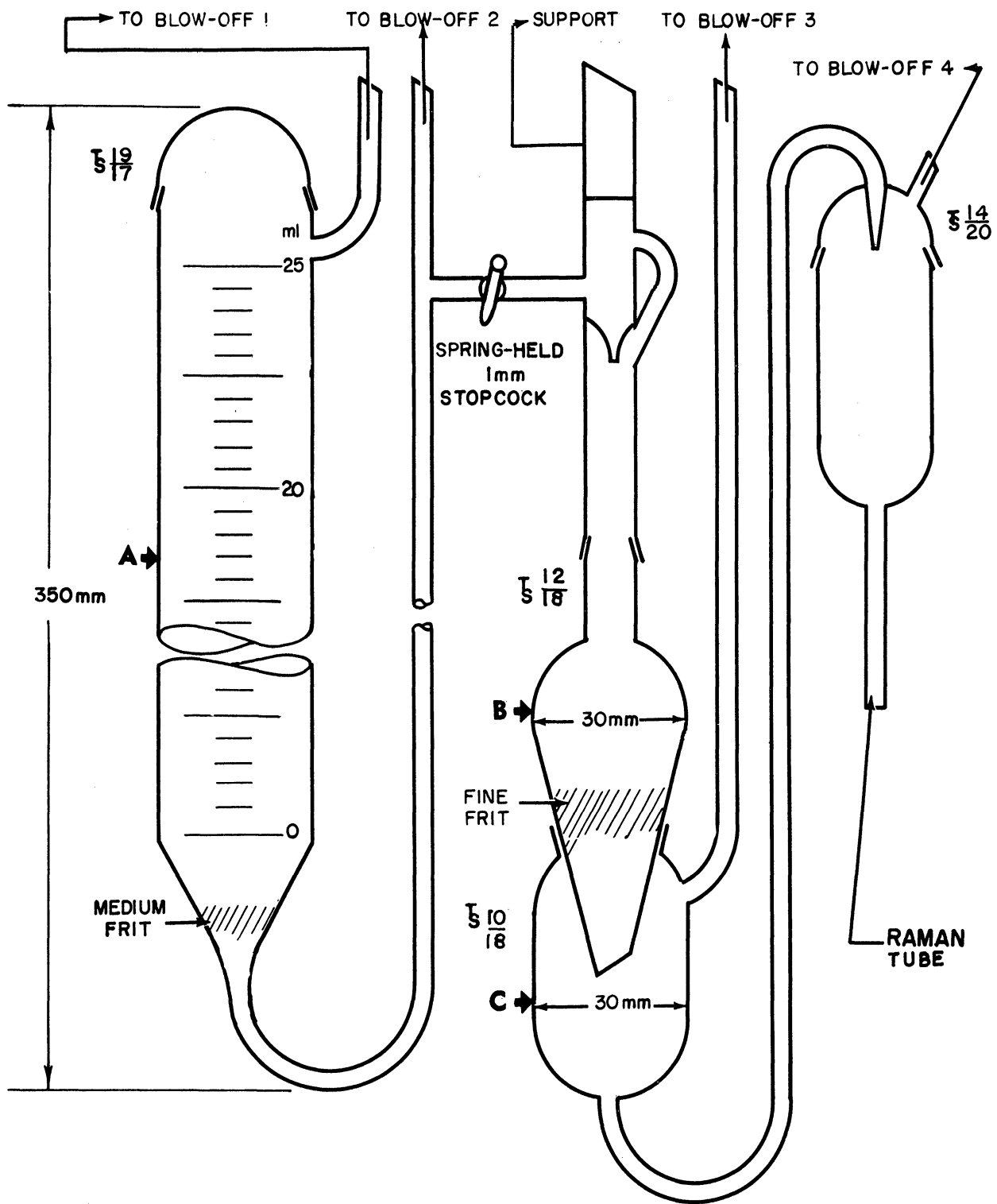


Fig. 1. Apparatus for purification and loading of samples in a Raman tube.



### c. Spectroscopic Equipment.

The Raman spectra were recorded photographically, using the spectrograph and light source described previously.<sup>3</sup> In general, exposure times ranged from 15 minutes to 5 hours and several exposures were made on more than one sample of each substance. Measurements were made directly on the plates with a Mann comparator and also on enlarged tracings made with a Leeds and Northrup microphotometer. The numerical values reported represent the average of all measurements. Many of the lines were weak and rather broad and, consequently, their maxima could not be measured as precisely as desired because of the general noise level of the tracings. Figures are given for the estimated probable errors with the data.

### Results and Discussion.

#### a. The Borohydride Ion.

The Raman frequencies observed for lithium, sodium, potassium, and ammonium borohydrides dissolved in liquid ammonia are listed in Table I, as are also the frequencies of lithium and potassium borodeuterides in the same solvent. There appears to be a small but real shift in the maxima of the bands in the different salts, which may be related to the polarizing ability of the cation. The solvent also affects the position of the bands since in two experiments on aqueous solutions of  $\text{KBH}_4$ , the B-H band maximum was measured at about  $2290 \text{ cm}^{-1}$  as compared to  $2269 \text{ cm}^{-1}$  in ammonia, and the shape of the band was altered. No other observations in aqueous media were tried due to the instability of the solutions. Since the hydrogens in  $\text{BH}_4^-$  are hydridic in nature, isotopic exchange with the hydrogens of ammonia does not occur at any detectable rate and it was possible to obtain the spectrum of the borodeuteride ion also in  $\text{NH}_3$ . In the following discussion, the data for the potassium salt are used; the shifts of frequencies with cation are sufficiently small so that no ambiguity results.

Assignments are based on a tetrahedral ion belonging to the point group  $T_d$ . This model predicts four fundamental frequencies, one totally symmetric stretching mode ( $A_1$ ), one doubly degenerate mode (E), and two triply degenerate modes, one stretching and one bending ( $F_2$ ). All fundamentals are allowed in the Raman effect, but only the  $F_2$  fundamentals are allowed in the infrared.

On the basis of its intensity and polarization properties, the  $A_1$  mode ( $\nu_1$ ) can immediately be assigned to the most intense band in the Raman spectrum, which, for the potassium salt, occurs at  $2269 \text{ cm}^{-1}$  in the hydrogen case and  $1568 \text{ cm}^{-1}$  in the deuterium. The frequency ratio observed is 1.45 instead of the harmonic value of 1.41, which may indicate either that the anharmonicity effect is not the normal one or that one of the fundamentals is involved in a Fermi resonance. Although as can be seen from Fig. 2, the B-H stretching region contains one or two bands which might be involved in this way, the relative intensities show that any such interaction must be weak and could not account for the size of the shift necessary

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3. G. L. Vidale and R. C. Taylor, J. Am. Chem. Soc., 78, 294 (1956).

TABLE I

RAMAN FREQUENCIES (IN  $\text{CM}^{-1}$ ) AND ASSIGNMENTS FOR LITHIUM, SODIUM, POTASSIUM, AND AMMONIUM BOROHYDRIDES AND FOR LITHIUM AND POTASSIUM BORODEUTERIDES DISSOLVED IN LIQUID AMMONIA

$\text{LiBH}_4$	$\text{NaBH}_4$	$\text{KBH}_4$	$\text{NH}_4\text{BH}_4$	$\text{LiBD}_4$	$\text{KBD}_4$	Assignment 1	Assignment 2
--	--	--	--	$824 \pm 5$	$827 \pm 5$	$\nu_4$	$\nu_4$
$1202 \pm 4$	$1205 \pm 4$	$1214 \pm 4$	$1205 \pm 4$	--	$862 \pm 10$	$\nu_2$	$\nu_2$
$2141 \pm 5$	$2151 \pm 5$	$2155 \pm 5$	$2146 \pm 5$	--	--	$2\nu_4$	$2\nu_4$
--	$2239 \pm 10$	--	--	$1662 \pm 3$	$1665 \pm 3$	$\nu_3$	$(\nu_2 + \nu_4)$ (for $\text{BH}_4^-$ only)
$2260 \pm 2$	$2264 \pm 2$	$2269 \pm 2^*$	$2264 \pm 2$	$1566 \pm 1$	$1568 \pm 1$	$\nu_1$	$\nu_1$
$2394 \pm 5$	$2402 \pm 5$	$2404 \pm 5$	$2400 \pm 5$	--	--	$2\nu_2$	$\nu_3$

\* Polarized.

to produce agreement with the harmonic value.

In order to assign the band at  $1214\text{ cm}^{-1}$  as the E mode,  $\nu_2$ , it is necessary to review the infrared data, since there are two H-B-H bending frequencies to be expected in this general region. Price<sup>4</sup> has reported a band at  $1080\text{ cm}^{-1}$  in a mull of  $\text{NaBH}_4$ , while Hornig<sup>5</sup> reports the same band at  $1121\text{ cm}^{-1}$  for a solid film of the same salt at liquid nitrogen temperatures. In this laboratory, a value of  $1122\text{ cm}^{-1}$  was obtained for  $\text{KBH}_4$  by the KBr pellet technique. These data on the solid indicate that the infrared active band  $\nu_4$  lies somewhere in the neighborhood of  $1100\text{ cm}^{-1}$  and that the  $1205\text{ cm}^{-1}$  band consequently is most likely  $\nu_2$ . Unfortunately, when liquid ammonia is used as a solvent, the region around  $1100\text{ cm}^{-1}$  is completely obscured by the very strong  $\nu_2$  band of the  $\text{NH}_3$  molecule so that the position of  $\nu_4$  in solution could not be established directly in the present work. However, the band appearing at about  $2155\text{ cm}^{-1}$  can hardly be explained except as the overtone of  $\nu_4$  and its position indicates that the fundamental is probably not far from  $1080\text{ cm}^{-1}$ . In the spectrum of the deuterated ion, two bands were observed in the low-frequency region, one at  $862\text{ cm}^{-1}$  and one at  $827\text{ cm}^{-1}$ . The former was quite weak but agrees with the shift expected for  $\nu_2$  and is so assigned. The latter was somewhat more intense and is assigned to  $\nu_4$ .

The assignment of the remaining  $F_2$  fundamental,  $\nu_3$ , is perhaps the least certain of the four because of the unexpected complexity of the B-H stretching region. Since this fundamental is infrared active, one might expect some help from infrared results. Price,<sup>4</sup> in his spectrum of solid  $\text{NaBH}_4$ , shows at least three poorly resolved bands in this region with a main maximum about  $2270\text{ cm}^{-1}$ . The spectrum of  $\text{KBH}_4$  in a KBr pellet shows a moderately intense band at about  $2278\text{ cm}^{-1}$ , a less intense but well-resolved band at  $2210\text{ cm}^{-1}$ , and a shoulder at about  $2340\text{ cm}^{-1}$ . These bands can be assigned with a high degree of confidence to  $\nu_3$ ,  $2\nu_4$ , and  $\nu_2 + \nu_4$ , respectively. Hornig<sup>5</sup> gives a value of  $2298\text{ cm}^{-1}$  with no mention of other bands. Although the shift between solid and solution is unknown, it appears that  $\nu_3$  probably lies in the neighborhood of  $\nu_1$ . In the Raman spectrum of the B-H stretching region (Fig. 1), at least four bands are present, including the  $A_1$  fundamental. The band at  $2155\text{ cm}^{-1}$  has already been assigned, while the band at  $2404\text{ cm}^{-1}$  appears to be  $2\nu_2$ . The remaining band, which is present as a shoulder on the  $2269\text{ cm}^{-1}$  peak, is most easily explained as the  $\nu_3$  fundamental. In a spectrum of  $\text{NaBH}_4$  taken with polarized light, the intensity of  $\nu_1$  was greatly reduced and the band in question, as near as could be determined, was depolarized with its maximum at about  $2240\text{ cm}^{-1}$ . Perhaps the chief objection to this assignment is the fact that in most other tetrahedral molecules,  $\nu_3$  occurs at a higher frequency than  $\nu_1$ . However, the alternative assignment (Assignment 2, Table I) implies a rather large shift between the solvent and solution for  $\nu_3$  and requires a rather large anharmonicity correction in the explanation of the  $2240\text{ cm}^{-1}$  band as  $\nu_2 + \nu_4$ .

4. W. C. Price, J. Chem. Phys., 17, 1044 (1949).

5. D. F. Hornig, Disc. Far. Soc., No. 9, p. 120 (1950).

In the borodeuteride spectrum,  $\nu_1$  is well isolated and  $\nu_3$  is assigned to the maximum of the strong band at  $1665 \text{ cm}^{-1}$ . The Teller-Redlich product-rule ratio for the  $F_2$  class calculated from the masses of the atoms involved is 1.77. Using the figures from Assignment 1, Table I, the approximate frequency product ratio is 1.76, while the ratio from Assignment 2 is 1.89. This provides strong support as to the correctness of the first assignment.

b. The Diammoniate of Diborane.

Previous work from this laboratory has supported the structure  $[\text{H}_2\text{B}(\text{NH}_3)_2^+](\text{BH}_4^-)$  for the classical "diammoniate of diborane"<sup>6</sup> rather than the currently accepted ammonium ion formulation of Schlesinger and Burg,  $(\text{NH}_4^+)(\text{H}_3\text{BNH}_2\text{BH}_3^-)$ .<sup>7</sup> Since most of the evidence presented is chemical in nature, a Raman study was carried out to supply additional information. The frequencies observed exclusive of solvent bands are tabulated in Table II and a tracing of the B-H stretching region is shown in Fig. 2.

TABLE II  
RAMAN FREQUENCIES (IN  $\text{CM}^{-1}$ ) OF THE DIAMMONIATE  
OF DIBORANE DISSOLVED IN LIQUID AMMONIA

Diammoniate of Diborane	$\text{NH}_4\text{BH}_4$ Decomposition Product	Product from $\text{NH}_4\text{Br}$ -Diammoniate Reaction
$772 \pm 3$	$733 \pm 3$	$773 \pm 3$
$839 \pm 5$	--	$852 \pm 10$
$882 \pm 5$	$884 \pm 8$ }	
$1209 \pm 4$	$1214 \pm 4$	$1208 \pm 4$
2140		
$2265 \pm 2 \text{ s}$	$2263 \pm 2 \text{ s}$	
$2321 \pm 3$	$2322 \pm 3$	$2322 \pm 3$
$2403 \pm 3$	$2405 \pm 3$	$2407 \pm 3$
$2437 \pm 3$	$2441 \pm 3$	$2437 \pm 3$

Comparison of the data in Table II with those in Table I shows that the frequencies of four characteristic bands of the borohydride ion agree with frequencies in the diammoniate spectrum within the experimental error in determining maxima and the change in position observed with the cation. A more striking comparison is made if one mentally subtracts the bands at  $2321$  and  $2437 \text{ cm}^{-1}$  from the diammoniate spectrum in Fig. 2 and compares the remainder with the borohydride

6. All earlier papers in this report.

7. H. I. Schlesinger and A. B. Burg, J. Am. Chem. Soc., 60, 290 (1938).

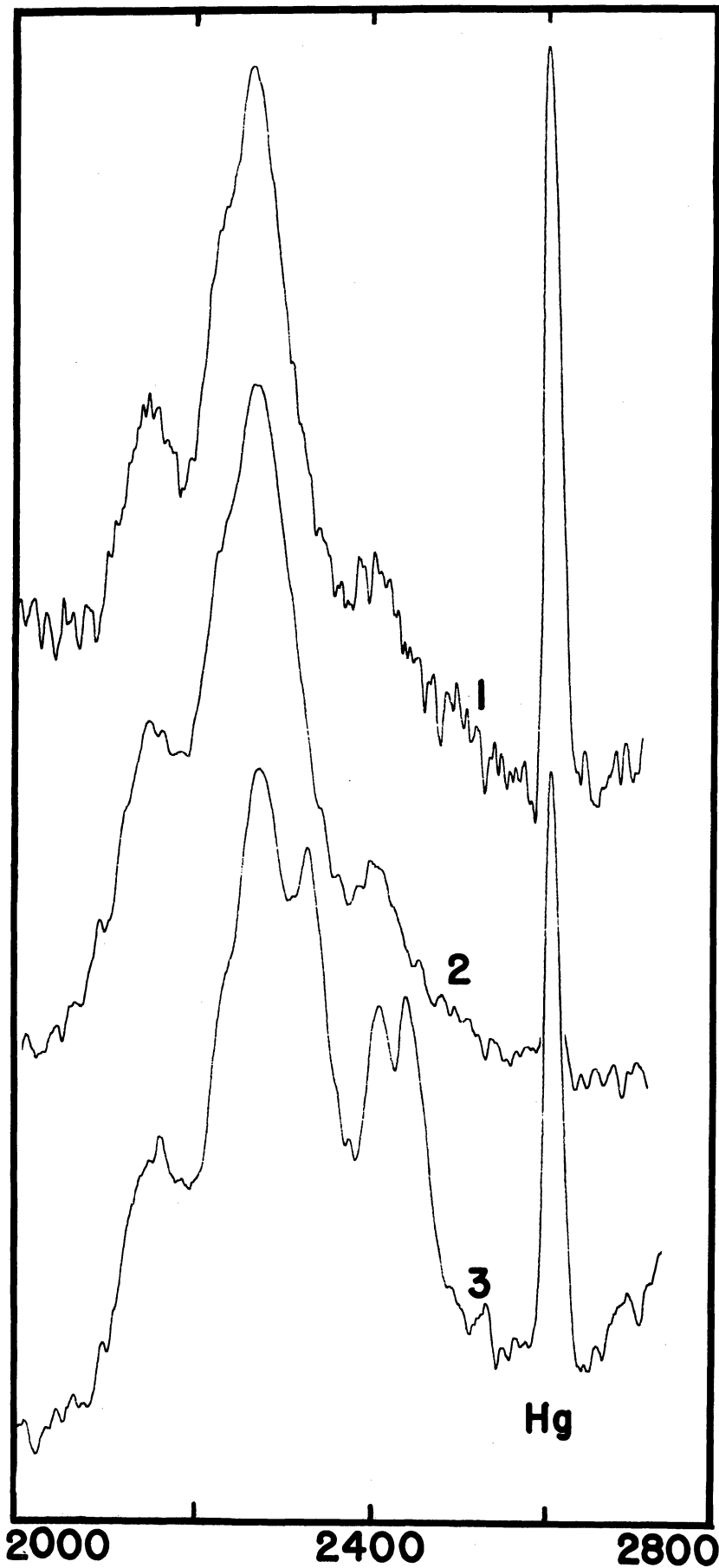


Fig. 2. The B-H stretching region in the Raman spectra of some borohydrides dissolved in liquid ammonia. Tracing 1,  $\text{LiBH}_4$ ; 2,  $\text{NaBH}_4$ ; 3, the diammoniate of diborane. (Frequency in  $\text{cm}^{-1}$ )

spectrum. The very close similarity furnishes strong evidence for the presence of a borohydride ion in the liquid ammonia solution of the diammoniate of diborane.

Conclusions which can be drawn solely from the spectroscopic evidence about the nature of the accompanying cation are more limited. The structure given above for this cation,  $[\text{H}_2\text{B}(\text{NH}_3)_2]^+$ , is isoelectronic with propane. In agreement with this formulation, only two B-H stretching frequencies, not found in the borohydride ion spectrum, are observed. Two frequencies are most consistent with the presence of a  $\text{BH}_2$  group since a  $\text{BH}_3$  group would contribute three unless it happened to be present in an ion having  $\text{C}_{3v}$  symmetry. The latter seems unlikely from chemical generalizations. No information could be obtained about the N-H modes due to the interference of solvent bands.

In the lower frequency region, three bands were observed at 772, 839, and  $882\text{ cm}^{-1}$ . The first was relatively sharp and agrees with what one might expect for a symmetrical stretching mode of the N-B-N skeleton. The latter two were weaker and much more diffuse members of a doublet. No lower frequency which might be assigned to a skeletal bending mode was observed, although this failure may have been caused by experimental difficulties. In propane, the symmetrical and unsymmetrical skeletal stretching modes occur at  $867$  and  $922\text{ cm}^{-1}$ , respectively.<sup>8</sup>

The recorded spectrum thus is reasonably consistent with the new formulation<sup>6</sup> but, of course, does not exclude other possibilities for the cation. On the other hand, the structure proposed by Schlesinger and Burg<sup>7</sup> for the diammoniate contains six B-H bonds which, judging from the spectra of analogous molecules such as propane and dimethyl ether, would be expected to give a very complicated spectrum in the B-H stretching region. That such a pattern fortuitously would match that obtained by superimposing two additional frequencies on the borohydride spectrum seems extremely unlikely, and to this extent, the spectral evidence does not agree with their proposed structure.

#### c. Decomposition Product of Ammonium Borohydride.

Chemical evidence has been given elsewhere<sup>9</sup> to the effect that if liquid ammonia solutions of  $\text{NH}_4\text{BH}_4$  are evaporated to dryness and the solid allowed to warm to room temperature, the solid evolves hydrogen and leaves a product which has the properties of the diammoniate of diborane. The spectrum of this decomposition product prepared as described was obtained in the present work largely to supply confirmatory evidence. Due to experimental difficulties, the solutions obtained were more dilute than those of the diammoniate and were not as "clean" optically. However, the frequency values in Table II match those of the diammoniate within experimental error and the band outline in the B-H stretching region

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8. G. Herzberg. Infrared and Raman Spectra of Polyatomic Molecules. New York: D. van Nostrand and Co., 1945, p.361.

9. R. W. Parry, D. R. Schultz, and P. R. Girardot, this Report, p. 4.

also agreed very closely. The identity of the decomposition product with the diammoniate thus appears confirmed.

d. Product of the Diammoniate—Ammonium Bromide Reaction.

As a consequence of the instability of solid ammonium borohydride at room temperature, treatment of the diammoniate with ammonium bromide under the proper conditions can result in the destruction of the borohydride ion present and its replacement by the bromide ion. In terms of the structure proposed previously,<sup>6</sup> the reaction can be written



Details of this reaction have been given elsewhere<sup>10</sup> and the properties of the product described. The Raman frequencies observed for this reaction product dissolved in liquid ammonia are given in Table II. Inspection shows that all values listed also appear in the diammoniate spectrum and, further, that the frequencies of the borohydride ion plus those of the  $\text{NH}_4\text{Br}$  reaction product together account for all bands observed in the diammoniate spectrum. The spectral evidence thus is strong that the reaction written above is correct and that in the reaction product one has the bromide salt of the cation which is present in the diammoniate. Two bands appear to be common to the spectrum of the cation and of the borohydride ion, namely, the bands at about  $1210 \text{ cm}^{-1}$  and their overtones at about  $2405 \text{ cm}^{-1}$ . Apparently the bending frequency of the  $\text{BH}_2$  group in the cation occurs at almost the identically same position as  $\nu_2$  of the borohydride ion. Due to the small, and in this case unknown, effect of the cation on the borohydride frequencies plus the inherent experimental uncertainty in measuring the positions of weak and rather broad bands, the two cannot clearly be distinguished.

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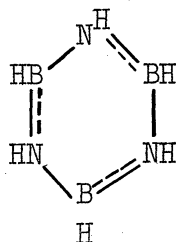
10. D. R. Schulz and R. W. Parry, this Report, p. 19.

IV. UNUSUAL COMPOUNDS RESULTING FROM THE BORANE GROUP



## A. BACKGROUND

Previous investigators have noted a formal resemblance between a B-N system and a C-C system. Since boron has one less electron than carbon and nitrogen has one more electron, the combination is isoelectronic with the C-C unit. From this analogy the cyclic compound borazene



is frequently referred to as "inorganic benzene." The physical properties show a striking resemblance to those of benzene, but the chemical properties differ. For example, all attempts to hydrogenate borazene to obtain an "inorganic cyclohexane" have failed. In the work described herein, an N, N', N"-trimethyl "inorganic cyclohexane" has been produced.

The second compound,  $F_3PBH_3$ , was of interest because of theoretical arguments against a bond between  $F_3P$  and boron. Such a bond can exist, but it is of limited stability.

B. PREPARATION AND PROPERTIES OF TRIMERIC N-METHYL-AMINOBORANE (T. C. Bissot and R. W. Parry)

Abstract

The compound N, N', N''-trimethyl "inorganic cyclohexane" or, more properly, trimeric N-methylaminoborane has been prepared and its properties are described.

Among the more interesting of the boron-nitrogen compounds are the borazenes. The structure and properties of these compounds have been well characterized and have been compared with those of benzene and its alkyl derivatives.

Hitherto there has been no report of a "saturated borazene" of the formula  $(R_2NBR_2)_3$  in which R is either hydrogen or a methyl radical, which would be structurally similar to cyclohexane or its methyl derivatives. The compound  $(CH_3)_2NBH_2$  is known to exist as a dimer at room temperature and as a monomer at higher temperatures, while  $H_2NBH_2$  is reported as a high polymer.<sup>1</sup> However, recent observations in this laboratory indicate that  $HCH_3-NBH_2$  is trimeric and is in all probability a six-membered ring composed of alternating boron and nitrogen atoms.

The new compound, trimeric N-methylaminoborane, was first isolated in low yield from the decomposition products obtained in the pyrolysis of O,N-dimethylhydroxylamineborane.<sup>2</sup> It can be prepared more conveniently and in yields of 80 to 90% by heating methylamine-borane at 100°.



The identity of the compound was proved by chemical analysis, molecular-weight determinations, and its decomposition at 200° into hydrogen and 1,3,5-trimethylborazene.

Although this compound does not display the extreme stability toward heat and hydrolysis which has been reported by Burg and his co-workers<sup>3</sup> for the trimeric P-dimethylphosphinoborane and the trimeric As-dimethylarsinoborane, it is very stable for a boron-nitrogen compound containing two active hydrogens per boron. It is unaffected after weeks in contact with moist air and is hydrolyzed only very slowly by cold water.

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1. A. B. Burg and C. L. Randolph, Jr., J. Am. Chem. Soc., 73, 953 (1951); E. Wiberg, A. Bolz, and P. Buckheit, Z. anorg. Chem., 256, 285 (1948); H. I. Schlesinger, et al., Univ. of Chicago, Signal Corps Contract W3434-SC-174 Final Report (1948-1949).

2. A study of the reaction of hydroxylamine and the five possible methyl-substituted hydroxylamines with diborane is being conducted in this laboratory and will be published in the near future.

3. A. B. Burg and R. I. Wagner, J. Am. Chem. Soc., 75, 3872 (1953); F. G. A. Stone and A. B. Burg, *ibid.*, 76, 386 (1954).

The pyrolysis of methylamine-borane has been studied by a number of previous investigators,<sup>4</sup> but this initial pyrolysis product never has been characterized.

### Experimental.—

#### a. Preparation of Trimeric N-Methylaminoborane.

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

The analysis of the product is summarized in Table I.

TABLE I

ANALYSIS FOR  $(\text{CH}_3\text{NHBH}_2)_3$ , %

	Obsd.	Calcd.
Carbon	28.00	28.00
Hydrogen	14.02	14.10
"Active" hydrogen	4.35	4.70
Boron	25.0	25.23
Nitrogen	32.78	32.66

#### b. Molecular-Weight Determinations.

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

The molecular weight was also determined by the vapor-pressure lowering of

4. H. I. Schlesinger, D. M. Ritter, and A. B. Burg, J. Am. Chem. Soc., 60, 1926 (1938); E. Wiberg, K. Hertwig, and A. Bolz, Z. anorg. Chem., 256, 177 (1948); G. W. Schaeffer and E. R. Anderson, J. Am. Chem. Soc., 71, 2143 (1949); A. B. Burg and L. C. Randolph, *ibid.*, 3451 (1949).

liquid ammonia solutions. The apparatus designed by D. R. Schultz<sup>5</sup> was modified by using a large slush bath of ethylene chloride as the constant-temperature medium. A molecular weight of 127 was obtained.

A trimer of  $\text{CH}_3\text{NHBH}_2$  has a calculated molecular weight of 128.7.

c. Decomposition into 1,3,5-Trimethylborazene.

A quantity, 0.2364 g of  $(\text{CH}_3\text{NHBH}_2)_3$  was placed in an evacuated sealed tube and heated at  $200^\circ$  for four hours. Upon opening the tube, 5.96 mmoles of hydrogen, identified by a molecular weight of 2.1, was found. This gives a ratio of hydrogen per mole of starting material of 3.24. The 1,3,5-trimethylborazene was purified by vacuum condensation, the portion collecting in a trap at  $-45^\circ$  being retained. A 74% yield was obtained based on the equation



The 1,3,5-trimethylborazene produced was characterized by vapor-pressure measurements over the temperature range  $50^\circ$  to  $75^\circ$  and by vapor-phase molecular-weight measurements based on vapor density (obsd. = 126; theor. = 122.5). The melting point of the solid was 0 to  $-1^\circ$  as compared to  $-9^\circ$  reported by Wiberg, Bolz, and Buckheit<sup>1</sup> and  $-7^\circ$  to  $-8^\circ$  reported by Schaeffer and Anderson.<sup>4</sup> It is believed that the higher value of 0 to  $-1^\circ$  indicates greater purity of the sample studied and does not negate the characterization of the borazene.

d. Properties of Trimeric N-Methylaminoborane.

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

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

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

e. X-Ray Powder Diffraction Data for Trimeric N-Methylaminoborane.

In Table II are listed the interplanar spacings ( $d$  values) and the relative

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5. D. R. Schultz, doctoral dissertation, Univ. of Mich., Ann Arbor, 1954.

line intensities found to be characteristic of the compound. The powder patterns were taken with copper  $K\alpha$  radiation in a cylindrical camera of 57.3-mm diameter. The low-absorbing glass capillaries used to hold the sample had a diameter of 0.2 mm and a wall thickness of 0.01 mm.

TABLE II

INTERPLANAR SPACINGS ( $\underline{d}$  VALUES) AND RELATIVE LINE  
INTENSITIES OF TRIMERIC N-METHYLAMINOBORANE

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

C. THE PREPARATION AND PROPERTIES OF PHOSPHORUS TRIFLUORIDE—BORANE AND PHOSPHORUS TRIFLUORIDE—BORANE- $d_3$  (R. W. Parry and T. C. Bissot)

Abstract

Phosphorus trifluoride and diborane react under pressure in sealed tubes at room temperature to give the new compound  $F_3PBH_3$ . Some physical and chemical properties of the new compound are described. Its properties show a striking resemblance to those of carbon monoxide—borane.

$NF_3$  does not add to the  $BH_3$  group, but under appropriate conditions  $B_2H_6$  is oxidized explosively by  $NF_3$ .

The compound  $Pt(PF_3)_2Cl_2$  prepared by Chatt and Williams<sup>1</sup> bears a striking resemblance to  $Pt(CO)_2Cl_2$ , and the complex  $Ni(PF_3)_4$  prepared by Irvine and Wilkinson<sup>2</sup> is very similar in properties to  $Ni(CO)_4$ . This experimental resemblance between the coordinating properties of CO and  $PF_3$  suggested the existence of the compound  $F_3PBH_3$ , which would be analogous to the  $OCBH_3$  of Burg and Schlesinger.<sup>3</sup> On the other hand, Chatt<sup>1</sup> pointed out that  $PF_3$  did not add to  $AlCl_3$ ,  $AlBr_3$ , or  $BF_3$ , and he invoked theoretical arguments as the basis for the prediction that a stable bond was unlikely between the boron in boron acids of the Lewis type and the phosphorus of phosphorus trifluoride. If, as suggested by Chatt, the acid-base type of reaction did not occur, the possibility of an oxidation-reduction reaction between  $B_2H_6$  and  $PF_3$  still merited consideration. In view of these interesting possibilities, an experimental study was conducted on the system  $B_2H_6$ - $PF_3$ . The formally analogous system  $B_2H_6$ - $NF_3$  has also been examined.

The Preparation and Physical Properties of Phosphorus Trifluoride—Borane,  $F_3PBH_3$ .—The high-pressure reaction between diborane and excess phosphorus trifluoride (8 atmospheres) proceeds slowly over the period of several days to yield the compound  $F_3PBH_3$  as the primary product. On prolonged standing, secondary reactions involving  $F_3PBH_3$  ensue which give as yet undefined liquid products along with appreciable amounts of hydrogen. The primary phosphorus trifluoride—borane adduct may also be obtained by displacing CO from carbon monoxide—borane using a smaller excess of  $PF_3$  (5 atmospheres).

Phosphorus trifluoride—borane is a colorless gas which is spontaneously inflammable in air. The melting point is  $-116.1^\circ \pm 0.2^\circ C$ . The vapor pressure of  $F_3PBH_3$  over the liquid range can be given by the equation

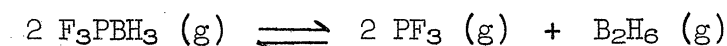
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1. J. Chatt and A. A. Williams, J. Chem. Soc., 3061, (1951); J. Chatt, *ibid.*, 3340, (1949).
  2. J. W. Irvine, Jr., and G. Wilkinson, Science, 113, 742 (1951); G. Wilkinson, J. Am. Chem. Soc., 73, 5501 (1951).
  3. A. B. Burg and H. I. Schlesinger, *ibid.* 59, 780 (1937).

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

Since the pure material resembles carbon monoxide—borane in that it will dissociate into  $\text{B}_2\text{H}_6$  and  $\text{PF}_3$ , it was necessary to purify the compound before each reading and to achieve temperature equilibrium rapidly. The vapor-pressure data extrapolate to give a boiling point of  $-61.8^\circ\text{C}$ , a heat of vaporization of 4760 calories per mole at the boiling point, and a Trouton constant of 22.5.

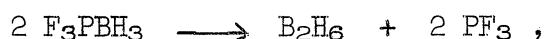
The molecular weight by vapor density at  $25^\circ\text{C}$  was 102.7 as compared to a theoretical value of 101.82.

The Dissociation Constant of Gaseous  $\text{F}_3\text{PBH}_3$  at  $25^\circ\text{C}$ .—The equilibrium constant for the reaction



was estimated by analyzing equilibrium mixtures according to the procedures described in the experimental sections. A value for  $K_{(\text{atm})}$  of  $1.0 \pm 0.3$  was obtained at  $25^\circ\text{C}$ . The uncertainty in the value can be attributed to three factors. First, a number of experimental difficulties were associated with the separation of the large excess of  $\text{PF}_3$  from the product and the unreacted diborane.<sup>4</sup> Second, since no effort was made to thermostat the reaction vessel, normal deviation of room temperature from  $25^\circ\text{C}$  would have some effect. Finally, secondary reactions involving the splitting out of  $\text{H}_2$  and the formation of less volatile products complicated the stoichiometry after longer periods of time.

Rate of Decomposition of  $\text{F}_3\text{PBH}_3$ .—In order to compare phosphorus trifluoride—borane with carbon monoxide—borane, their rates of decomposition at room temperature were compared. The decomposition reaction,



produces an increase in pressure, and the rate of pressure change with time can be used as a measure of reaction velocity. Rate data are shown in Fig. 1 along with comparable data of Burg and Schlesinger<sup>3</sup> for the  $\text{OCBH}_3$ . The similarity of the rates is striking, particularly in the early phases where side reactions have not complicated the interpretation of pressure measurements.

The mechanism for the decomposition of carbon monoxide—borane has been the subject of some recent controversy.<sup>5</sup> Unfortunately, the current data do not aid in resolving the question; however, they do suggest that the mechanism which explains

4. The problem is simplified in the case of carbon monoxide—borane since the CO is not condensable with liquid nitrogen, whereas the other components are. Since  $\text{PF}_3$  boils at  $-95^\circ\text{C}$  and  $\text{B}_2\text{H}_6$  at  $-92^\circ\text{C}$ , chemical procedures had to be employed for analysis.

5. A. B. Burg, J. Am. Chem. Soc., 74, 3482 (1952); S. H. Bauer, paper presented before the 127th Meeting, American Chemical Society, Cincinnati, Ohio, April, 1955.

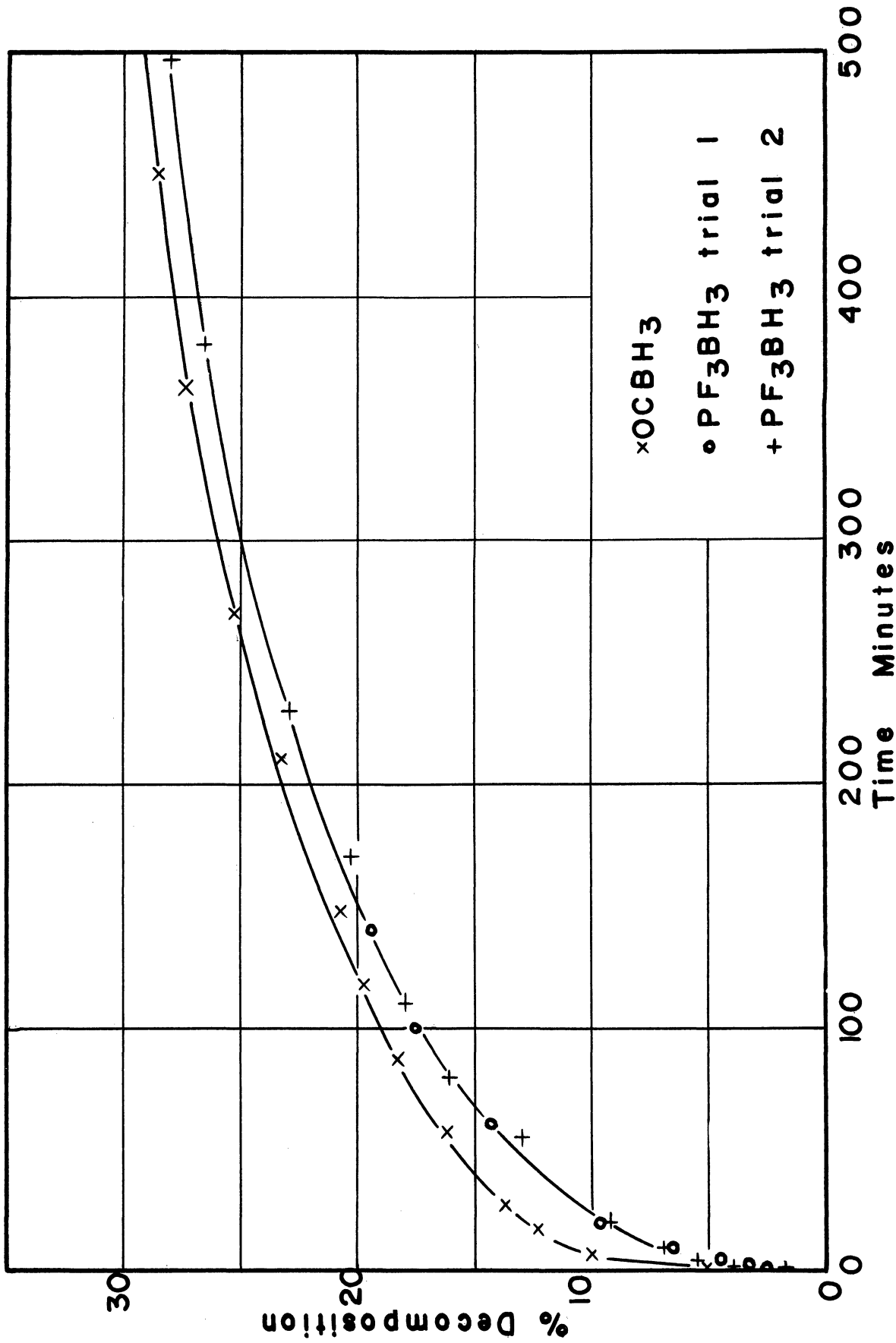


Fig. 1. Decomposition of OCBH<sub>3</sub> and PF<sub>3</sub>BH<sub>3</sub> at room temperature.



OCBH<sub>3</sub> will also explain F<sub>3</sub>PBH<sub>3</sub>. It is perhaps significant that both CO and PF<sub>3</sub> might be classed as "secondary bases" as mentioned by Bauer.<sup>5</sup>

Reaction of F<sub>3</sub>PBH<sub>3</sub> with Trimethylamine and with Ammonia.—When stoichiometric quantities of F<sub>3</sub>PBH<sub>3</sub> and trimethylamine are mixed, the trimethylamine displaces the PF<sub>3</sub> quantitatively to form (CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub> and free PF<sub>3</sub>. If an excess of trimethylamine is used, the PF<sub>3</sub> which is liberated reacts with the excess trimethylamine in a one-to-one ratio to give gases and a solid which have not been fully characterized.

When F<sub>3</sub>PBH<sub>3</sub> reacts with excess ammonia over the temperature range of -128° to -80°C, five molecules of ammonia will be picked up by each molecule of the borane adduct. The reaction product is a white solid which begins to decompose at room temperature with evolution of hydrogen and development of a yellow color. When the solid was heated to about 55°C, 1.62 moles of ammonia were evolved per mole F<sub>3</sub>PBH<sub>3</sub>. It is probable that the original solid product is a mixture. The reaction, which appears to be rather complex, is being studied further. Data suggest rupture of the phosphorus-fluorine bond by the ammonia.

The Properties of Phosphorus Trifluoride—Borane-d<sub>3</sub>.—The compound F<sub>3</sub>PBD<sub>3</sub> was needed for Raman spectral studies. The deuterated compound had a melting point of -115.1° ± .1°C. The vapor pressure of the liquid can be given by the equation

$$\text{Log}_{10} P = -1010.8/T + 7.6171 .$$

Extrapolating this vapor-pressure data yields a boiling point of -59.8°C, a heat of vaporization of 4630 calories per mole, and a Trouton constant of 22.

The Reaction Between NF<sub>3</sub> and Diborane.—NF<sub>3</sub>, which is formally analogous to PF<sub>3</sub>, is known to have essentially no basic properties. It was nonetheless interesting to compare the behavior of NF<sub>3</sub> and PF<sub>3</sub> in their reaction with diborane. Results can be summarized as follows: (1) under conditions similar to those used in making F<sub>3</sub>PBH<sub>3</sub> and OCBH<sub>3</sub> no compound formation between NF<sub>3</sub> and B<sub>2</sub>H<sub>6</sub> was observed; (2) in these experiments, mixtures of NF<sub>3</sub> and B<sub>2</sub>H<sub>6</sub> were stable in the gas phase even under high pressures; (3) mixtures of NF<sub>3</sub> and B<sub>2</sub>H<sub>6</sub> can be violently explosive at temperatures which are low enough to give condensed phases in the system. The conditions necessary to initiate explosive reaction between the two liquids were not clearly defined, but spontaneous explosive reaction was observed only when the contents of the reaction tube were liquefied after the gases had been standing for several days under pressure. This explosion was undoubtedly an oxidation-reduction process with N<sub>2</sub>, HF, and BF<sub>3</sub> as probable products. The possibility that the reaction was triggered by very small amounts of impurities in the NF<sub>3</sub>, such as N<sub>2</sub>O, NO, or NO<sub>3</sub>F, or by decomposition products of B<sub>2</sub>H<sub>6</sub>, remains reasonable.

Discussion.—The striking similarity between the physical properties of phosphorus trifluoride—borane and carbon monoxide—borane is illustrated by the data in Table I. Even the differences between the deuterated and nondeuterated compounds are comparable. The stability of F<sub>3</sub>PBH<sub>3</sub> is somewhat greater than the comparable OCBH<sub>3</sub> (see K values in Table I). Its rate of dissociation at room temperature also is somewhat lower than the carbonyl adduct. These facts correlate well with the observations of Chatt and Williams<sup>1</sup> to the effect that PF<sub>3</sub> adducts of the platinum (II) halides are more stable than the corresponding carbonyl compounds.

TABLE I

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

	OCBH <sub>3</sub>	OCBD <sub>3</sub> <sup>6</sup>	F <sub>3</sub> PBH <sub>3</sub>	F <sub>3</sub> PBD <sub>3</sub>
Melting Point	-137.0	-134.4	-116.1	-115.1
Boiling Point	-64	-62.2	-61.8	-59.8
H Vaporization	4750	4760	4760	4630
Trouton Constant	23	23	22	22
Dissociation Constant				
K <sub>atm</sub> at 25°C	2.5 <sup>5</sup>	--	1.0 ± .3	--
Percent Decomposed				
After 1 hr at 25°C	17%	--	14%	--

The initial reaction of F<sub>3</sub>PBH<sub>3</sub> with trimethylamine parallels closely the corresponding reaction involving carbon monoxide—borane. Differences are noticed, however, in secondary reactions because the liberated PF<sub>3</sub> reacts directly with trimethylamine whereas CO does not. The reactions of both OCBH<sub>3</sub> and F<sub>3</sub>PBH<sub>3</sub> with ammonia are more complex and require further study.

The spontaneous inflammability of F<sub>3</sub>PBH<sub>3</sub> in air correlates well with the general observation that the reactivity toward oxidizing agents and moisture of the simple borane adducts is inversely related to the strength of the base to which it is bound. The weak base strength of PF<sub>3</sub> produces a highly inflammable adduct.

The most reasonable model for the molecule would be an ethane-like structure with a sigma bond between the boron and the phosphorus. Double bonding of the type postulated by Chatt<sup>1</sup> for the metal adducts of PF<sub>3</sub> is ruled out by the absence of d electrons on the boron. Other systems involving addition of PF<sub>3</sub> to Lewis acids are under investigation. Further speculation on bonding can best await more complete experimental information.

Experimental.

## a. Preparation of Phosphorus Trifluoride.

The phosphorus trifluoride was prepared by the reaction between phosphorus trichloride and zinc fluoride, using a minor modification of the procedure of Chatt and Williams.<sup>1</sup> The crude products were passed through a reflux column at -80°C in order to recover unreacted PCl<sub>3</sub>, then the impure PF<sub>3</sub> was trapped in a liquid nitrogen trap and purified by fractionation in the vacuum line.

## b. Diborane

Diborane was prepared by the reaction between lithium aluminum hydride and

<sup>6</sup> A. B. Burg, J. Am. Chem. Soc., 74, 1340 (1952).

boron trifluoride etherate in ether solution.<sup>7</sup> After purification by low-temperature fractionation, the vapor pressure at  $-111.8^{\circ}\text{C}$  was 225 mm. Diborane- $d_6$  was prepared using lithium aluminum deuteride. The  $\text{LiAlD}_4$  was prepared in situ from lithium deuteride and aluminum chloride.

c. The Preparation of  $\text{F}_3\text{PBH}_3$ .

A measured amount of diborane, together with a large excess of  $\text{PF}_3$ , was condensed in a heavy-walled Pyrex bomb tube of 60-ml capacity. The techniques resemble closely the procedures used by Burg and Schlesinger for the preparation of  $\text{OCBH}_3$ .<sup>3</sup> The bomb tube was allowed to stand several days at room temperature. Maximum yields were usually obtained after four days; longer periods of time frequently resulted in the formation of secondary products, although the factors responsible for the secondary reaction were never completely delineated. After standing, the bomb tube was frozen with liquid nitrogen and the tube opened to the line by means of the vacuum-tube opener. Noncondensable gases were removed with a Toepler pump, measured, and identified by molecular-weight measurements. The condensable portions were distilled through a trap at  $-155^{\circ}\text{C}$ , at which temperature the  $\text{F}_3\text{PBH}_3$  is quantitatively retained. The excess  $\text{B}_2\text{H}_6$  and  $\text{PF}_3$  was measured and analyzed by a sealed-tube hydrolysis, using the amount of hydrogen generated to determine the portion of  $\text{B}_2\text{H}_6$  in the mixture. The  $\text{F}_3\text{PBH}_3$  was freed from less volatile impurities by distilling it through a trap at  $-128^{\circ}\text{C}$ . The pure  $\text{F}_3\text{PBH}_3$  showed a vapor pressure of 23.0 mm at  $-111.8^{\circ}\text{C}$ .

The less volatile materials formed from secondary reactions were easily separated from the more volatile components by fractional distillation in the vacuum line. Upon hydrolysis of these materials, only small amounts of hydrogen were liberated. In one case the less volatile materials were separated by fractional condensation and a liquid with a vapor pressure of 5 mm at  $-80^{\circ}\text{C}$  was isolated. A measurement of molecular weight by vapor density gave a value of 120. It appeared stable in the vapor phase but polymerized in the liquid phase to give a nonvolatile oil. No hydrogen was liberated on addition of water, indicating that it contained no active hydrogens. However, the compound was destroyed by water. These observations, plus the fact that the secondary reaction results in the liberation of gaseous hydrogen, suggest the tentative formula  $\text{F}_2\text{PBF}_2$  for the monomeric liquid. The characterization is still incomplete since only very small amounts of material were available and the conditions which favor its formation have not been completely determined. Data for representative runs are summarized in Table II.

d. Analysis and Characterization of the  $\text{F}_3\text{PBH}_3$ .

Hydridic hydrogen in the compound was determined by condensing a weighed sample of gas in the 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 hydrogen was measured; observed hydridic hydrogen is 2.89%; theoretical for  $\text{F}_3\text{PBH}_3$  is 2.97%.

7. I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik, and G. B. L. Smith, J. Am. Chem. Soc., 74, 901 (1952).

The  $\text{PF}_3$  is partially hydrolyzed by the above procedure, and the resulting HF attacks the Pyrex glass enough to make a boron analysis meaningless. Small amounts of  $\text{PF}_3$  were always obtained after water hydrolysis; a contaminant which appeared to be  $\text{SiF}_4$  was always present, as would be expected.

The addition compound was hydrolyzed by 40% NaOH as the first step in obtaining a phosphorus analysis; the P-F bond is cleaved rapidly in alkaline solution.<sup>8</sup> The resulting solution was acidified and the phosphorous acid was oxidized to 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  $\text{F}_3\text{PBH}_3$  (30.43% P).

TABLE II

DATA ON REACTIONS BETWEEN PHOSPHORUS TRIFLUORIDE AND DIBORANE

	Run Number				
	3	4	5	6	8
<u>Conditions</u>					
Volume of bomb, ml	62.5	62.9	63.5	61.7	61.7
Initial mmoles $\text{B}_2\text{H}_6$	3.28	3.20	3.16	3.22	5.42
Initial mmoles $\text{PF}_3$	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
<u>Products</u>					
Mmoles $\text{B}_2\text{H}_6$	1.24	0.69	0.27	0.44	2.12
Mmoles $\text{PF}_3$	14.65	13.17	11.37	12.31	4.87
Mmoles $\text{PF}_3\text{BH}_3$	4.26	5.01	4.34	4.73	4.50
Mmoles of less volatile by-products	0.01	0.08	1.40	0.38	0.84
Mmoles $\text{H}_2$	0.03	0.55	-	1.29	2.10
Yield $\text{PF}_3\text{BH}_3$ based on $\text{B}_2\text{H}_6$	65%	78.3%	68.7%	73.5%	41.5%
Apparent equilibrium constant $K_{\text{atm}}$	5.73	1.86	0.71	1.18	0.98

e. Measurement of Physical Properties of  $\text{H}_3\text{BPF}_3$ .

Conventional techniques were used for vapor-density and vapor-pressure measurements (Tables III and IV). Temperatures were measured with ethylene and carbon dioxide vapor-pressure thermometers. The melting point was obtained in the vacuum line, using the method of Stock.<sup>9</sup>

8. H. S. Booth and A. R. Bozarth, J. Am. Chem. Soc., 61, 2927 (1939).

9. A. Stock, Ber., 50, 156 (1917).

TABLE III

## VAPOR PRESSURES OF PHOSPHORUS TRIFLUORIDE—BORANE

Temp. °C	Observed Pressure mm	Calculated Pressure mm	$\Delta P$ (Cal. - Obs.)
-127.7	4.1 (s)		
-119.7	11.4 (s)		
-111.8	23.0	23.4	+0.4
-101.5	56.6	57.0	+0.4
-98.1	76.4	74.6	-1.8
-95.7	90.6	89.7	-0.9
-87.6	162.1	161.6	-0.5
-79.9	267	270	+3.0

TABLE IV

VAPOR PRESSURES OF PHOSPHORUS TRIFLUORIDE—BORANE- $d_3$ 

Temp. °C	Observed Pressure mm	Calculated Pressure mm	$\Delta P$ (Cal. - Obs.)
-119.4	8.0 (s)		
-112.0	20.9	22.2	+1.3
-101.5	54.2	53.7	-0.5
-95.6	85.2	84.2	-1.0
-84.1	186	187	+1.0
-79.0	260	259	-1.0

f. Reaction of  $F_3PBH_3$  with Trimethylamine.

One and ninety three hundredths mmoles of  $F_3PBH_3$  were condensed in a 250-ml bulb with 2.31 mmoles of trimethylamine. When the mixture was warmed to room temperature, there was an immediate reaction in which a white solid was produced. The bulb was cooled to  $-80^\circ C$ ; the more volatile products were distilled out; the bulb was weighed; the trimethylamine-borane was sublimed out; and the bulb was reweighed. A 97% yield (0.1362 g) of  $(CH_3)_3NBH_3$  was obtained. Vacuum-line distillation of the volatile gases yielded 79.3% of the theoretical  $PF_3$ . This was characterized by vapor-pressure and molecular-weight measurements (obs. 87.6; theor. 87.98). The unrecovered  $PF_3$  (0.4 mmole) corresponded exactly to the excess of trimethylamine (0.38 mmole), a fact which suggests that a reaction between  $PF_3$  and  $N(CH_3)_3$  had taken place to yield the unidentified solid and gaseous products. This postulate 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.

g. Reaction of  $F_3PBH_3$  with Ammonia.

A quantity of dry ammonia, 14.70 mmoles, was condensed on the walls of the reaction tube. Then, 2.20 mmoles of  $F_3PBH_3$  were added and the temperature was raised from  $-128^\circ$  to  $-80^\circ C$  over the period of 2-1/2 hours. The excess ammonia was then sublimed from the reaction tube at  $-80^\circ C$ . The amount of ammonia recovered was 3.69 mmoles, meaning that 5.0 moles of ammonia react with one mole of  $F_3PBH_3$ .

The reaction product was a white solid which began to decompose at room temperature by turning yellow and giving off small amounts of hydrogen. Upon heating the solid to about  $55^\circ C$ , an amount of ammonia equivalent to 1.62 moles of the original 5.0 was recovered. During the decomposition a small amount of a white solid of very low vapor pressure was collected in a Dry-Ice trap. This white solid burst into flame when the trap was cleaned with concentrated nitric acid.

h. Preparation of Nitrogen Trifluoride.

Nitrogen trifluoride was prepared by a modification of the method of Ruff.<sup>10</sup> A closed electrolysis cell was substituted for Ruff's open cell.

The impure  $NF_3$  was bubbled slowly through a warm KI solution. Final purification was achieved by low-temperature fractionation in the vacuum line. The gas was passed slowly through a trap cooled to  $-183^\circ C$  with liquid oxygen. The impurities, principally small amounts of  $N_2O$ , condensed, while the  $NF_3$  passed through into a third trap cooled to  $-208^\circ C$  with low-pressure liquid nitrogen (maintained at 100-mm pressure by pumping through a manostat). Small amounts of dissolved oxygen and nitrogen were pumped from the  $NF_3$  in the third trap to give a product of high purity. The molecular weight of the gas, as determined by vapor density, was 71.2. The theoretical value for  $NF_3$  is 71.01.

i. The Reaction of Nitrogen Trifluoride with Diboranes.

The sealed-tube, high-pressure techniques described for the preparation of  $F_3PBH_3$  were employed. In a typical run 2.61 mmoles  $B_2H_6$  and 18.84 mmoles  $NF_3$  were sealed into a bomb tube and allowed to stand for eight days at room temperature. When the tube was opened to the line, the amount of noncondensable gas was negligible. A mixed pentane bath at  $-155^\circ C$  was placed around the tube and the entire contents distilled into the vacuum system. On further fractionation in the vacuum line, no fraction could be retained in the  $-155^\circ C$  trap. Finally, during a transfer distillation a violent explosion occurred. The temperature of the vessel at the time of the explosion was estimated to be about  $-170^\circ C$ , since a liquid nitrogen Dewar had just been removed and another low-temperature bath was to be substituted. The explosion occurred before the second bath was put in place. In a second trial under similar circumstances an explosion occurred while the contents of the reaction tube were being distilled into the vacuum line.

10. O. Ruff, J. Fischer, and F. Luft, Z. anorg. Chem., 172, 417-25 (1928).

V. THE REACTIONS OF DIBORANE WITH HYDROXYLAMINE  
AND ITS METHYL DERIVATIVES

### Abstract

Free hydroxylamine and all its O- and N- methyl derivatives have been prepared in pure form. Melting points, vapor pressures, and heats of vaporization have been determined for the entire series. Values are those expected from considerations of hydrogen bonding.

The basic constants for the series have been determined. Variations in the series are compared to variations found in the series ammonia, methyl amines.

Although all the methyl derivatives of hydroxylamine have been mentioned 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 the reaction of the hydroxylamines with diborane, and since the properties of the bases are of interest in their own right, a study of the pure-methyl-substituted hydroxylamines has been conducted. Results are reported herein.

### Experimental.

#### a. The Preparation of Hydroxylamine and Its Methyl Derivatives.

1. Hydroxylamine—The free base was liberated from a suspension of hydroxylammonium chloride in butanol, using sodium butoxide as the base.<sup>1</sup> The salt was thoroughly dried at 110°C before use. Since the free base undergoes rapid decomposition at temperatures above 15°C and is very hygroscopic, it was stored under anhydrous butanol at -10°C until used. Cold samples were filtered rapidly, washed with cold anhydrous ether, and weighed in a special vacuum-jacketed weighing bottle.

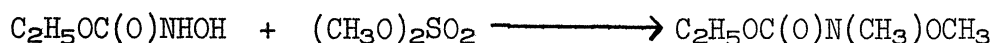
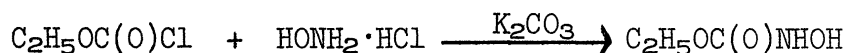
2. O-methylhydroxylamine—Methoxyamine hydrochloride (Eastman Organic Chemicals) was treated with an excess of 50% KOH in a small one-piece distillation apparatus. The fraction boiling at 45°-50° was distilled onto KOH pellets contained in a receiver which was immersed in an ice-water bath. The free base was then decanted into a tube containing BaO and equipped with a  $\text{S}$  joint. The tube was attached to the line and the O-methylhydroxylamine was allowed to stand in contact with the BaO for several days. The  $\text{CH}_3\text{ONH}_2$  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.

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1. C. D. Hurd, in Inorganic Synthesis. Vol. I. New York: McGraw-Hill Book Co., Inc., 1939, p. 87.

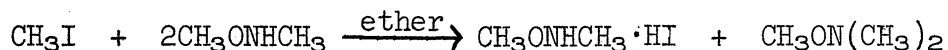


3. O,N-dimethylhydroxylamine—This methyl-substituted hydroxylamine was prepared by the following reactions:



The literature directions<sup>2,3</sup> 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 was frozen in the bottom of a tube which was equipped with a  $\text{F}$  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), was within the experimental error of the measurement.

4. O,N,N-trimethylhydroxylamine—The trimethyl derivative was prepared as described by Jones and Major,<sup>4</sup> using the reaction of methyl iodide with the O,N-dimethylhydroxylamine.



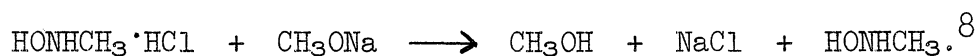
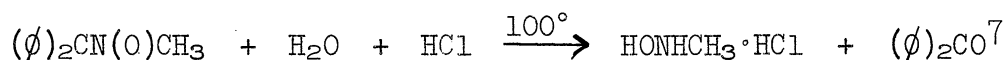
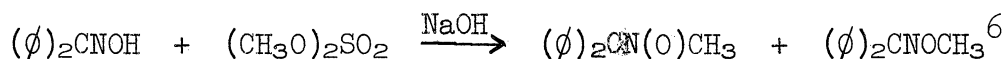
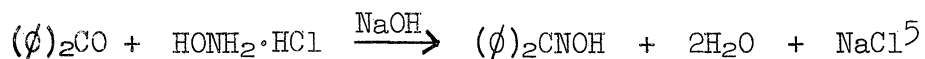
The ether solution was filtered and phenyl isocyanate was added to remove any unreacted  $\text{CH}_3\text{ONHCH}_3$  as the N-phenyl-N'-methyl-N'-methoxy urea derivative. The ether and the free O,N,N-trimethylhydroxylamine were distilled out and dry HCl passed into the ether solution. The recrystallized 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).

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

2. L. W. Jones, *Am. Chem. J.*, 20, 38 (1898).

3. R. T. Major and E. E. Fleck, *J. Am. Chem. Soc.*, 50, 1479 (1928).

4. L. W. Jones and R. T. Major, *ibid.*, 2742 (1928).



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).

6. N,N-dimethylhydroxylamine—This hydroxylamine was prepared by the action of a methyl Grignard reagent upon ethyl nitrate in ether solution.<sup>9</sup> 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 thoroughly dried under high vacuum on the vacuum line. The melting point observed was 103°-106°. Hepworth<sup>9</sup> listed an mp of 102°, while Cope and co-workers<sup>10</sup> 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

5. A. I. Vogel. Practical Organic Chemistry. London: Longmans, Green and Co., Inc., 1948, p. 704.

6. The structural isomers



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.

7. L. Semper and L. Lichtenstadt, Ber., 51, 933 (1918).

8. C. Kjellin, ibid., 26, 2377 (1893).

9. H. Hepworth, J. Chem. Soc., 119, 255 (1921).

10. A. C. Cope, T. T. Foster, and P. H. Towle, J. Am. Chem. Soc., 71, 3929 (1949).

of water and amine obtained in the distillation, it was found that all 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  $\text{HON}(\text{CH}_3)_2 \cdot \text{HCl}$  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  $\text{HON}(\text{CH}_3)_2$  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, mp 17.7°, bp 100.7°. Nitrogen analyses, 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.

<u>Temperature</u> °C	<u>Apparent</u> <u>Molecular Weight</u>
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.

#### b. Physical Properties.

1. 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.<sup>11,12</sup> A sample of the amine was condensed with liquid nitro-

11. A. Stock, Ber., 50, 156 (1917).

12. R. S. Sanderson. Vacuum Manipulations of Volatile Compounds. New York: John Wiley and Sons, Inc., 1948.

gen 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-dimethylhydroxylamine 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 Table I.

TABLE I  
MELTING POINTS OF HYDROXYLAMINE AND ITS  
METHYL-SUBSTITUTED DERIVATIVES

Compound	Melting Point °C	Investigator
HONH <sub>2</sub>	33.05 32-33	Lobry de Bruyn <sup>13</sup> Brühl <sup>14</sup>
HONHCH <sub>3</sub>	42 38.2, 38.7	Kjellin <sup>8,15</sup> This investigation
HON(CH <sub>3</sub> ) <sub>2</sub>	17.5 -17.8	This investigation
CH <sub>3</sub> ONH <sub>2</sub>	-86.4	This investigation
CH <sub>3</sub> ONHCH <sub>3</sub>	-97.0	This investigation
CH <sub>3</sub> ON(CH <sub>3</sub> ) <sub>2</sub>	-97.2	This investigation

13. C. A. Lobry de Bruyn, *Rec. trav. chim.*, 10, 100 (1891).

14. J. W. Brühl, *Ber.*, 26, 2508 (1893).

15. The early observations of Kjellin were apparently rather crude. The boiling point which he reported for HONHCH<sub>3</sub> was in error by a large factor (Table VI). Extensive purification in this investigation failed to raise the melting point above the reported value.

2. 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. 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.

(a)  $-80^{\circ}$  to  $0^{\circ}$ . Four different two-phase systems were used as constant-temperature baths in this region. These were slush baths of chloroform ( $-63.5^{\circ}$ ), chlorobenzene ( $-45.3^{\circ}$ ), carbon tetrachloride ( $-22.8^{\circ}$ ), and ice-water ( $0^{\circ}$ ). A Dry Ice—*isopropyl alcohol* bath was used at  $-78^{\circ}$ . 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  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_5\text{Cl}$ , and  $\text{H}_2\text{O}$ .

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

(b)  $0^{\circ}$  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  $0.01^{\circ}$  graduations, which had been calibrated and certified by the National Bureau of Standards, was used to measure the temperature of the bath.

(c) Above room temperature. An immersible tensimeter designed after the one described by Burg and Schlesinger<sup>16</sup> was used to determine vapor pressures above room temperature. The tensimeter was immersed in a constant-temperature bath controlled to  $\pm 0.05^{\circ}$ . Two National Bureau of Standards calibrated thermometers,  $-5^{\circ}$  to  $50^{\circ}$  and  $50^{\circ}$  to  $110^{\circ}$ , were used with stem corrections applied where they were significant.

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

$$\text{Log}_{10} P = -A/T + B - C \log T .$$

Data are summarized in Tables II to V. The heats and entropies of vaporization at the boiling point were estimated from the vapor-pressure data. Comparative physical data for all the methyl derivatives of hydroxylamine are summarized in Table VI.

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16. A. B. Burg and H. I. Schlesinger, J. Am. Chem. Soc., 59, 780 (1937).

TABLE II

## THE VAPOR PRESSURE OF O-METHYLHYDROXYLAMINE

$$\text{Empirical Equation } \log_{10} P = -2433.7/T + 23.9284 - 5.3746 \log T$$

Temperature °C	Observed Pressure mm	Calculated Pressure mm	$\Delta P$ Cal.-Obs.
-63.5	.75	.69	-0.06
-45.3	3.55	3.76	+0.21
-22.8	20.5	20.7	+0.2
-20.4	24.2	24.4	+0.2
-17.6	29.0	29.2	+0.2
-13.3	38.2	38.5	+0.3
-10.4	45.6	46.1	+0.5
-6.8	56.4	57.0	+0.6
0.0	83.9	83.8	-0.1
9.4	138.8	138.5	-0.3
10.1	143.5	143.6	+0.1
12.6	162.9	162.5	-0.4
14.4	177.3	177.4	+0.1
16.0	192.1	192.6	+0.5
17.7	208.4	208.6	+0.2
19.1	222.8	222.6	-0.2
20.1	233.6	232.7	-0.9
21.1	243.9	245.4	+1.5
24.8	291.1	290.5	-0.6
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	765	+4

TABLE III

## THE VAPOR PRESSURE OF O,N-DIMETHYLHYDROXYLAMINE

$$\text{Empirical Equation } \log_{10} P = -2282.9/T + 22.1065 - 4.7976 \log T$$

Temperature °C	Observed	Calculated	$\Delta P$ Cal. - Obs.
	Pressure mm	Pressure mm	
-45.2	6.1	6.0	-0.1
-42.0	8.0	8.0	0
-36.5	11.8	11.7	-0.1
-31.4	16.8	17.0	+0.2
-27.0	23.1	23.0	-0.1
-22.6	30.6	30.8	+0.2
-18.0	40.8	41.2	+0.4
-13.3	54.9	54.5	-0.4
-7.3	77.8	77.2	-0.6
-4.2	91.5	92.0	+0.5
0.0	114.4	115.3	+0.9
4.0	141.1	141.3	+0.2
8.0	173.2	173.5	+0.3
12.0	210.9	210.7	-0.2
16.0	253.8	253.7	-0.1
19.7	301.4	301.0	-0.4
23.9	361.5	361.7	+0.2
28.0	430.4	431.0	+0.6
32.9	526.6	527.1	+0.5
37.5	630.2	631.1	+0.9
42.4	765	762.6	-2.4

TABLE IV

A. THE VAPOR PRESSURE OF O,N,N-TRIMETHYLHYDROXYLAMINE  
 Empirical Equation  $\text{Log}_{10} P = -2296.9/T + 27.3690 - 6.8151 \text{ Log } T$

Temperature °C	Observed Pressure mm	Calculated Pressure mm	$\Delta P$ Cal.-Obs.
-78.5	0.9	0.9	0
-63.5	3.6	3.9	+0.3
-45.2	17.3	16.8	-0.5
-39.0	26.5	25.8	-0.7
-35.0	35.5	33.7	-1.8
-29.8	47.5	46.8	-0.7
-25.2	61.7	61.5	-0.2
-20.0	81.5	82.9	+1.4
-14.1	113.6	113.4	-0.2
-9.3	144.4	145.8	+1.4
-4.8	186.0	181.3	-4.7
0.0	226.9	227.7	+0.8
3.9	270.7	271.0	+0.4
8.3	328.0	328.7	+0.7
11.8	379.1	379.8	+0.7
15.9	448.0	448.1	+0.1
20.0	525.4	524.9	-0.5
23.3	597.5	595.3	-2.2

B. THE VAPOR PRESSURE OF N-METHYLHYDROXYLAMINE

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

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 V

## THE VAPOR PRESSURE OF N,N-DIMETHYLHYDROXYLAMINE

$$\text{Empirical Equation } \log_{10} P = -3780.1/T + 39.4125 - 10.2693 \log T$$

Temperature °C	Observed Pressure mm	Calculated Pressure mm	$\Delta P$ Cal.-Obs.
17.6	13.0	13.0	0.0
19.1	14.5	14.4	-0.1
25.2	21.4	21.4	0.0
29.8	28.5	28.6	0.1
34.7	38.0	38.1	0.1
40.3	52.4	52.5	0.1
44.9	67.3	67.3	0.0
50.3	90.1	89.8	-0.3
55.1	114.6	114.2	-0.4
60.2	146.0	146.8	0.8
65.1	183.3	183.8	0.5
70.2	229.7	231.2	1.5
75.1	284.4	285.2	0.8
80.2	351.7	351.2	-0.5
85.0	427.0	426.3	-0.7
90.0	521	518	-3

TABLE VI

MELTING POINTS, BOILING POINTS, HEATS OF VAPORIZATION, AND  
TROUTON CONSTANTS OF METHYL-SUBSTITUTED HYDROXYLAMINES

Compound	Melting Point °C	Boiling Point °C 760 mm	$\Delta H$ Vap. cal/mol	$\Delta H/T$ e.u.
HONHCH <sub>3</sub>	38.5	115.0	11,880	30.6
HON(CH <sub>3</sub> ) <sub>2</sub>	17.6	100.6	9,670	25.9
CH <sub>3</sub> ONH <sub>2</sub>	-86.4	48.1	7,710	24.0
CH <sub>3</sub> ONH(CH <sub>3</sub> )	-97.0	42.3	7,440	23.6
CH <sub>3</sub> ON(CH <sub>3</sub> ) <sub>2</sub>	-97.2	30.0	6,410	21.1

c. Chemical Properties.

1. 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 100-ml 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 Beckmann model G pH meter with a combination glass-calomel electrode system was carefully standardized against a potassium acid phthalate buffer. Both the four-necked titration flask and the buffer solution were thermostated at  $25 \pm 0.1^\circ$ .

The dilute solution of the amine hydrochloride was then titrated with 0.05 N NaOH from a 5-ml microburette. 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

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

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.<sup>17</sup> In order to estimate the magnitude of the errors in the procedure, the constant for  $\text{NH}_4\text{OH}$  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,<sup>18</sup> 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  $\pm 0.03$  pK unit. Data are summarized in Table VII.

17. D. M. Yost and H. Russell, Jr. Systematic Inorganic Chemistry. New York: Prentice-Hall, Inc., 1944, p. 97.

18. R. G. Bates and G. D. Pinching, Res. Paper 1982, J. Res. Natl. Bur. Std., 42, 419 (1949).

TABLE VII

pKa VALUES FOR AMMONIA, HYDROXYLAMINE, AND  
METHYL-SUBSTITUTED HYDROXYLAMINES

Compound	Ionic Strength	$\sqrt{\mu}$	Average Apparent pKa	Value of pKa at Infinite Dilution
NH <sub>3</sub>	0.058	0.241	9.310	4.73 ± 0.02
	0.0213	0.146	9.298	
	0.0025	0.050	9.277	
	0.00	0.00	9.27	
HONH <sub>2</sub>	0.0226	0.150	6.012	8.03 ± 0.02
	0.0075	0.087	5.997	
	0.0023	0.048	5.985	
	0.00	0.00	5.97	
HONHCH <sub>3</sub>	0.0226	0.150	6.002	8.04 ± 0.02
	0.0100	0.100	5.968	
	0.0034	0.058	5.969	
	0.0026	0.051	5.983	
	0.00	0.00	5.96	
HON(CH <sub>3</sub> ) <sub>2</sub>	0.0626	0.252	5.276	8.80 ± 0.02
	0.0212	0.145	5.246	
	0.0026	0.051	5.218	
	0.00	0.00	5.20	
CH <sub>3</sub> ONH <sub>2</sub>	0.100	0.316	4.674	9.40 ± 0.02
	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	
CH <sub>3</sub> ONHCH <sub>3</sub>	0.0615	0.248	4.780	9.25 ± 0.02
	0.205	0.143	4.768	
	0.00223	0.048	4.752	
	0.0	0.00	4.75	
CH <sub>3</sub> ON(CH <sub>3</sub> ) <sub>2</sub>	0.0672	0.259	3.746	10.35 ± 0.02
	0.0206	0.144	3.704	
	0.00223	0.047	3.671	
	0.00	0.00	3.65	

The base strengths of hydroxylamine and methoxyamine have been reported previously in the literature. The basic ionization constant usually reported for hydroxylamine<sup>19,20</sup> is the early value of Winkelbleck,<sup>21</sup>  $6.6 \times 10^{-9}$ , corresponding to a pK<sub>b</sub> of 8.18. The pK<sub>b</sub> value, 7.40, given by Ishikawa and Aoki<sup>22</sup> appears to be erroneous. The value closest to that found in this investigation (8.03) is that of Kolthoff and Stenger<sup>23</sup> who listed the pK<sub>b</sub> of hydroxylamine as 7.97. The ionization constant for methoxyamine of  $2.4 \times 10^{-5}$  reported by Vodrazka<sup>24</sup> corresponds to a pK<sub>a</sub> of 4.62. This is within the assigned error of the value obtained, pK<sub>a</sub> 4.60.

Discussion.—Brown and co-workers<sup>5</sup> have 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 were the only factor in determining the strength of the base, the order expected would be  $\text{NH}_3 < \text{NH}_2\text{CH}_3 < \text{NH}(\text{CH}_3)_2 < \text{N}(\text{CH}_3)_3$ . The order actually observed with a proton and with trimethylborane as reference acids is  $\text{NH}_3 < \text{N}(\text{CH}_3)_3 < \text{NH}_2\text{CH}_3 < \text{NH}(\text{CH}_3)_2$ . A number of theories have been proposed to explain this order of base strengths of alkyl amines.<sup>26-28</sup> The opinion is divided as to whether the inductive effect of the alkyl group is opposed to a steric factor or by solvent interaction. Brown<sup>25</sup> has argued that the decrease in the basicity of  $(\text{CH}_3)_3\text{N}$  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<sup>26</sup> 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.

19. D. M. Yost and H. Russell, Jr. Systematic Inorganic Chemistry. New York: Prentice-Hall, Inc., 1944, p. 98.
20. W. Latimer. Oxidation Potentials. New York: Prentice-Hall, Inc., 1938, p. 89.
21. K. Winkelbleck, Z. Phys. Chem., 36, 574 (1901).
22. F. Ishikawa and I. Aoki, Bull. Inst. Phys. and Chem. Research, 19, 136 (1940).
23. I. M. Kolthoff and V. A. Stenger. Volumetric Analysis. Vol. I. 2nd ed. New York: Interscience Publishers, 1942, Table II, p. 284.
24. Z. Vodrazka, Chem. Listy., 46, 208 (1952).
25. H. C. Brown, H. Bartholomay, and M. D. Taylor, J. Am. Chem. Soc., 66, 435 (1944).
26. A. F. Trotman-Dickenson, J. Chem. Soc., 1293 (1949); R. B. Bell and A. F. Trotman-Dickenson, *ibid.*, 1288 (1949).
27. R. G. Pearson, J. Am. Chem. Soc., 70, 204 (1948); R. G. Pearson and F. V. Williams, *ibid.*, 76, 258 (1954).
28. K. S. Pitzer and R. Spitzer, *ibid.*, 70, 1261 (1948).

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 Fig. 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 to two substituents 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 O-methylhydroxylamine 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,  $\text{CH}_3\text{OCH}_2\text{COOH}$  (pKa 3.48), which is a stronger acid than glycolic acid,  $\text{HOCH}_2\text{COOH}$  (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 were 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.

Data summarized in Table VI show that the replacement of hydrogen by a methyl group on the oxygen lowers the boiling points and the melting points of the compounds. The removal of the relatively strongly protonic hydrogen on the oxygen eliminates hydrogen bonding through the hydroxyl group. The same effect, though to a much smaller degree, is expected upon replacement of one of the hydrogens on the nitrogen by a methyl group. For comparable compounds the Trouton constant and the boiling point are reduced by substitution of methyl for hydrogen on nitrogen.

Although it is frequently assumed that the entropy of vaporization for a liquid under a constant pressure of one atmosphere (Trouton constant) is related to the degree of association in the liquid phase, Hildebrand<sup>29</sup> showed that the entropy of vaporization at a constant vapor-phase concentration is of more fundamental significance. The so-called Hildebrand-Trouton constant is the entropy of vaporization at a constant vapor-phase concentration of .00507 mole/liter. The Hildebrand-Trouton constant for a group of amines is compared with the value of  $\Delta H_{\text{vap.}}/T$  at 200-mm pressure for the same series in Table VIII. It will be noticed that according to the Trouton-Hildebrand constant all the amines except the trimethyl derivatives show a roughly comparable degree of association in the liquid phase prior to vaporization, a fact which may be ascribed to hydrogen bonding.

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29. J. H. Hildebrand, J. Am. Chem. Soc., 37, 970 (1915).

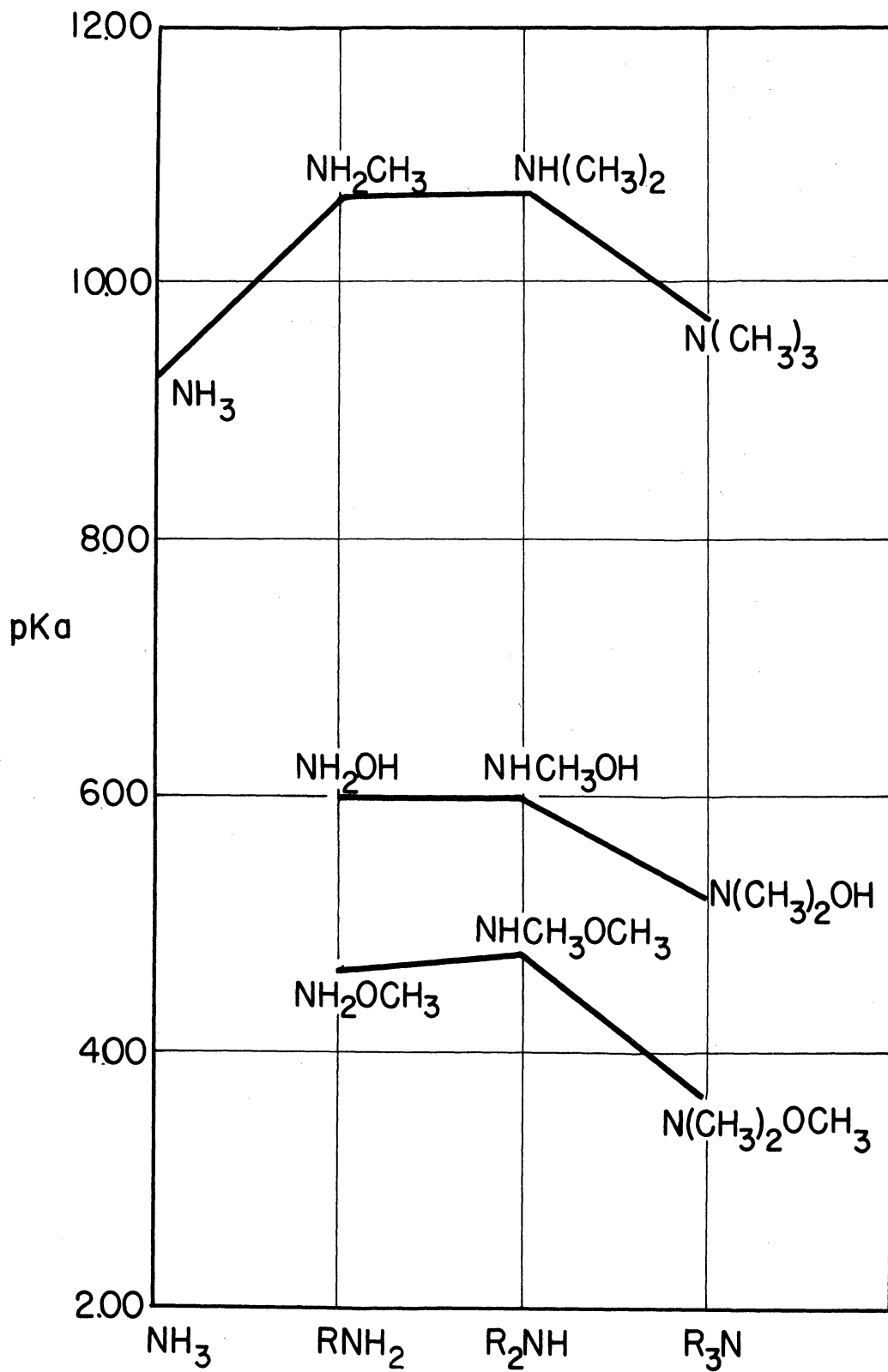


Fig. 1. The pKa values for  $\text{CH}_3$ ,  $\text{OH}$ , and  $\text{OCH}_3$  substituted amines.

TABLE VIII

A COMPARISON OF THE "TROUTON CONSTANT" AT A PRESSURE OF 200 MM WITH THE HILDEBRAND-TROUTON CONSTANT AT A UNIFORM VAPOR CONCENTRATION OF 0.00507 MOLE/LITER FOR A SERIES OF AMINES

Compound	$\Delta H_{\text{vap.}}$ 200 mm cal/mole	$T^{\circ}$ A	$\frac{\Delta H_{\text{vap.}}}{T}$	Temp. for Vap. Conc. of .00507 mole/liter	P for Vap. Conc. mm	$\Delta H_{\text{vap.}}$ at This Temp. cal/mole	$\frac{\Delta H}{T}$	Ref.
NH <sub>3</sub>	5,860	216	27.1	200	63	6,041	30.2	(a)
CH <sub>3</sub> NH <sub>2</sub>	6,770	240	28.2	224	72	6,860	30.5	(b)
(CH <sub>3</sub> ) <sub>2</sub> NH	7,100	252	28.2	236	76	7,330	31.1	(c)
(CH <sub>3</sub> ) <sub>3</sub> N	6,090	245	24.8	227	72	6,150	27.0	(c)
N <sub>2</sub> H <sub>4</sub>	10,230	351	29.1	337	107	10,280	30.5	(d)
NH <sub>2</sub> OH	16,600	361	46.0	352	106	17,266	49.0	(a)
NH <sub>2</sub> OCH <sub>3</sub>	8,400	290	29.0	273	84	8,483	31.0	(e)
H <sub>2</sub> O	10,070	340	29.6	325	105	10,202	31.3	(a)
CCl <sub>4</sub> (Ref.)	7,680	311	24.7	294	48	7,938	27.0	(a)

- (a) D. R. Stull, *Ind. Eng. Chem.*, **39**, 540 (1947).  
 (b) Aston *et al.*, *J. Am. Chem. Soc.*, **59**, 1743 (1937).  
 (c) T. E. Jordan. Vapor Pressures of Original Compounds. New York: Interscience Publishers, 1954, pp. 176 and 178.  
 (d) L. F. Audrieth and B. A. Ogg. Hydrazine. New York: John Wiley and Sons., Inc., 1951, p. 74.  
 (e) This investigation.

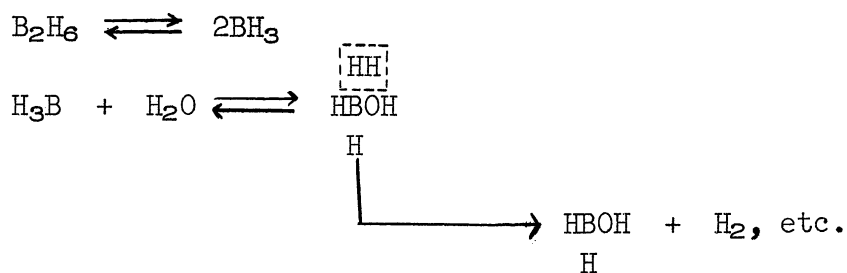
The value of 49.0 e.u. calculated from the literature data for the vapor pressure of hydroxylamine deserves further consideration. In comparison to the corresponding constants for the closely related water, hydrazine, ammonia, and O-methylhydroxylamine (Table VIII), this value is unusually high. In view of the instability of free hydroxylamine above 10°C, it is almost certain that the high value of  $\Delta S$  indicates some decomposition of the sample during the vapor-pressure measurement. Such an error in vapor pressure would result in a low value for the boiling point. The data for the more stable methyl derivatives of hydroxylamine suggest that the true boiling point of hydroxylamine is indeed above the recorded value of 111°C. For N-methylhydroxylamine the value is 115°C and for the N,N'-dimethylhydroxylamine the value is 100.6°C. These values suggest 125°C as a more reasonable boiling point for the pure H<sub>2</sub>NOH.

B. THE REACTION OF HYDROXYLAMINE AND ITS N-METHYL DERIVATIVES WITH DIBORANE (D. H. Campbell, T. C. Bissot, and R. W. Parry)

Abstract

Hydroxylamine-borane and N-methylhydroxylamine-borane have been prepared in impure form as solids at  $-112^{\circ}\text{C}$ . These lose  $\text{H}_2$  on warming to room temperature. Pure N,N-dimethylhydroxylamine-borane has been prepared as a volatile liquid, which is relatively stable at room temperature. The decomposition of the borane complex is catalyzed by  $\text{B}_2\text{H}_6$  and by the decomposition residues. The role of  $\text{B}_2\text{H}_6$  in the decomposition is interpreted in terms of a proposed reaction scheme.

Many of the reactions of the boron hydrides are assumed to occur through the addition of a Lewis base to the borane group followed by internal decomposition of the adduct. One of the mechanisms suggested for the hydrolysis of diborane<sup>1</sup> illustrates the transitory existence of the unstable addition complex:



The internal decomposition of such borane adducts is a question of some interest, yet many of these addition complexes, suggested as intermediates, are too unstable to make their direct study practical. In contrast, the N-methylhydroxylamineboranes seemed particularly suitable for such a study since the boron-nitrogen bonds should be of moderate stability and secondary reactions such as oxidation of the boron by the hydroxylamine and loss of hydrogen through interaction of protonic and hydridic hydrogens in the molecule should proceed with some ease. In addition, a study of the hydroxylamine addition compounds was of some practical interest because of the possibility of B-N-O polymer formation. The formation and decomposition of the borane adducts of hydroxylamine and of its N-methyl derivatives have been studied and the results are interpreted here in terms of a reaction mechanism for complex decomposition.

The Reaction of Diborane and Hydroxylamine.—Diborane and solid anhydrous hydroxylamine gave no evidence for reaction over the temperature range  $-186^{\circ}$  to  $-96^{\circ}\text{C}$ ; however, after the solid and gas had been standing in contact for several hours at  $-96^{\circ}\text{C}$ , the system was warmed up slightly and explosive interaction occurred.

1. H. G. Weiss and I. Shapiro, J. Am. Chem. Soc., 75, 1221 (1953).



In order to moderate the reaction, diethyl ether was used as a reaction medium.<sup>2</sup> Diborane reacted very slowly with a stirred ether suspension of anhydrous hydroxylamine at  $-112^{\circ}\text{C}$  without the liberation of significant amounts of hydrogen. Under these conditions the approximate stoichiometry of the process was given by the equation



In every run the ratio  $\text{NH}_2\text{OH}/\text{B}_2\text{H}_6$  deviated somewhat from the theoretical value of 2 and the deviation was always larger than the experimental error of measurement. This was a general observation applicable to hydroxylamine and both of its N-methyl derivatives but not to the O-methyl hydroxylamines.<sup>3</sup> See Table I. This fact is considered later.

TABLE I

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

Compound	Melting Point	Volatility	Ratio Amine/ $\text{B}_2\text{H}_6$ in Prep.**	Approx. Temp. at which 50% Decomp. in 24 hr, $^{\circ}\text{C}$
$\text{HONH}_2\text{BH}_3$	Solid at $-78^{\circ}$	None (Decomp.)	1.80	$-75$ (impure)
$\text{HONHCH}_3\text{BH}_3$	Liquid* at $-78^{\circ}$	None	1.92	15 (impure)
$\text{HON}(\text{CH}_3)_2\text{BH}_3$	$2^{\circ} - 4^{\circ}$	6 mm at $25^{\circ}$	1.92	25 (impure) 55 (pure)

\* Sample impure; low melting point may be due to impurities.

\*\* Each value is a result of several runs. The theoretical value is 2.

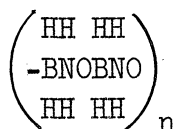
If the temperature of the ether insoluble hydroxylamine adduct of diborane was to rise slowly above  $-112^{\circ}\text{C}$ , hydrogen was liberated, probably through the interaction

2. The advantages of diethyl ether as a solvent in some boron hydride reactions have been demonstrated previously. Emeleus and Stone [J. Chem. Soc., 840-1 (1951)] failed to obtain exact stoichiometry for the reaction between diborane and non-solvated hydrazine, but Steindler and Schlesinger [J. Am. Chem. Soc., 75, 756 (1953)] obtained the compound  $\text{H}_3\text{BNH}_2\text{NH}_2\text{BH}_3$  with excellent stoichiometry in the presence of diethyl ether.

3. T. C. Bissot, D. H. Campbell, and R. W. Parry, this Report, p. 147.

of the hydroxyl hydrogen of hydroxylamine and the hydridic hydrogen of a borane group. The total amount of hydrogen liberated at various temperatures is shown in Fig. 1. The moles of hydrogen lost per mole of hydroxylamine used approached 1 at about 25°C and 2 at about 125°C. The product remaining after the loss of one mole of hydrogen was a white solid which dissolved in water, methanol, and ethanol with the evolution of small amounts of hydrogen. The material was insoluble in liquid ammonia, ether, benzene, toluene, and 1,4-dioxane. The product remaining after the loss of two moles of hydrogen dissolved only with difficulty in water, but readily in dilute acid or base.

The above facts suggest the formula



for the 25°C decomposition product; however, it is difficult to harmonize the above formulation with the data for hydrogen evolution at different temperatures shown in Fig. 1. One would expect that the temperature—hydrogen-evolution curve should show a break after the loss of one mole of hydrogen per hydroxylamine-borane. The curve shows a break after loss of only 2/3 of a mole of H<sub>2</sub> per HONH<sub>2</sub>BH<sub>3</sub>. This anomaly is attributed to the fact that increasing rigidity of the polymer prevented free interaction of the acidic and hydridic hydrogen in the addition complex. This postulate receives support from the observation that in a similar type of decomposition process the presence of a polyglycol ether solvent eliminated the change in rate after loss of 2/3 of a mole of hydrogen.<sup>3</sup> As the temperature was raised, the stoichiometry was complicated by the interaction of the protonic hydrogens attached to the nitrogen and the hydridic hydrogens of the borane group. Finally, direct pyrolysis of the borane group added further complication at temperatures above about 70°C.

The Reaction of Diborane and N-methylhydroxylamine.—This reaction, conducted only in ether, resembled the reaction of diborane and hydroxylamine except for minor points. The addition product of the N-methylhydroxylamine was a clear ether soluble liquid at -78°C. Above -78° hydrogen was lost, and the liquid increased in viscosity until the mass solidified near room temperature. No volatile products other than hydrogen were observed until the temperature was raised to 100°C and above. At this temperature methylamine contaminated with traces of ammonia was obtained. About 19% of the total nitrogen in the complex was recovered as methylamine. The polymerization upon loss of hydrogen parallels closely the process described previously for the hydroxylamine-borane.

The residue remaining in the tube after pyrolysis at 220°C was a yellow solid. Upon hydrolysis with dilute HCl enough additional hydrogen was obtained from the residue to bring the total "hydridic" hydrogen per molecule of complex up to two instead of the expected three. The recovery of methylamine at high temperatures and the loss of a hydridic hydrogen from the boron indicate a shift of the oxygen group to the boron and of a hydrogen to the nitrogen. This shift is considered elsewhere.<sup>3</sup>

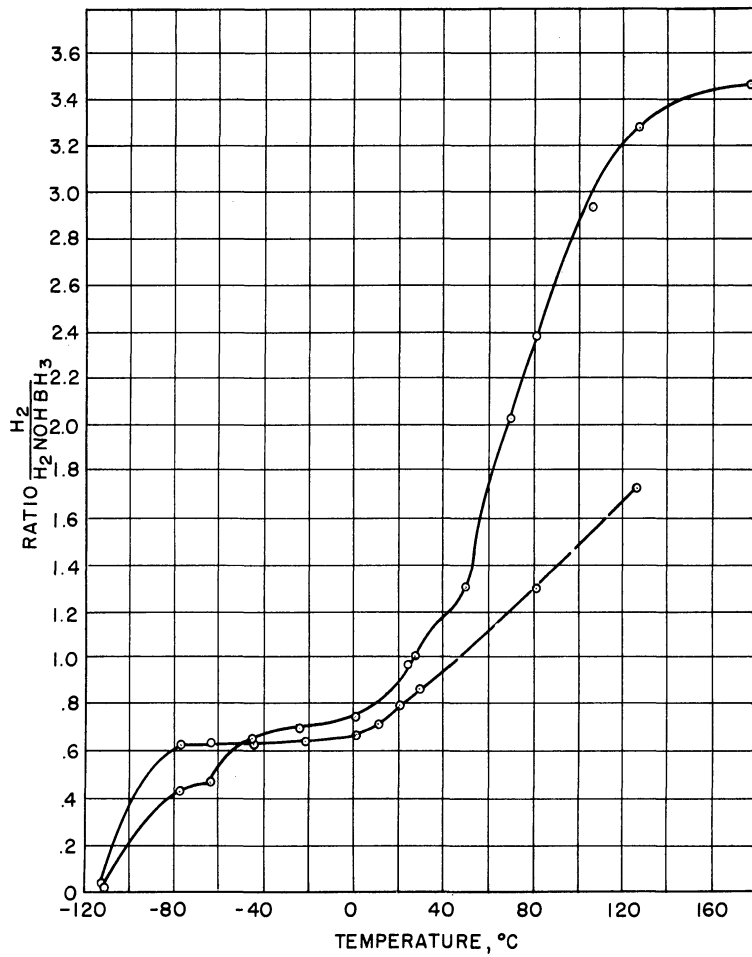


Fig. 1a. Mole ratio of hydrogen to  $H_2NOHBH_3$ .

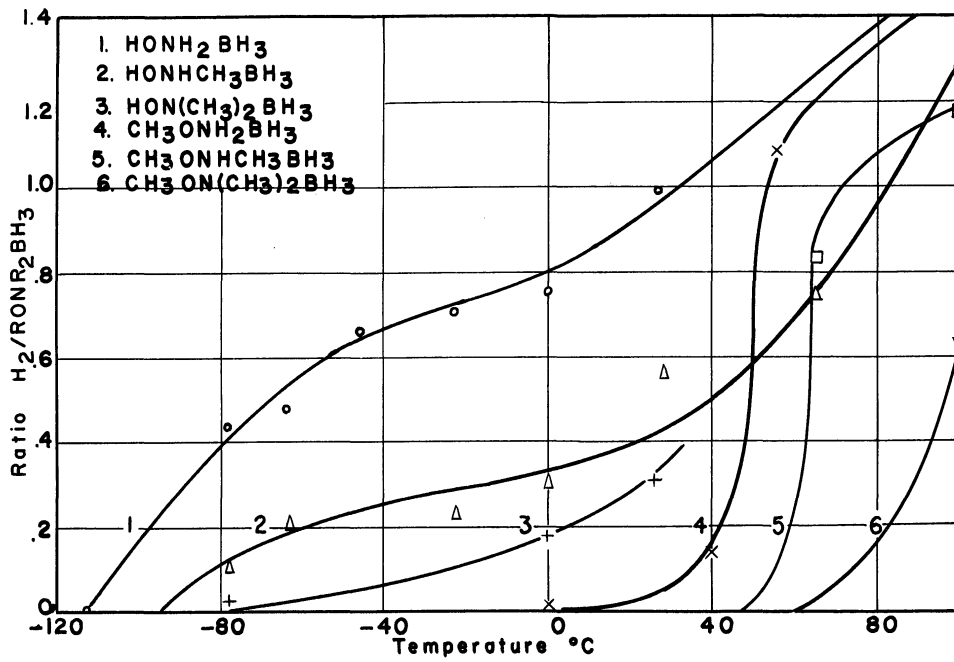


Fig. 1b. Decomposition curves of hydroxyl- and methyl-substituted hydroxylamine boranes.

The Reaction of N,N-Dimethylhydroxylamine and Diborane.—This addition reaction was conducted with and without ether as a solvent. In contrast to the observations with hydroxylamine, the reaction without a solvent was not explosive and gave stoichiometry comparable to that observed in the presence of ether. As in the two preceding cases, the ratio of  $\text{NOH}(\text{CH}_3)_2$  to  $\text{B}_2\text{H}_6$  deviated from the expected value of two; fortunately, however, the isolation of the pure N,N-dimethylhydroxylamine-borane and a study of its properties gave a reasonable explanation for the observed deviations in the entire series.

In the decomposition of the two previous compounds no volatile product other than hydrogen separated at temperatures below  $100^\circ\text{C}$ . In contrast, the pure N,N-dimethylhydroxylamine-borane could be distilled from the reaction mixture at  $25^\circ\text{C}$  as a liquid. The liquid had a vapor pressure of 6 mm at  $25^\circ\text{C}$ , a melting point of 2 to  $4^\circ\text{C}$ , and a molecular weight by vapor density at room temperature of  $70 \pm 6$ . (Theoretical for  $\text{HON}(\text{CH}_3)_2\text{BH}_3$  is 74.9.) The small weight of the sample, resulting from its low vapor pressure at  $25^\circ$ , accounted for the large experimental uncertainty. This uncertainty plus the known association of N,N-dimethylhydroxylamine in the vapor phase prevented the use of the pressure measurements for evaluating the degree of dissociation of the complex. The following analytical results were obtained for the pure N,N-dimethylhydroxylamine-borane:

	Observed	Theoretical
Hydridic Hydrogen	3.92	4.04
Boron	14.4	14.44
Nitrogen	18.6	18.69

When the pure complex was distilled from the rapidly decomposing system at room temperature, it turned out to be surprisingly stable. A pure sample standing at  $25^\circ\text{C}$  for five days was less than 5% decomposed. If, however, the pure liquid was returned to the tube containing the initial decomposition products, rapid evolution of hydrogen began immediately at room temperature. The yield of pure  $\text{HON}(\text{CH}_3)_2\text{BH}_3$  obtained from the early preparations, in which excess diborane was used, was found to correlate with the amount of undecomposed compound calculated from the observed hydrogen evolution. The results are shown in Table II.

When extra diborane was added to the pure compound, vigorous hydrogen evolution began. Data are summarized in Table III. Although small amounts of diborane were used up in the reaction, most of it was recovered and at least 12 moles of hydrogen were liberated for every mole of diborane consumed. The high ratio indicates that the effect of the diborane was definitely catalytic and no primary stoichiometric process including diborane was involved. On the other hand, the fact that small amounts of diborane were used up in a secondary process justifies the poor stoichiometry in all the reactions of diborane and the hydroxylamines.

The observation that excess  $\text{B}_2\text{H}_6$  catalyzes the decomposition suggested that better results would be obtained if an excess of amine were used rather than an excess of diborane. The prediction was verified by experiment. When the amine was

TABLE II

REACTION BETWEEN N,N-DIMETHYLHYDROXYLAMINE AND EXCESS DIBORANE

Solvent	Run Number		
	1 Ether	2 None	3 Ether
Ratio $\text{HON}(\text{CH}_3)_2/\text{B}_2\text{H}_6$	1.94	1.91	1.91
$\text{H}_2/\text{HON}(\text{CH}_3)_2$	0.43	0.72	0.32
% Complex Not Decomposed*	57	28	68
% Pure Complex Recovered	50	30	65

\*Based on hydrogen evolution.

TABLE III

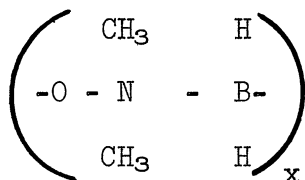
CATALYTIC DECOMPOSITION OF PURE N,N-DIMETHYLHYDROXYLAMINE-BORANE BY DIBORANE  
AT 25°C

	Trial 1	Trial 2
Mmoles $\text{B}_2\text{H}_6$ added per mmole of pure $\text{HON}(\text{CH}_3)_2\text{BH}_3$	.78	.14
Moles $\text{H}_2$ liberated per mole of pure $\text{HON}(\text{CH}_3)_2\text{BH}_3$	0.82 (0.5 hr)	1.07 (28 hr)
% added $\text{B}_2\text{H}_6$ which was recovered unchanged	91	35
Mmoles $\text{B}_2\text{H}_6$ consumed for each mmole of pure $\text{HON}(\text{CH}_3)_2\text{BH}_3$ decomposed	.07	.09
Mmoles $\text{H}_2$ released for each mmole $\text{B}_2\text{H}_6$ consumed	16	12

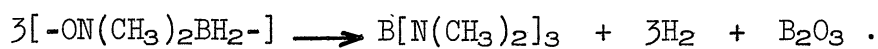
in excess, hydrogen evolution, prior to separation of the pure complex, corresponded to only 2.3% decomposition; when diborane was in excess, hydrogen evolution under comparable conditions corresponded to from 50 to 70% decomposition. Unfortunately, the N,N-dimethylhydroxylamine and its borane adduct have vapor pressures which are too close together to permit easy vacuum-line fractionation. Due to mechanical purification losses, only a 70% yield of the pure N,N-dimethylhydroxylamine-borane was recovered, although better separation procedures would undoubtedly have given higher yields. These observations suggest that pure hydroxylamine-borane and

N-methylhydroxylamine-borane might be prepared as stable compounds if a way could be found to minimize contact between the complex and the excess diborane. Unfortunately, the fact that these two amines are solids in ether at the reaction temperature means that diborane must be present in excess since separation of the unreacted amine from the adduct is difficult at low temperatures.

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



Since no suitable solvent was found, the value of x was not determined. The  $[\text{ON}(\text{CH}_3)_2\text{BH}_2-]$  polymer underwent further decomposition upon heating to high temperatures. A sample of  $\text{HON}(\text{CH}_3)_2\text{BH}_3$  upon prolonged pyrolysis at 100° yielded hydrogen equivalent to 1.25 moles  $\text{H}_2$  per mole  $\text{HON}(\text{CH}_3)_2\text{BH}_3$  plus small amounts of a high-boiling liquid. The type of thermal decomposition which might be expected is explained by the equation



The compound  $\text{B}[\text{N}(\text{CH}_3)_2]_3$  is reported as a liquid with low volatility at room temperature.<sup>4</sup>

In contrast to the behavior of the N-methylhydroxylamine-borane there was no evidence for a shift of oxygen group from nitrogen to boron and of a hydridic hydrogen from boron to nitrogen in the thermal decomposition of the N,N-dimethylhydroxylamine-borane.

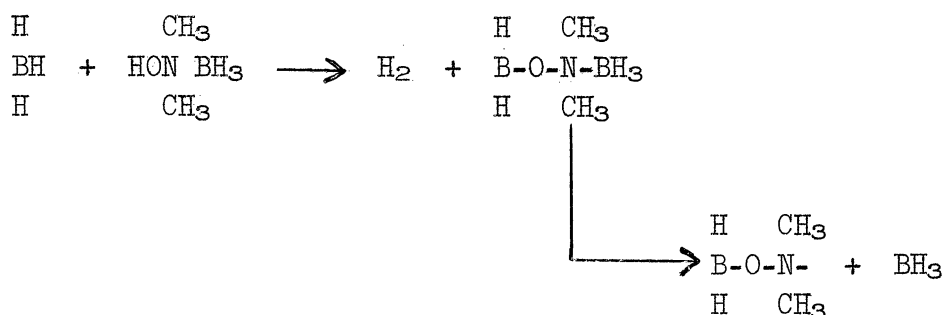
A sample of the N,N-dimethylhydroxylamine-borane was allowed to react with a small excess of trimethylamine. An 80% yield of  $(\text{CH}_3)_3\text{NBH}_3$  was obtained, and the amine displaced was identified as N,N-dimethylhydroxylamine.

Discussion.—The thermal decomposition of the N,N-dimethylhydroxylamine-borane was different in several respects from that of  $\text{HONH}_2\text{BH}_3$  and  $\text{HONCH}_3\text{HBH}_3$ . In the decomposition of the latter two compounds there was a range of about 100°C between the temperature at which a significant amount of hydrogen was first produced and the temperature at which one mole was collected. Furthermore, a change in rate of  $\text{H}_2$  evolution was noticed after loss of 2/3 of a mole of hydrogen but not after loss of one mole. On the other hand, pure  $\text{HON}(\text{CH}_3)_2\text{BH}_3$  was relatively stable at 25°C but decomposed rapidly when the temperature was raised just 30°. In addition, the rate

4. E. Wiberg and K. Schuster, Z. anorg. Chem., 213, 77 (1933).

of hydrogen evolution decreased almost to zero at 55°C after the expected one mole of hydrogen had been liberated. This difference can be attributed to the volatility of the N,N-dimethylhydroxylamine-borane and to the fact that the pure liquid product and the decomposition product do not appear to be mutually soluble. Since they separated as distinct phases, the polymerization which accompanied the loss of hydrogen did not impede the decomposition of the unreacted material. Furthermore, the decomposition of the dimethyl compound was not complicated by the loss of the hydrogen attached directly to nitrogen, as was the case with the other two complexes.

When carefully purified,  $\text{HON}(\text{CH}_3)_2\text{BH}_3$  was amazingly stable for a compound containing a protonic and hydridic hydrogen in the same molecule. The role of  $\text{B}_2\text{H}_6$  in promoting  $\text{H}_2$  evolution suggests a reasonable explanation for the stability of this pure material. In general, the coordination of the  $\text{BH}_3$  group to a base reduces the hydridic character of the attached hydrogens, the degree of reduction being almost proportional to the strength of the coordinate link which is formed. For example, a weakly complexed addition compound such as  $\text{F}_3\text{PBH}_3$  or  $\text{OCBH}_3$  is almost as reactive as diborane itself and inflames spontaneously in moist air. In contrast, the strongly complexed trimethylamine-borane is stable indefinitely in dry air and is only slowly hydrolyzed by liquid water. In  $\text{HON}(\text{CH}_3)_2\text{BH}_3$  it is logical to assume that the hydridic hydrogens of the borane group are sufficiently deactivated through coordination to prevent their interaction with the weakly acidic hydrogen of the  $-\text{OH}$  group. However, the unstabilized hydrogens on the diborane are basic enough to react readily with this protonic hydrogen. After formation of the B-O-N bond, the  $\text{BH}_3$  which was originally attached to the amine could be released to attack another molecule or to reform  $\text{B}_2\text{H}_6$ :



It would be logical to assume that the first step in the above process is the coordination of the  $\text{BH}_3$  to the  $\text{OH}$  group of the amine, though this is not proved. An explanation for the fact that a slight excess of diborane was always consumed in the reactions of the hydroxylamines with diborane can be based on the above mechanism. It is probable that this process occurs to some extent during complex formation and the second step of the interaction, involving release of the  $\text{BH}_3$  group, is not always quantitative. Excellent stoichiometry was obtained in the reaction of diborane and the O-methylhydroxylamines where the above process would be blocked.<sup>3</sup> It was also noticed that loss of hydrogen from the pure methoxyamine boranes was not catalyzed by diborane, an observation which is consistent with the above mechanism.

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

plosions were ever encountered in heating a hydroxylamine-borane after the addition compound was once formed. A sample of the N,N-dimethyl derivative was heated directly up to 100°C.

The explosion of the diborane-hydroxylamine mixture at low temperatures can be attributed to sudden vigorous interaction of previously unreacted condensed phases or perhaps to impurities. Hydroxylamine itself will detonate if subjected to sudden intense heating, but the free base is much less subject to detonation if coordinated.<sup>3</sup>

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

The displacement of N,N-dimethylhydroxylamine by trimethylamine is consistent with the fact that the latter is the stronger base.<sup>5</sup>

### Experimental.—

#### a. Materials.

1. Hydroxylamine, preparation and handling—Free hydroxylamine was prepared by the reaction of sodium butoxide with hydroxylammonium chloride suspended in butanol.<sup>6</sup> The free base decomposes rapidly above 15°C and it picks up water and carbon dioxide avidly. These properties necessitated the use of the special cooled weighing bottle shown in Fig. 2. In such a device the amine was kept cool, yet weighable.

The plate-like hydroxylamine crystals were stored in anhydrous butanol at -10°C until needed; they were then filtered off, washed rapidly with cold ether, sucked dry, and transferred to the cooled weighing bottle (Fig. 2). After weighing, the crystals were dumped into the reaction tube, which was immediately cooled with ice-water; the tube was rapidly attached to the vacuum line and evacuated. The special weighing bottle was tared. In order to determine the accuracy which can be obtained by handling the hydroxylamine in this manner, weighed samples of the free base were titrated with standard acid. Results on several samples indicated that the weight of the sample was reproducibly about 8% above the theoretical weight obtained from the titration. The discrepancy is undoubtedly due to ether adhering to the crystals. An 8% correction was applied to the weights of all samples handled in the above manner.

2. N-methyl and N,N-dimethylhydroxylamines—The preparation and properties of these free bases are described elsewhere.<sup>5</sup>

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5. T. C. Bissot and R. W. Parry, this Report, p. 118.

6. C. D. Hurd in Inorganic Synthesis. Vol. I. New York: McGraw-Hill Book Co., Inc., 1939, p. 87.



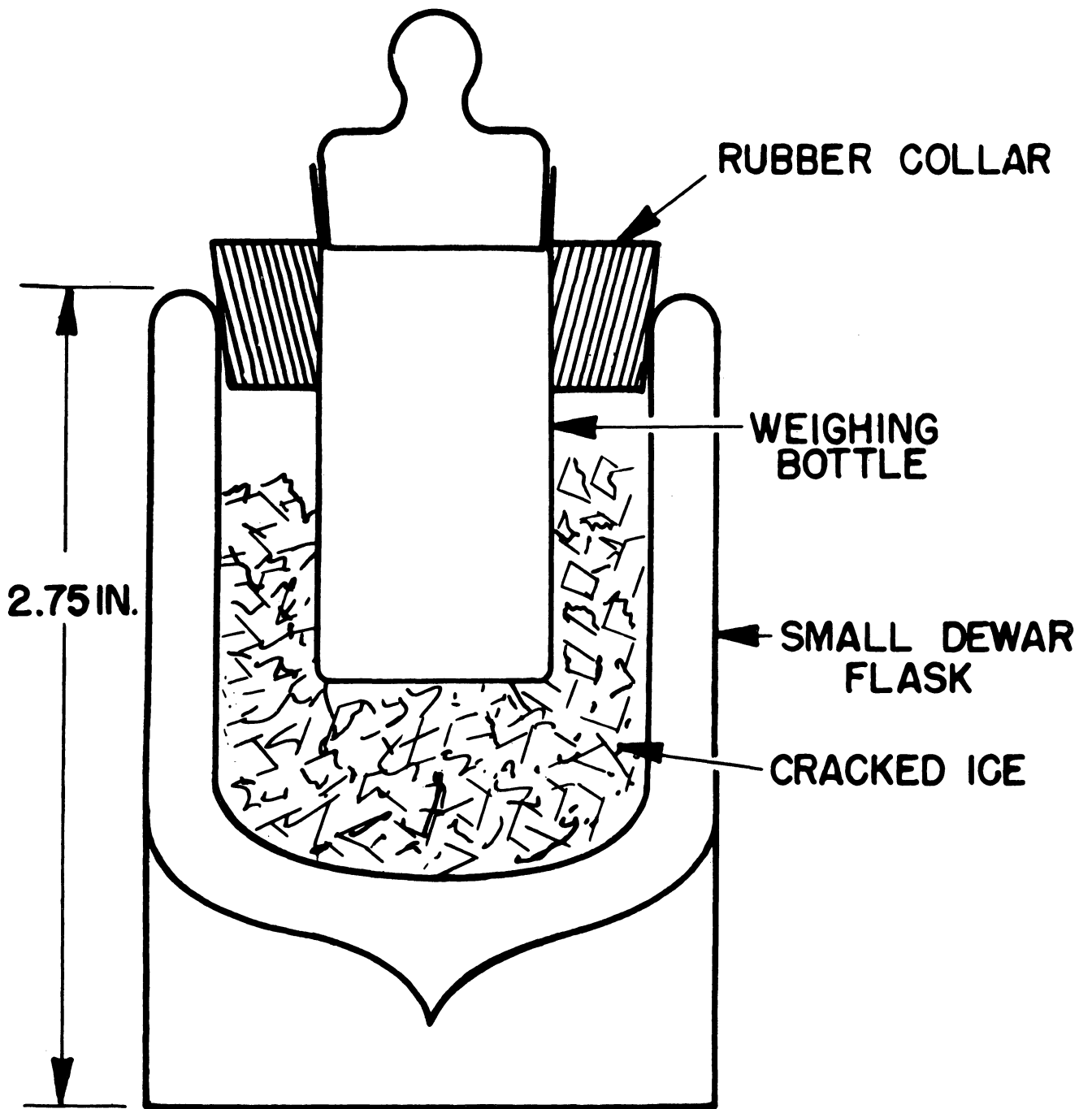


Fig. 2. Special weighing unit for hydroxylamine.

3. Diborane—Diborane was prepared from  $\text{LiAlH}_4$  and boron trifluoride etherate as described elsewhere.<sup>7</sup>

b. General Procedure for Compound Formation.

The generalized procedure for conducting reactions is described below. Some minor deviations from this procedure were used in specific cases; such details are available in dissertation form.<sup>8,9</sup>

1. Diborane in excess—The reaction vessel was a 20-mm Pyrex tube, about 8 inches long, attached to the conventional high-vacuum system by means of a 24/40  $\text{S}$  joint. The tube was equipped with an automatic, electromagnetically operated, plunger-type stirrer. In a typical run an approximately 2-to-6-mmole sample of the amine was weighed out in an evacuated micro weighing tube or in the previously described chilled weighing bottle.  $\text{HON}(\text{CH}_3)_2$  and  $\text{HON}(\text{CH}_3)\text{H}$  were vacuum distilled directly into the reaction vessel from the weighing tube; hydroxylamine was transferred as described earlier. A 1-to-6-ml aliquot of anhydrous diethyl ether, which had been dried for several days over  $\text{CaH}_2$ , was distilled into the reaction tube and the system was stirred until a solution of uniform suspension was obtained. (When no solvent was used, this step was omitted.)

The system was then frozen with liquid nitrogen and a carefully measured amount of diborane, about 10 to 20% in excess of the stoichiometric amount, was distilled into the tube. The system was then warmed to  $-112^\circ\text{C}$  by means of a  $\text{CS}_2$  slush bath and stirring was continued for the required period. The free hydroxylamine, which was insoluble in ether, reacted very slowly and required up to 20 hours for nearly complete reaction. The more ether soluble methyl and dimethyl derivatives gave complete reaction in two hours or less at  $-112^\circ\text{C}$ .

The system was frozen with liquid nitrogen; noncondensable gases were pumped off with a Toepler pump and passed through a packed trap cooled with liquid nitrogen. The total amount of gas was measured and was identified by a molecular-weight determination. The temperature of the original reaction vessel was raised to  $-78^\circ\text{C}$ ;  $\text{H}_2$  was collected until its rate of evolution approached zero, then it was pumped off and measured; the excess diborane and the ether solvent were distilled out and very carefully fractionated in the vacuum line. The recovered diborane was measured and the amount used in the reaction was calculated.

Because of the extremely slow reaction between diborane and hydroxylamine, some question as to the stoichiometry arose. For this reason the rate of absorption of  $\text{B}_2\text{H}_6$  by an ether suspension of hydroxylamine was studied at  $-112^\circ\text{C}$ .

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7. I. Shapiro, H. G. Weiss, M. Schmick, S. Skolnik, and G. B. L. Smith, *J. Am. Chem. Soc.*, 74, 901 (1952).

8. T. C. Bissot, doctoral dissertation, Univ. of Mich., Ann Arbor, 1955.

9. D. H. Campbell, doctoral dissertation, Univ. of Mich., Ann Arbor, 1953.

At definite time intervals unreacted  $B_2H_6$  was distilled from the system, purified, measured, and returned to the reactor. Quantitative removal of  $B_2H_6$  from an ether solution at  $-112^\circ C$  was a slow and difficult operation; hence, a standard separation procedure was used which gave almost complete recovery and when applied to an ether solution of diborane would give an apparent rate of  $B_2H_6$  absorption somewhat greater than the actual rate, but the ultimate stoichiometry would be unaffected. Data plotted in Fig. 3 show that the rate of complex formation is slow, but the ratio of  $B_2H_6$  to  $NH_2OH$  approaches the theoretical value of 0.5 as a limit.

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

c. Thermal Decomposition of the Borane Adducts.

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

d. Analytical Methods.

1. Hydridic hydrogen—Determined by heating the sample for several hours in a sealed tube with 6 N HCl. The hydrogen gas evolved was measured and identified in the vacuum system.

2. Boron—A modification<sup>10</sup> of the identical pH method of Foote<sup>11</sup> was applied to the microdetermination of boron in the presence of nitrogen compounds. The acid solution from hydrolysis was adjusted to a pH value very close to 7; the solution was then saturated with mannitol and the boric acid complex was titrated by bringing the system back to the same pH of 7. Excellent results were obtained when the method was applied to known standards.

3. Nitrogen—Nitrogen was usually determined by the micro Kjeldahl method. The hydroxylamines were reduced to ammonia by digestion with glucose in the presence of a  $K_2SO_4$ - $CuSO_4$  catalyst.

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10. R. W. Parry, D. H. Campbell, D. R. Schultz, S. G. Shore, T. C. Bissot, and R. C. Taylor. The Chemistry of Boron Hydrides. Eng. Res. Inst., Univ. of Mich., Annual Report Project 1966-1-P (1954).

11. F. J. Foote, Ind. Eng. Chem., Anal. Ed., 4, 39 (1932).

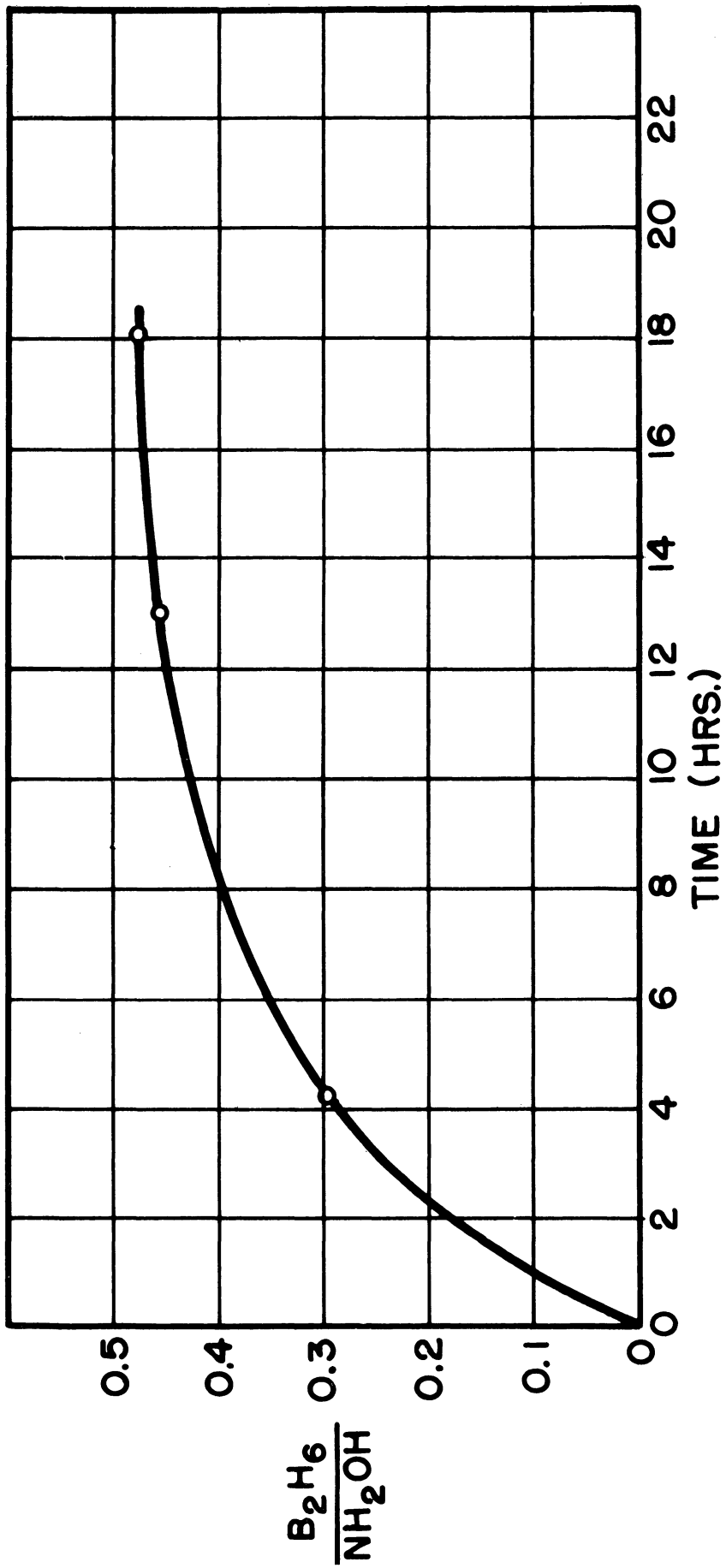


Fig. 3. Reaction of diborane with hydroxylamine at  $-112^{\circ}C$ .

C. THE REACTION OF O-METHYLHYDROXYLAMINE AND ITS N-METHYL DERIVATIVES WITH DIBORANE<sup>1</sup>  
(T. C. Bissot, D. H. Campbell, and R. W. Parry)

Abstract

The borane adducts of O-methyl, O,N-dimethyl, and O,N,N-trimethyl hydroxylamine have been prepared. Their thermal decomposition and hydrolysis have been studied. A mechanism for the shift of a methoxy group from nitrogen to boron and of a hydrogen from boron to nitrogen is suggested.

In another publication<sup>2</sup> the reaction of diborane with hydroxylamine and its N-methyl derivatives was considered. Structural and mechanistic arguments suggested that the chemistry of O-methylhydroxylamine-borane, and its N-methyl derivatives, ( $\text{CH}_3\text{ONR}_2\text{BH}_3$ ,  $\text{R} = \text{H}$  or  $\text{CH}_3$ ), should differ appreciably from that of hydroxylamine-borane and its N-methyl derivatives, ( $\text{HONR}_2\text{BH}_3$ ). The preparation, properties, and chemistry of the O-methyl-hydroxylamine boranes are considered herein.

O-Methylhydroxylamine-Borane,  $\text{CH}_3\text{ONBH}_3$  ---  
 $\begin{matrix} \text{HH} \\ | \\ \text{B} \\ | \\ \text{HH} \end{matrix}$

a. Preparation and Characterization.

In the presence of diethyl ether pure O-methylhydroxylamine and pure diborane react to produce O-methylhydroxylamine-borane. The observed stoichiometric ratios of  $\text{CH}_3\text{ONH}_2$  to  $\text{B}_2\text{H}_6$  for five separate runs were in the range 1.98-2.01. In the absence of ether the stoichiometry was poor in some cases and hydrogen gas was evolved at low temperatures. The pure white solid addition compound melts sharply at 55°C, with rapid evolution of hydrogen gas. Its solubility in ether is appreciable at room temperature but falls off as the temperature is lowered. Some of the solid could be sublimed slowly and with difficulty at 40°C in high vacuum. Decomposition was a competing process.

After hydrolysis of  $\text{CH}_3\text{ONH}_2\text{BH}_3$  with dilute hydrochloric acid, the following analytical data were obtained: hydridic hydrogen: obs. 4.63%, theor. 4.96%; boron: obs. 17.8%, theor. 17.77%. The amount of O-methylhydroxylamine hydrochloride in the hydrolysis product was estimated roughly from a titration curve on an aliquot. At least 93% of the nitrogen was still present as  $\text{CH}_3\text{ONH}_2$ .

When an ethereal solution of  $\text{CH}_3\text{ONH}_2\text{BH}_3$  was treated with a slight excess of  $\text{BF}_3$ , no  $\text{B}_2\text{H}_6$  was released. In view of earlier mechanistic arguments,<sup>2</sup> it is significant to note that  $\text{B}_2\text{H}_6$ , which catalyzed hydrogen loss from pure N-methylhydroxylamine-borane, did not catalyze the decomposition of pure O-methylhydroxylamine-borane. Attempts to displace  $\text{CH}_3\text{ONH}_2$  from the complex by the stronger base<sup>3</sup>  $\text{N}(\text{CH}_3)_3$  gave only a 22% yield of  $(\text{CH}_3)_3\text{NBH}_3$ . A competing reaction was loss of hydrogen from the complex, a process which appeared to be catalyzed by the presence of trimethylamine. Thirty-three percent of the original

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1. Abstracted from doctoral dissertations submitted to the Horace H. Rackham School of Graduate Studies of The University of Michigan by T. C. Bissot and D. H. Campbell.

2. D. H. Campbell, T. C. Bissot, and R. W. Parry, this Report, p. 134.

3. T. C. Bissot and R. W. Parry, this Report, p. 118.

complex decomposed through hydrogen loss. The foregoing observation was of importance in interpreting data obtained in early attempts to synthesize  $\text{CH}_3\text{ONH}_2\text{BH}_3$ .

In early synthetic trials the adduct lost hydrogen at low temperatures and a viscous liquid remained after the ether was removed. It was found that a small amount of ammonia, contaminating the O-methylhydroxylamine, was responsible for the low-temperature hydrogen loss; very pure O-methylhydroxylamine gave a relatively stable borane adduct. The ammonia was surprisingly effective; a mixture containing nine mole percent  $\text{NH}_3$  with ninety-one mole percent  $\text{CH}_3\text{ONH}_2$  reacted with diborane in ether to give off hydrogen such that the ratio  $\text{H}_2/\text{CH}_3\text{ONH}_2\text{BH}_3$  (theor.) was 0.48 after one hour. After low-temperature hydrogen loss, varying amounts of a weakly complexed, approximately one-to-one mixture of diethyl ether and  $\mu$ -monoamino-diborane,  $\text{H}_2\text{NB}_2\text{H}_5$ , were isolated from the system. The production of  $\text{H}_2\text{NB}_2\text{H}_5$  by such a low-temperature reaction is unexpected. The foregoing data suggest that O-methylhydroxylamine is effective in catalyzing low-temperature hydrogen loss from the ammonia-borane addition compounds in the presence of excess  $\text{B}_2\text{H}_6$ .  $\text{H}_2\text{NB}_2\text{H}_5$  is a product.<sup>4</sup> On the other hand, both ammonia and trimethylamine were effective in catalyzing hydrogen loss from  $\text{CH}_3\text{ONH}_2\text{BH}_3$ . This was the only O- or N-methylhydroxylamine-borane which was shown to be unstable in the presence of these bases. The mode of base action is not clear.

#### b. Pyrolysis of O-Methylhydroxylamine-Borane.

The thermal decomposition of  $\text{CH}_3\text{ONH}_2\text{BH}_3$  occurred in two ways. If it was heated rapidly to approximately  $90^\circ\text{C}$ , a violent detonation resulted. If it was heated slowly, hydrogen was evolved at a slow rate until the solid melted at  $55^\circ\text{C}$ . The rate of  $\text{H}_2$  evolution increased markedly when the liquid phase appeared; within ten minutes or less at  $55^\circ\text{C}$  the amount of hydrogen evolved was such that the ratio  $\text{H}_2/\text{CH}_3\text{ONH}_2\text{BH}_3$  amounted to 0.66. At this point the liquid became increasingly viscous and the rate of hydrogen evolution dropped sharply. After four days at  $55^\circ\text{C}$  the last one-third of a mole of  $\text{H}_2$  was obtained.

During heating at  $55^\circ\text{C}$  a complex solid mixture of  $\text{NH}_3$ ,  $\text{B}(\text{OCH}_3)_3$ , and in some cases  $\text{CH}_3\text{OH}$  sublimed from the reaction vessel. The chief component of the mixture was the weakly associated solid  $\text{H}_3\text{NB}(\text{OCH}_3)_3$ . In the vapor phase the complex dissociated completely to  $\text{H}_3\text{N}$  and  $\text{B}(\text{OCH}_3)_3$ . The volatile solid always contained a slight excess of boron over nitrogen.

Hydrogen evolution from the original viscous mass did not stop at one mole but continued at a slow rate. After the loss of one mole of hydrogen and the evolution of considerable trimethylborate from the system, the residue could be heated safely above  $90^\circ\text{C}$ . The viscous mass changed slowly into a white solid as the temperature was raised. After heating to  $300^\circ\text{C}$ , the residue was analyzed. The empirical formula for the solid was  $\text{BN}_{1.12}(\text{OCH}_3)_{0.1}\text{H}_{1.3}$ . It is important to

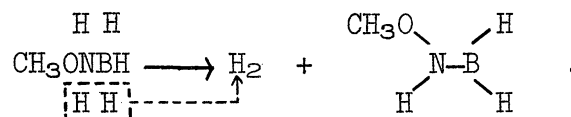
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4. All variables important in obtaining good yields of  $\text{H}_2\text{NB}_2\text{H}_5$  from mixtures of  $\text{NH}_3$ ,  $\text{B}_2\text{H}_6$ , and  $\text{CH}_3\text{ONH}_2$  were not studied systematically. Yields of  $\text{H}_2\text{NB}_2\text{H}_5$  were rather erratic, varying from good to poor. Catalysis of hydrogen loss was definite.

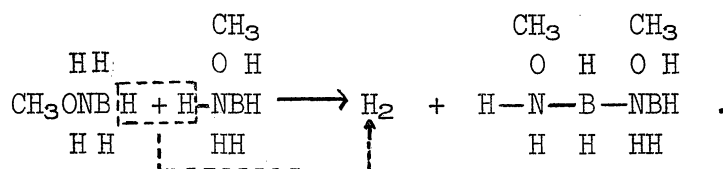
note that more than 90% of the original methoxy content of the compound was sublimed from the system, largely as trimethylborate.

The sharp break in the rate of hydrogen evolution after loss of only two-thirds of one mole of hydrogen was difficult to correlate with structural or mechanistic arguments for the process. Accordingly, pure O-methylhydroxylamineborane was prepared, and its rate of decomposition at 55°C was studied in solution as a function of dilution. Diethyleneglycol dimethylether was chosen as a suitable solvent. Figure 1 shows decomposition rate data for (1) the pure compound, (2) a 50% solution of the complex in the polyglycol ether, and (3) a 10% solution. The previously unexplained sharp break in rate after loss of only two-thirds of a mole of hydrogen disappeared when the solvent was introduced. Such an observation suggests that the break is associated with the rapidly increasing viscosity of the decomposing mass. Reduced mobility of interacting groups reduces the rate of gas evolution. More detailed treatment of the data given below lend further support to such an argument.

The rate data of Fig. 1 can be used to differentiate between intramolecular and intermolecular loss of hydrogen from the complex. If the liberated hydrogen were produced by an intramolecular reaction, the process would be first order and one mole of hydrogen would be evolved per mole of borane adduct:



The resulting unsaturated product would be expected to polymerize. If the hydrogen were produced by an intermolecular process, the kinetics should be higher than first order, but the stoichiometry would be the same as for the first-order process:



Further reaction between the monomer and the dimer or polymer should give long chains. Both intra- and intermolecular processes would be complicated by the partial loss of a second mole of hydrogen, since hydrogens are still available on boron and nitrogen. Crosslinking of chains would thus be expected.

In Fig. 1 the fraction of complex 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  $\text{CH}_3\text{ONH}_2\text{BH}_3$ . The first-order rate equation can be converted to the form

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

From this form it is apparent that the fraction decomposed at any time would be

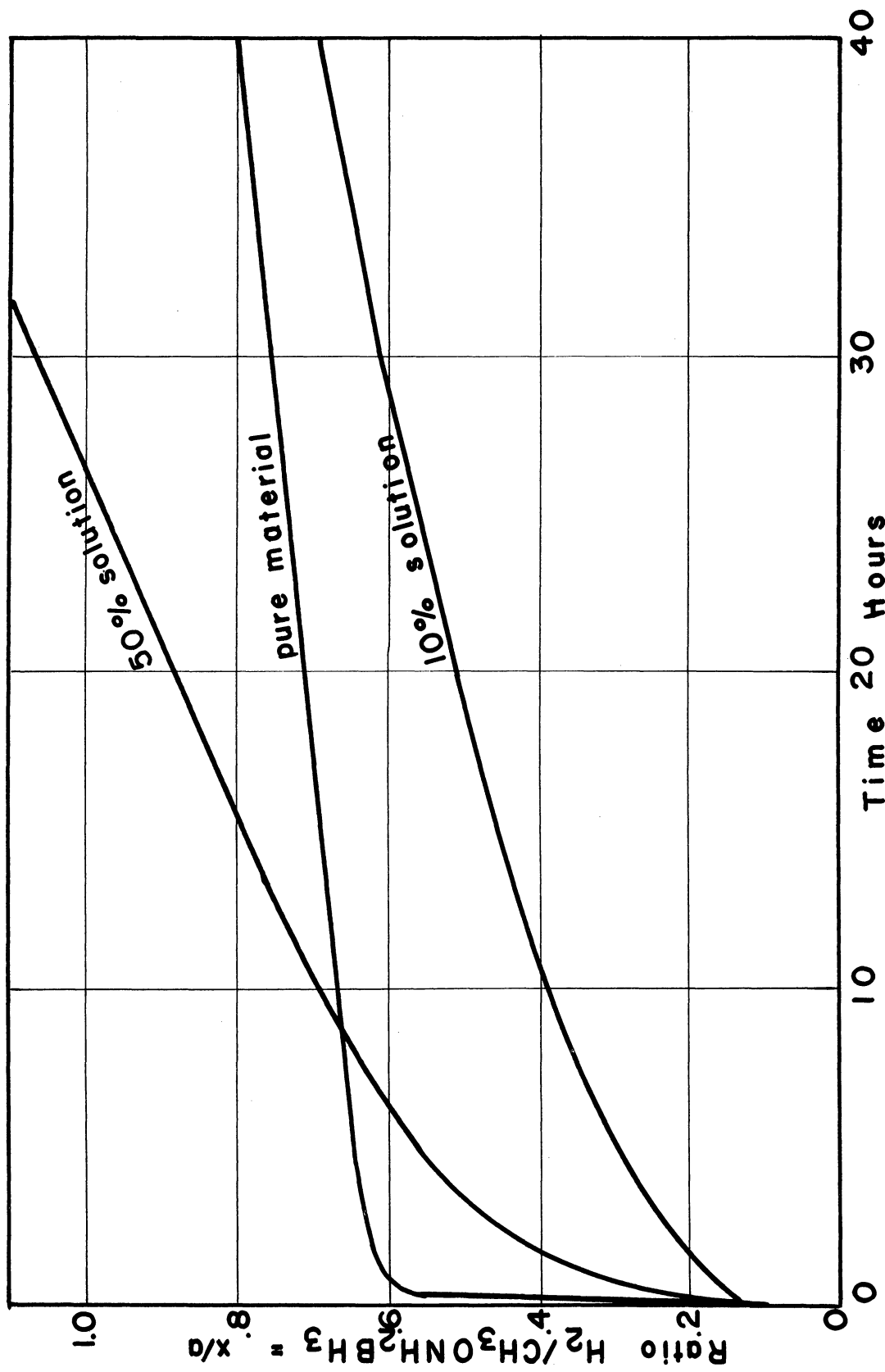


Fig. 1. Decomposition of  $\text{NH}_2\text{OCH}_3 \cdot \text{BH}_3$  at  $55^\circ\text{C}$ .

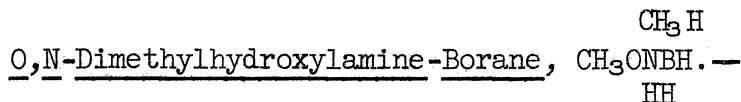


independent of the volume of the solution if the reaction were first order. The data in Fig. 1 thus provide strong evidence against intramolecular loss of hydrogen under the conditions used. A simplified treatment of the solution curves in Fig. 1 gives an apparent order of about 2 for the process.

The intermolecular decomposition indicated by the rate data produces polymerization, a result which is consistent with the increasing viscosity of the residue as hydrogen is lost. Increasing viscosity of the system would be expected to retard an intermolecular process but not an intramolecular process.

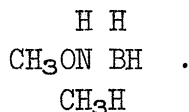
c. Hydrolysis of O-Methylhydroxylamine-borane.

Acid hydrolysis of  $\text{CH}_3\text{ONH}_2\text{BH}_3$  gave the expected hydrochloride salt of the base along with boric acid; in contrast, basic hydrolysis of the complex gave reduction of the O-methylhydroxylamine to ammonia and only two of the expected three hydridic hydrogens of the borane group. A shift of hydrogen from boron to nitrogen and of a methoxy group from nitrogen to boron took place in basic solution. The shift is comparable to that observed in the thermal decomposition process.



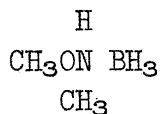
a. Preparation and Characterization.

O,N-dimethylhydroxylamine will react with diborane to produce



Ether was acceptable but not necessary as a solvent. In contrast to the case of O-methylhydroxylamine, excellent stoichiometry and a pure product resulted from the interaction of diborane and the free, nonsolvated base. See Table I.

The liquid



froze at about  $-22^\circ\text{C}$ . Vapor pressure at room temperature could not be measured with the mercury manometer on the system, but the liquid could be distilled at room temperature under high vacuum without decomposition. Analysis gave a B/N/hydridic H ratio of 1/0.97/2.92. Upon hydrolysis with hydrochloric acid the original amine was recovered and identified as the hydrochloride salt.

When an ether solution of  $\text{CH}_3\text{ONHCH}_3\text{BH}_3$  was stirred overnight with an excess of  $\text{N}(\text{CH}_3)_3$  at  $0^\circ\text{C}$ , an 86% yield of  $(\text{CH}_3)_3\text{NBH}_3$  was recovered. There was no hydrogen evolution in this displacement reaction, as there was in the similar experiment with  $\text{CH}_3\text{ONH}_2\text{BH}_3$ .

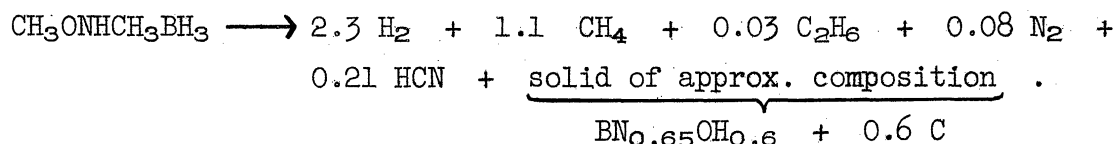
TABLE I

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

Compound	Melting Point	Volatility	Ratio Amine/B <sub>2</sub> H <sub>6</sub> in Preparation	Approx. Temp. at Which 50% Decomp. in 24 hr., °C
HONH <sub>3</sub> BH <sub>3</sub>	Solid decomp.	Nonvolatile	1.80	-75
HONHCH <sub>3</sub> BH <sub>3</sub>	Liquid	Nonvolatile	1.92	15
HON(CH <sub>3</sub> ) <sub>2</sub> BH <sub>3</sub>	2°-4°	6 mm 25°	1.92	25 as prep. 55 pure
CH <sub>3</sub> ONH <sub>2</sub> BH <sub>3</sub>	55°	Slightly volatile 40°	2.00	55
CH <sub>3</sub> ONHCH <sub>3</sub> BH <sub>3</sub>	-23° to -21°	Slightly volatile 25°	1.97	65
CH <sub>3</sub> ON(CH <sub>3</sub> ) <sub>2</sub> BH <sub>3</sub>	-16.5°	3.8 mm 26°	1.99	90

## b. Pyrolysis of O,N-Dimethylhydroxylamine-Borane.

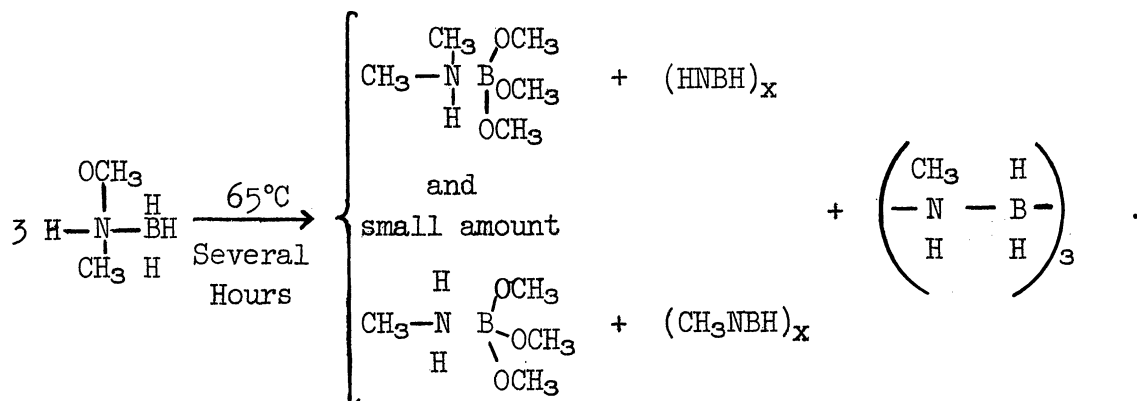
CH<sub>3</sub>ONHCH<sub>3</sub>BH<sub>3</sub> is more stable than the O-monomethylhydroxylamine adduct. Only traces of H<sub>2</sub> were liberated in its preparation and storage at room temperature. As in the previous case, both explosive and nonexplosive decomposition were observed. Explosive decomposition, brought about by heating the compound rapidly to 100°C, is obviously a very complex process. The stoichiometry for one sample was obtained from an overall analysis of explosion products. The process is approximated by the following empirical equation:



The quantitative features of the above equation probably vary from one explosion to another, but the qualitative features are of interest. Hydrogen is to be expected in view of the ease with which hydrogen evolution occurs from compounds of this type; nitrogen is a normal explosion product of nitrogen compounds. The appearance of methane and ethane suggests methyl radicals as an intermediate; their reduction gives methane, their combination gives ethane. The appearance of HCN was rather unexpected, but can be rationalized in terms of the original

HCN linkage in the molecule.

The nonexplosive decomposition which results from storage of the compound at 65°C for several hours differs markedly from the explosive decomposition. The overall stoichiometry is approximated by the following equation:



The compound  $(\text{CH}_3\text{NHBH}_2)_3$ , first prepared as a definite compound by the above process, has been described elsewhere.<sup>5</sup> It is significant that the amine bound to trimethylborate was largely dimethylamine. Much smaller amounts of methylamine were found. A shift of methyl groups from one nitrogen to another in a controlled disproportionation reaction is implied.

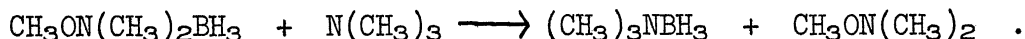
#### c. Hydrolysis of O,N-Dimethylhydroxylamine-Borane.

Hydrolysis reactions followed closely the pattern set in the hydrolysis of O-methylhydroxylamine-borane. Acid hydrolysis produced boric acid and the salt of O,N-dimethylhydroxylamine. Hydrolysis with 50% KOH in a sealed tube at 100°C produced a shift of methoxy and hydrogen to give methylamine as the principal basic product (27% yield) in a complex mixture of amines. Pure  $\text{CH}_3\text{ONHCH}_3$  was not decomposed when heated under similar conditions with 50% KOH. Only two of the three hydridic hydrogens on the borane group were ever released as  $\text{H}_2$ .

#### O,N,N-Trimethylhydroxylamine-Borane.

##### a. Preparation and Characterization.

$\text{CH}_3\text{ON}(\text{CH}_3)_2$  reacted with diborane without a solvent to give  $\text{CH}_3\text{ON}(\text{CH}_3)_2\text{BH}_3$ . Stoichiometry of the process was excellent. The pure addition compound melts at -16.5° to -16.0°C and has a vapor pressure of 3.8 mm at 25°C. An equimolar mixture of  $\text{CH}_3\text{ON}(\text{CH}_3)_2\text{BH}_3$  and trimethylamine,  $\text{N}(\text{CH}_3)_3$ , reacted as indicated:



Ninety-eight percent of the original  $\text{CH}_3\text{ON}(\text{CH}_3)_2$  was recovered. No  $\text{H}_2$  was evolved.

##### b. Pyrolysis of O,N,N-Trimethylhydroxylamine-Borane.

In contrast to the behavior of O-methyl and O,M-dimethylhydroxylamine boranes,

5. T. C. Bissot and R. W. Parry, J. Am. Chem. Soc., 77, 3481 (1955).

O,N,N-trimethylhydroxylamine-borane did not undergo an explosive decomposition when heated rapidly to 100°C in a sealed tube. At this temperature slow decomposition took place. All products were volatile. The molar ratio of hydrogen produced to O,N,N-trimethylhydroxylamine-borane used was 0.64. Trimethylborate,  $B(OCH_3)_3$ , was isolated as one of the products. The remainder of the volatile components were fractionated extensively, but no pure compounds could be separated.

c. Hydrolysis of O,N,N-Trimethylhydroxylamine-Borane.

Hydrolysis of  $CH_3ON(CH_3)_2BH_3$  with 50% KOH for two hours at 100° in a sealed tube gave no evidence for a shift of methoxy or hydrogen as had been observed in the two preceding cases. About 92% of the original base and 90% of the hydridic hydrogen in the compound were recovered after hydrolysis.

Discussion.—

a. Loss of Hydrogen from the Borane Adducts of the Methylhydroxylamine Derivatives.

The role played by both the complexed amine and the free diborane in the loss of hydrogen from the amine-borane complex is of interest in connection with mechanistic arguments suggested earlier.<sup>2</sup> If one assumes that hydrogen evolution from the impure complex results from the interaction of a protonic hydrogen on the amine and a hydridic hydrogen on the attacking borane group, then the temperature for loss of hydrogen from the complex should correlate with the relative acidity of the hydrogen atoms on the amine.<sup>6</sup>

In Table I selected chemical properties of all hydroxylamine-borane addition compounds are summarized. The temperatures at which 50% decomposition of the impure complex occurred in 24 hours are listed. As expected, the O-methylhydroxylamine-borane adducts are more stable than the compounds containing a free hydroxyl group. Furthermore, if one assumes the usual electron-donating power attributed to alkyl radicals, the inductive effect of the methyl groups would reduce the acidic character of the remaining hydrogen atoms on the amine whenever a hydrogen is replaced by an alkyl radical. In general, the decomposition temperature of the amine-borane adducts increases where a methyl group replaces a hydrogen attached to the nitrogen. Other factors such as entropy of activation also contribute to this result.

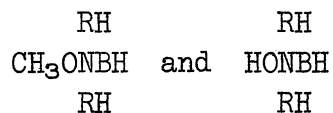
The poor stoichiometry observed in the reaction between diborane and those hydroxylamines which contain a free -OH group has been attributed to interaction of the -OH and borane groups.<sup>2</sup> This argument finds support in the current study since stoichiometry was always excellent in the reaction between diborane and pure O-methylhydroxylamines where no free -OH group was present.

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6. The relative acidic character of the secondary hydrogens on the amines is not necessarily the reverse of the primary basic strength of the amines as measured in water.<sup>3</sup>

b. The Hydride-Methoxy Shift in Pyrolysis.

The pyrolysis of



(R = methyl or H) produced striking contrasts in behavior. Rapid heating of the O-methyl and O,N-dimethylhydroxylamine boranes invariably led to violent explosion. Rapid heating of hydroxyl and N-methylhydroxylamine boranes led to rapid H<sub>2</sub> evolution, but no violent explosion was ever observed.<sup>7</sup> The explosions in the former case appeared to be triggered by the sudden exothermic shift of methoxy groups from nitrogen to boron. Such shifts were never necessary in the latter case. Slower, more gentle heating of the O,N-dimethylhydroxylamine-borane adducts led to a controlled shift of methoxy groups from nitrogen to boron and of hydrogen from boron to nitrogen. Loss of hydrogen from the compound always preceded the low-temperature shift. Prior to the loss of hydrogen from the borane adduct, acid hydrolysis always yielded the original O-methylhydroxylamine and three molecules of hydrogen per borane group. After loss of hydrogen, B(OCH<sub>3</sub>)<sub>3</sub>, ammonia, methyl and dimethyl amines were obtained. Clearly, group transfer had occurred after or concurrent with hydrogen loss. The difficult pyrolysis of CH<sub>3</sub>ON(CH<sub>3</sub>)<sub>2</sub>BH<sub>3</sub> below 100°C also suggested that hydrogen loss was an important initial step in the shifting of groups.

These facts imply that in those cases where a hydrogen is still attached to the nitrogen of a methoxyamine the pyrolysis proceeds by an initial splitting out of hydrogen from boron and nitrogen followed by rapid CH<sub>3</sub>O group transfer to the newly opened site on the boron. In explosive decomposition rapid heating produces more violent fragmentation, probably involving breaking of B-H and O-CH<sub>3</sub> bonds to give free radicals and atoms. This mode of decomposition undoubtedly involves a higher energy of activation, hence higher localized temperatures. Temperatures may build up rather rapidly in small volumes of the solid as a result of the exothermic low-temperature process, hence the low-temperature shift in the O-methyl and O,N-dimethylhydroxylamine boranes could be easily converted to the explosive decomposition process if heating were rapid and heat were not dissipated.

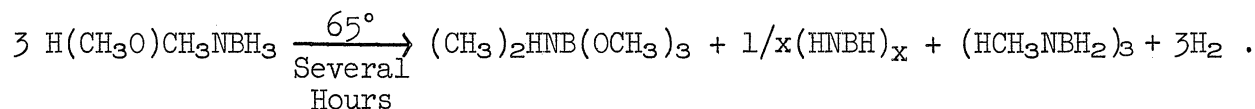
Although it was found that explosive decomposition of pure methoxyamine could be initiated by both spark and heat, it was shown that attachment of a nonoxidizable Lewis acid such as BF<sub>3</sub> to the base decreased its sensitivity to explosion. The compound CH<sub>3</sub>ONH<sub>2</sub>BF<sub>3</sub> was prepared in benzene as a white solid melting at 86°-88°C. The compound was heated in a sealed tube to 300°C. There was no explosion, but at the higher temperature the solid turned dark. This evidence indicates that the explosive decomposition is associated with the reducing character of the BH<sub>3</sub> group and not alone with the properties of the coordinated amine.

The following equation was written for the low-temperature decomposition of

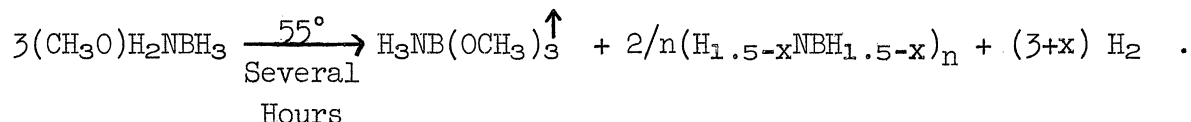
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7. D. H. Campbell, T. C. Bissot, and R. W. Parry, this Report, p. 134.

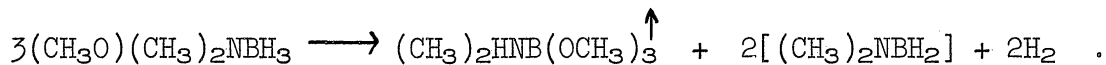
O,N-dimethylhydroxylamine-borane:



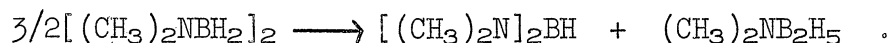
Data for the pyrolysis of O-monomethylhydroxylamine-borane suggest a similar process, but the trimeric compound  $(\text{H}_2\text{NBH}_2)_3$ , the inorganic analog of cyclohexane, was not isolated despite several experimental attempts. A polymerization beyond the trimer stage was probably responsible for the difference. The expected equation would be



The O,N,N-trimethylhydroxylamine-borane also underwent the methoxyl-hydride shift to give products which were rather similar in a formal sense to those outlined above:



Although all the products of the reaction were volatile, only trimethoxyborane could be isolated and characterized as a pure compound. Despite extensive fractionation, the expected compound  $[(\text{CH}_3)_2\text{NBH}_2]$  could not be separated. The explanation is found in a report by Burg and Randolph<sup>8</sup> to the effect that N,N-dimethylamine-borane, in addition to participating in a monomer-dimer equilibrium, can enter into the reaction:



They reported that the mixture could not be separated into its components by conventional trap-to-trap distillation. The vapor pressure of the decomposition product in this investigation was in the same range as that expected for the mixture of the above compounds.

Despite the formal similarity, the actual decomposition process, the pyrolysis of O,N,N-trimethylhydroxylamine-borane must differ significantly from that suggested for the O-methyl and O,N-dimethyl derivatives. The absence of hydrogen attached to nitrogen renders impossible a low-temperature hydrogen loss followed by a shift of a methoxy group. Any mechanism which would impose a coordination number of five on boron or nitrogen is equally distasteful. Since the decomposition occurred at high temperatures where there would be partial dissociation of the complex to give free  $\text{BH}_3$  groups, it is suggested that the mechanism involved  $\text{BH}_3$  groups. A temporary coordination of  $\text{BH}_3$  with the oxygen on the amine would give an unstable intermediate which could shift a hydrogen over to the nitrogen while the boron retained the methoxyl group. A disproportionation of methoxyborane to trimethoxyborane and diborane would give the ob-

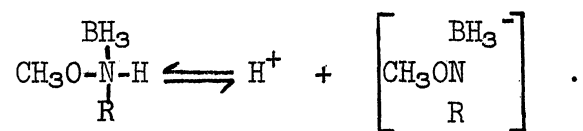
8. A. B. Burg and C. L. Randolph, J. Am. Chem. Soc., 73, 953 (1951).

served products. The rate for such a process, involving a high-energy intermediate, would be slow compared to the shift over the unsaturated intermediate, and would not be expected to achieve explosive proportions even at 100°C. Such was the case.

c. The Methoxyl-Hydride Shift During Hydrolysis with a Strong Base.

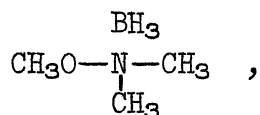
Hydrolysis of  $\text{CH}_3\text{ONH}_2\text{BH}_3$  and  $\text{CH}_3\text{ONHCH}_3\text{BH}_3$  by 50% KOH invariably resulted in transfer of the methoxyl group to the boron and of the hydrogen to the nitrogen. In contrast, hydrolysis of  $\text{CH}_3\text{ON}(\text{CH}_3)_2\text{BH}_3$  simply liberated the base unchanged and produced hydrogen and borates from the  $\text{BH}_3$  group. No shift of the methoxyl group was ever detected in the latter case. Clearly, the hydrogen attached to the nitrogen played a dominant role in group transfer. The following mechanism is suggested.

In a strongly alkaline solution the equilibrium shown below would be displaced to the right:



The resulting anion could then rearrange by shift of a hydrogen to the nitrogen and of a methoxyl group to the boron. Since the hydrolysis of such B-H bonds in alkaline solution is a rather slow reaction, the reduction of the amine would occur before the original compound was decomposed.

For the compound



acid ionization is impossible and no shift would be expected. Experimental facts support the expectation.

d. Physical Properties of the Methyl-Substituted Hydroxylamine Boranes.

Although the boiling points, melting points, and heats of vaporization for the methyl-substituted hydroxylamines are those expected from considerations of the hydrogen bond, the physical properties of the hydroxylamine boranes cannot be treated so easily. Data are summarized in Table I. The melting points, for example, do not show any definite trends. Although hydrogen bonding directly to the nitrogen is blocked by coordination of the borane group, bridging to the oxygen atom is still possible. The relatively low vapor pressures of the methyl-substituted hydroxylamine boranes and the slight increase in volatility with alkyl substitution on the nitrogen suggest that hydrogen-bond formation is still of some small importance for these compounds. On the other hand, the fact that  $\text{HON}(\text{CH}_3)_2\text{BH}_3$  is more volatile than  $\text{CH}_3\text{ON}(\text{CH}_3)_2\text{BH}_3$  is contrary to results expected

from hydrogen-bonding considerations. A relatively large dipole moment for these compounds is indicated.

### Experimental.--

#### a. Reagents.

1. The O-methylhydroxylamines were prepared and purified as described earlier.<sup>9</sup>

2. Diborane was prepared and purified as described earlier.<sup>10</sup>

3. Ether--Reagent-grade diethyl ether was stored over CaH<sub>2</sub> for several days and distilled under low pressure before use. Commercial diethyleneglycol dimethylether was handled in a similar fashion.

#### b. Preparation and Reactions of Compounds.

The general procedure for conducting reactions of this type has been described earlier.<sup>10</sup> Ether as a solvent was necessary for the preparation of the O-methylhydroxylamine-borane, but not for the O,N-dimethyl or O,N,N-trimethyl derivatives.

It has been noted elsewhere that ammonia or trimethylamine as a contaminant in the O-methylhydroxylamine makes the resulting borane adduct lose hydrogen. When 9% ammonia was added to carefully purified O-methylhydroxylamine and the reaction with diborane was effected as described above, the resulting mixture of CH<sub>3</sub>ONH<sub>2</sub>BH<sub>4</sub> and B<sub>2</sub>H<sub>6</sub>·2NH<sub>3</sub> changed into a liquid at room temperature and evolved hydrogen. After only one hour, the ratio H<sub>2</sub>/CH<sub>3</sub>ONH<sub>2</sub>BH<sub>3</sub> was 0.48. A weakly complexed 1:1 liquid mixture of H<sub>2</sub>NB<sub>2</sub>H<sub>5</sub> and (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O was distilled from the system. Although the complexing of H<sub>2</sub>NB<sub>2</sub>H<sub>5</sub> with (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O has not been reported previously, it is not unexpected since ammonia and trimethylamine adducts of H<sub>2</sub>NB<sub>2</sub>H<sub>5</sub> are known. If the 1:1 mixture is completely dissociated in the vapor state, it would have a molecular weight of 58.4. The observed values determined by vapor density, were 61.5 and 63.7.

Essentially pure H<sub>2</sub>NB<sub>2</sub>H<sub>5</sub> was recovered from the mixture by complexing the ether with either AlCl<sub>3</sub> or BF<sub>3</sub>. Both worked satisfactorily. A 7.7-mg sample of aminodiborane purified by this technique was characterized on the basis of the evidence listed in Table II.

Conventional high-vacuum techniques were used for effecting reaction between the methoxylamine-borane adducts and reagents such as BF<sub>3</sub> or NR<sub>3</sub>. Details are available elsewhere.<sup>11</sup>

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9. T. C. Bissot, R. W. Parry, and D. H. Campbell, this Report, p. 118.

10. D. H. Campbell, T. C. Bissot, and R. W. Parry, this Report, p. 134.

11. T. C. Bissot, Ph.D. dissertation, Univ. of Mich., Ann Arbor, 1955.



TABLE II  
CHARACTERIZATION OF  $\mu$ -MONOAMINODIBORANE

	Observed	Literature (a)
Molecular Weight	46.6	42.7
Vapor Pressure		
-23	7.8 mm	7.6 mm
0	32.4 mm	32.3 mm
18.9	85.4 mm	86.8 mm
Melting Point	Above $-78^{\circ}$	$-66.4^{\circ}$
B/N/Hydridic H Ratio	1/1.99/4.86	1/2/5

(a) H. I. Schlesinger, D. M. Ritter, and A. B. Burg, J. Am. Chem. Soc., 60, 2297 (1938).

c. Low-Temperature Decomposition of Compounds.

Samples were maintained in the preparation vessel at the desired temperature and products were isolated and characterized. The most difficult phase of the operation was the resolution of the complex solid mixture of  $\text{NH}_3$ ,  $\text{B}(\text{OCH}_3)_3$ , and, on occasion,  $\text{CH}_3\text{OH}$  which resulted.

Ammonia was identified by a potentiometric titration curve. Upon hydrolysis of the mixture, no hydridic hydrogen was found. Boron analysis indicated 9.22% B; nitrogen found was 7.52%. This is equivalent to 88.4%  $\text{B}(\text{OCH}_3)_3$  and 9.15%  $\text{NH}_3$ , a mixture which should have a molecular weight of 70.0 when completely dissociated. The observed molecular weight by vapor density was 70.3.

Synthetic "mixtures" of  $\text{H}_3\text{N}$ ,  $\text{B}(\text{OCH}_3)_3$ , and  $\text{CH}_3\text{OH}$  were identical to the solid mixtures in terms of physical appearance, vapor pressure, and dissociation pressures in the vapor phase.

In the mixture resulting from the decomposition of  $\text{CH}_3\text{ONCH}_3\text{HBH}_3$ , the mixture of  $\text{R}_2\text{HN}$ ,  $\text{B}(\text{OCH}_3)_3$ , and  $\text{CH}_3\text{OH}$  was separated by tying up the amines and alcohol with excess diborane, then separating the  $\text{B}(\text{OCH}_3)_3$  and  $\text{B}_2\text{H}_6$  by vacuum-line distillation. The purified  $\text{B}(\text{OCH}_3)_3$  was characterized by vapor pressure at four temperatures, by melting point ( $-29.0^{\circ}$  obs. and  $-29.3^{\circ}$  literature), by molecular weight (114.6 vs 103.9 literature), by absence of active hydridic H, and by boron analysis (10.05% vs 10.41% theory).

d. Explosive Decomposition.

Explosive decomposition was conducted by heating a well-annealed bomb tube

containing the sample to 100°. The tube was opened to the vacuum line by means of the vacuum-tube opener. Noncondensable gases such as H<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> were pumped off and separated by conventional techniques. C<sub>2</sub>H<sub>6</sub> and HCN in the condensable products were separated by fraction distillation in the vacuum line. The HCN was characterized by molecular weight, melting point, vapor pressures, and reaction with silver nitrate.

e. Analytical Methods.

These have been described elsewhere (this report, p. 145).

VI. THE REDUCTION OF CHLOROPHOSPHINES WITH LITHIUM ALUMINUM HYDRIDE  
AND WITH LITHIUM HYDRIDE (J. T. Yoke, G. Kodama, and R. W. Parry)

## Abstract

Alkyl phosphines have been prepared by the reduction of alkylchlorophosphines with lithium aluminum hydride. Coordination compounds of the general form  $\text{LiAl}(\text{PHR})_4$ ,  $\text{LiAl}(\text{PR}_2)_4$ , and  $[\text{LiAl}(\text{PR})_2]_n$  result from the interaction of alkyl phosphines with  $\text{LiAlH}_4$ . Because of complex formation, direct distillation of alkyl phosphines from the reaction mixture is retarded. Simple  $\text{PH}_3$  can be distilled directly from the mixture of  $\text{PCl}_3$  and  $\text{LiAlH}_4$  since it escapes at low temperatures before complexing.

Lithium hydride reacted with  $\text{PCl}_3$  to give large amounts of elemental phosphorus and less than 10%  $\text{PH}_3$ .

The reduction of boron or silicon halides with  $\text{LiAlH}_4$  represents an effective method for the synthesis of hydrides of boron or silicon.<sup>1</sup> The corresponding reduction of phosphorus trichloride to give phosphine was studied briefly by Paddock<sup>2</sup> and the preparation of  $\text{C}_6\text{H}_5\text{PH}_2$  from  $\text{C}_6\text{H}_5\text{PCl}_2$  was reported by Horvat and Furst<sup>3</sup> while this investigation was in progress. The reduction of alkyl chlorides of phosphorus to give alkyl phosphines and their lithium aluminum complexes has been studied in this investigation.

The Reduction of Phosphorus Trichloride.—In the presence of diethyl ether or tetrahydrofuran,  $\text{PCl}_3$  was reduced rapidly at  $-60^\circ\text{C}$  to give recovered yields of  $\text{PH}_3$  ranging from 60 to 80%. An earlier observation of Paddock<sup>2</sup> to the effect that the reaction would not go properly at room temperature in the absence of a suitable solvent was confirmed.

In the preparation of  $\text{B}_2\text{H}_6$ ,  $\text{LiH}$  can be substituted for  $\text{LiAlH}_4$  to reduce  $\text{BF}_3$ . The corresponding substitution of  $\text{LiH}$  for  $\text{LiAlH}_4$  in the reduction of  $\text{PCl}_3$  produced only about a 6% yield of  $\text{PH}_3$ . The major reaction was

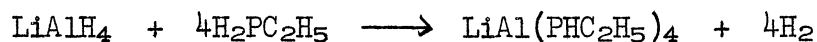


More than 70% of the theoretical phosphorus was consistently recovered. Variation of the temperature of the reaction from  $-60^\circ$  to  $25^\circ\text{C}$  and the presence or absence of  $\text{LiAlH}_4$  produced no major change in products.

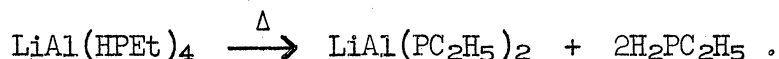
The Reduction of Monoalkyl Phosphorus Dichlorides.—The reduction of  $\text{EtPCl}_2$  with  $\text{LiAlH}_4$ , using the procedure outlined above for the reduction of  $\text{PCl}_3$ , gave very low yields of directly recoverable product. With  $\text{LiAlH}_4$  the alkyl phosphine

1. A. E. Finholt, A. C. Bond, and H. I. Schlesinger. J. Am. Chem. Soc., 69, 1199 (1947).
2. N. L. Paddock, Nature, 167, 1070 (1951).
3. R. J. Horvat and A. Furst, *ibid.*, 74, 562 (1952).

underwent a secondary reaction to give hydrogen and a mixture of lithium tetrakis ethyl monohydrogen phosphido aluminate (III) and lithium bis ethyl phosphide aluminate (III). The ratio was dependent upon conditions, all of which have not yet been completely delineated.



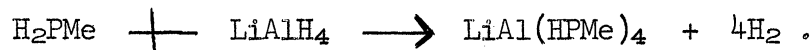
The alkyl phosphine could be released from either of the solid products by hydrolysis. Heating the monohydrogen coordination compound brought about release of a portion of the coordinated phosphine through a disproportionation type of reaction:



The reaction between ethyl phosphine and  $\text{LiAlH}_4$  was very similar to that observed with a primary amine and  $\text{LiAlH}_4$  (Ref. 1, p. 162, and Table II, p. 169) except that the amine reaction was much faster than the phosphine process under comparable conditions. This appears to be somewhat strange since the phosphine is usually considered to be a somewhat stronger acid than the amine.

In the reduction of  $\text{PCl}_3$  with  $\text{LiAlH}_4$  appreciable amounts (60-80% yields) of  $\text{PH}_3$  could be distilled directly from the reaction mixture and no evidence of complex formation was noted. In the reduction of chlorophosphines only small amounts (0-25%) of alkyl phosphine could be distilled and complex formation was indicated by hydrogen evolution. This difference is attributed to the fact that  $\text{PH}_3$  is volatile at the low temperature of the reduction ( $-63^\circ$ ), hence further reaction with  $\text{LiAlH}_4$  is difficult. On the other hand, the  $\text{EtPH}_2$  produced from  $\text{EtPCl}_2$  is not volatile at  $-63^\circ\text{C}$  and is retained in the ether solution where loss of hydrogen occurs.

The Reaction of Methyl Phosphines with  $\text{LiAlH}_4$ .—Although attempts to synthesize methyl phosphine by reduction of a product believed to be  $\text{MePCl}_2$  were inconclusive due to experimental difficulties, the direct reaction between methyl phosphine and  $\text{LiAlH}_4$  was studied in some detail. Results summarized in Table II, p. 169, support representation of the process by the equation



The presence of some of the bis product,  $\text{LiAl}(\text{PM}_3)_2$ , is also suggested by the data.

A comparable reaction involving diethyl monohydrogen phosphine gave evidence for the formation of  $\text{LiAl}(\text{PMe}_2)_4$ , Table II, p. 169. The complex was destroyed by water to liberate the original phosphine.

The Synthesis of Mixed Alkyl Chlorides of Phosphorus.—The use of the foregoing reduction process for the preparation of phosphines is limited in practical application by the comparative unavailability of the alkyl chlorophosphines. Ethyl dichlorophosphine,  $\text{EtPCl}_2$ , can be prepared by the alkylation of  $\text{PCl}_3$  with tetra-

ethyl lead.<sup>4</sup> Normal propyl dichlorophosphine was also prepared by an extension of the tetraethyl lead alkylation procedure. In an attempt to prepare methyl dichlorophosphine from  $\text{Pb}(\text{Me})_4$  and  $\text{PCl}_3$ , a precipitate of  $\text{PbCl}_2$  was obtained in the original step, as expected, but difficulties encountered during the reduction step prevented isolation and characterization of  $\text{MePH}_2$  which was needed for positive identification of methyl phosphorus (III) chloride.

Fox<sup>5</sup> suggested the use of dialkyl cadmium as an alkylating agent for the preparation of alkyl dichlorophosphines. The procedure worked well. On the other hand, the Grignard reagent as conventionally handled in diethyl ether gave no  $\text{EtPCl}_2$  when equal molar quantities of  $\text{MgRX}$  and  $\text{PCl}_3$  were allowed to react.

The Vapor Pressures of Mono- and Diethyl Phosphines.—Since vapor-pressure data for mono- and diethyl phosphines have not been recorded in the literature, data for carefully purified samples were obtained. For ethyl phosphine the vapor pressure is given by the equation

$$\log_{10} P = - \frac{1766.2}{T} - 3.5850 T + 17.7567 .$$

The molar heat of vaporization at the normal boiling point of 20°C is 6000 cal. For diethyl phosphine the equation is

$$\log_{10} P = \frac{2359.6}{T} - 4.5931 \log T + 21.1877 .$$

The molar heat of vaporization at the normal boiling point of 86°C is 7520 cal. Trouton's constants of 20.5 cal/mole x deg for monoethyl and 21.0 cal/mole x deg for diethyl phosphine are normal for nonassociated liquids. Data are given in Table I.

The Reaction Between Ethyl Phosphine and an Ether Solution of Aluminum Hydride.—Although ethyl phosphine reacted rapidly with hydridic hydrogens of  $\text{LiAlH}_4$  to liberate gaseous hydrogen, it was found that  $\text{EtPH}_2$  would not react with a solution of aluminum hydride in ether at room temperature. It is well known that coordination to a strong uncharged base such as  $\text{N}(\text{CH}_3)_3$  of a species containing hydridic hydrogen such as  $\text{BH}_3$  reduces the hydridic character of the hydrogen. For example, trimethylamine-borane shows very little hydridic character, even less than  $\text{LiBH}_4$ . An extrapolation of this argument suggests that the strong coordination of solvent ether to the aluminum hydride reduces the hydridic character of the hydrogens to such an extent that reaction with the protonic hydrogens of phosphine is not observed at room temperature. On the other hand, the corresponding reaction with the more hydridic  $\text{LiAlH}_4$  proceeds easily at -65°C.

4. M. S. Kharasch, E. V. Jensen, and S. Weinhouse, *J. Org. Chem.*, 14, 429 (1949).

5. R. B. Fox, *J. Am. Chem. Soc.*, 72, 4147 (1950).

TABLE I

## VAPOR PRESSURES OF MONO- AND DIETHYL PHOSPHINES

A. Monoethyl Phosphine $\text{PEtH}_2$				B. Diethyl Phosphine $\text{PEt}_2\text{H}$			
Temp. °C	Pressure mm Hg (obs.)	Pressure mm Hg (calc.)	$\Delta$	Temp. °C	Pressure mm Hg (obs.)	Pressure mm Hg (calc.)	$\Delta$
-83.6	1.9	1.9	0	-35.3	2.1	2.26	- .1
-63.5	10.1	10.3	+ .2	-22.6	5.8	5.67	- .1
-45.2	36.4	36.1	- .3	0.0	23.9	22.9	-1.0
-35.3	64.7	65.1	+ .4	5.5	31.2	31.0	- .2
-22.6	128.2	128.4	+ .2	31.5	108.3	108.4	+ .1
0.0	363.5	360.6	-3.5	42.4	170.7	170.8	+ .1
5.2	446.7	445.1	-1.6	51.6	244.6	243.7	- .9
16.9	690.2	692.2	+2.0	52.9	255.3	255.8	+ .5
				61.4	343.7	347.0	+3.3
				71.4	484.0	485.4	+1.4
				75.1	549.1	546.6	-2.5
				80.6	653.8	648.2	-5.6

$$\log P = -1766.2/T - 3.5850 \log T + 17.7567$$

Boiling Point = 20°C from equation

$$\Delta H_{\text{vap}} \text{ at } 760 \text{ mm} = 6000 \text{ cal at } 293^\circ\text{K}$$

$$\Delta S_{\text{vap}} \text{ at } 760 \text{ mm} = 20.5 \text{ cal/mole} \times \text{deg.}$$

$$\log P = -2359.6/T - 4.5931 \log T + 21.1877$$

Boiling Point = 86°C from equation

$$\Delta H_{\text{vap}} \text{ at } 760 \text{ mm} = 7520 \text{ cal at } 293^\circ\text{K}$$

$$\Delta S_{\text{vap}} \text{ at } 760 \text{ mm} = 21.0 \text{ cal/mole} \times \text{deg}$$

## Experimental.—

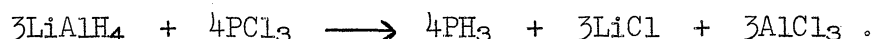
### a. Reagents.

Analytical reagent grade Mg, C<sub>2</sub>H<sub>5</sub>Br, PCl<sub>3</sub>, and AlCl<sub>3</sub> were used without further purification. LiAlH<sub>4</sub> and LiH were commercial products obtained from Metal Hydrides, Inc.

Tetrahydrofuran (Eastman Kodak) was distilled from mineral oil through a Snyder column, dried over sodium, and refractionated. Boiling point = 63.0-63.3°C uncorrected.

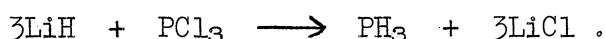
### b. The Reduction of Phosphorus Trichloride with Lithium Aluminum Hydride.

The reaction vessel was a 500-cc three-neck  $\text{E}$  flask. One neck was connected through a vacuum stopcock to a conventional high-vacuum fractionating system. The center neck was equipped with a cold finger, the top of which led to a column packed with glass helices and surrounded by a jacket for a cooling bath. This column led to a train consisting of a similarly packed U-trap, a mercury bubbler, a stopcock, and a second U-trap which could be opened on the end to a Toepler pump or the vacuum fractionation system. See Fig. 1. A stream of nitrogen was passed through the apparatus. Slush baths at -75°C were placed around the flask, the packed column, and the packed U-trap. The final U-trap was immersed in liquid nitrogen. In a typical run about .012 mole of PCl<sub>3</sub> (1 cc liquid) in 25 cc of diethyl ether was added dropwise with magnetic stirring to about 1 g (.026 mole) LiAlH<sub>4</sub> in 75 cc of diethyl ether (temp. -75° to -65°C). After addition was complete, the cooling bath was removed from the reaction flask. The highly volatile PH<sub>3</sub> product passed through the train to the final trap. After purification in the high-vacuum line, the PH<sub>3</sub> was characterized by vapor pressure and molecular weight. Yields of recovered PH<sub>3</sub> ranged from 55 to 70% of theory, based on the equation

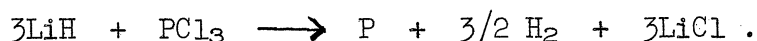


### c. The Reduction of Phosphorus Trichloride with Lithium Hydride.

The apparatus and technique were roughly the same as described above. About .013 mole PCl<sub>3</sub> in 20 cc of tetrahydrofuran was added dropwise to .0315 g of 200-mesh LiH suspended in 75 cc of tetrahydrofuran under N<sub>2</sub>. Vigorous stirring was achieved by a magnetic stirrer. The PH<sub>3</sub> formed was about 6% of the theoretical based on the equation



Red phosphorus formed in the flask was filtered on a ground-glass crucible, dried, and weighed. Yield was 72%, based on the equation





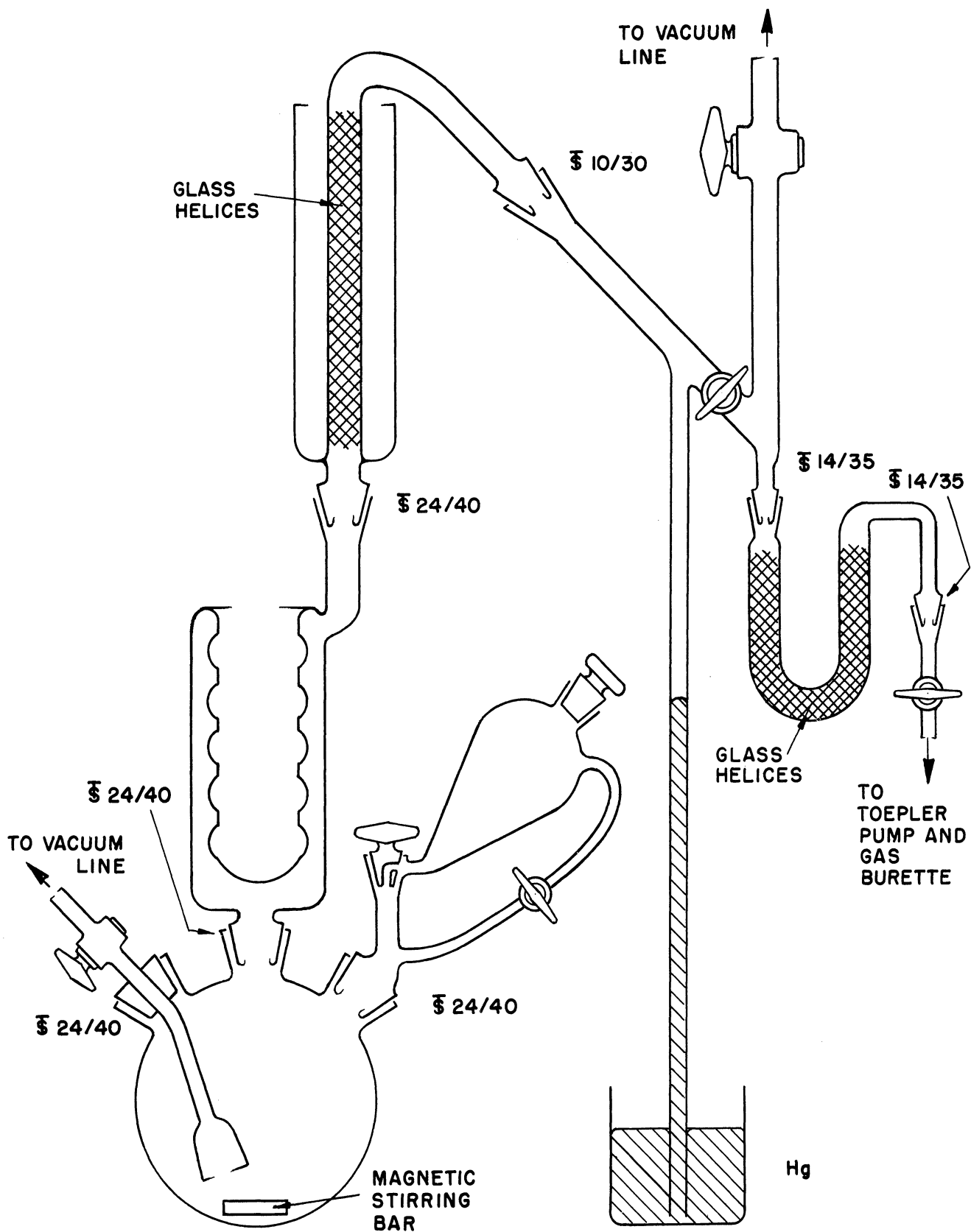


Fig. 1. Apparatus for production of phosphines by reduction of chlorophosphines with  $\text{LiAlH}_4$ .

d. The Reduction of Ethyl Dichlorophosphine with  $\text{LiAlH}_4$ .

About 5 g (.04 mole) of ethyl dichlorophosphine was distilled under vacuum into the reaction flask along with 25 cc of tetrahydrofuran which had been distilled directly from  $\text{LiAlH}_4$ . A chloroform slush bath ( $-63^\circ\text{C}$ ) was placed in the cold finger and the packed column was surrounded with powdered Dry Ice. The reaction flask was kept at a low temperature by refluxing of the solvent from the cold finger in the evacuated system.

A large excess of lithium aluminum hydride (7.0 g) was stirred with 75 cc of dry tetrahydrofuran. Since all the hydride does not dissolve (impure), the mixture was centrifuged and the supernatant liquid transferred with a dry hypodermic syringe to the dropping funnel (under  $\text{N}_2$ ). The solution was then added dropwise with magnetic stirring to the reaction flask. Condensable and noncondensable gases were separated, identified, and measured.

Usually very little phosphine was distilled from the system at the end of the run, but the alkyl phosphine was easily obtained from the solid residues by hydrolysis, using a 20% solution of water in tetraethyleneglycol diethyl ether.

e. The Direct Reaction Between Methyl Phosphines and  $\text{LiAlH}_4$  and Methyl Amine and  $\text{LiAlH}_4$ .

Commercial Ansul polyether No. 141 was dried by warming with sodium wire overnight. It was distilled under reduced pressure.  $\text{LiAlH}_4$  was stirred in the ether and the mixture centrifuged to get a clear solution. Concentration of the  $\text{LiAlH}_4$  solution was estimated by hydrolyzing 1 cc of the solution and measuring evolved hydrogen.

The reaction vessel for the process was essentially the same as that described earlier. The  $\text{LiAlH}_4$  solution (about 1.5 cc of about 1 molar solution) was placed in the flask. After cooling the solution to  $-78^\circ\text{C}$  and evacuating, stopcocks were closed and the system held at room temperature for 1/2 hour. Traces of evolved hydrogen were removed, then a measured amount (in vacuum line) of  $\text{PH}_2(\text{CH}_3)$ ,  $\text{PH}(\text{CH}_3)_2$ , or  $\text{NH}_2\text{CH}_3$  was condensed into the vessel from the vacuum system. Ice water was placed in the cold finger and the reaction vessel was allowed to warm to  $0^\circ\text{C}$ . Near  $0^\circ\text{C}$  hydrogen evolution was quite rapid. At intervals hydrogen was pumped from the frozen system and measured. Any amine or phosphine distilling from the system was returned.

When gas evolution was complete about 3 or 4 cc of water was condensed into the flask and the system warmed. The liberated  $\text{H}_2$  and  $\text{P}(\text{CH}_3)_2\text{H}$  or amine were purified in the vacuum system and measured. Detailed data are summarized in Table II.

f. The Preparation of Alkyl Dichlorophosphines.

Fifty grams of tetraethyl lead (0.15 mole) and 68.7 g (0.5 mole) of  $\text{PCl}_3$  were refluxed for 30 hours in a nitrogen atmosphere. Distillation of the re-

TABLE II  
THE REACTION OF PHOSPHINES AND AMINES WITH  $\text{LiAlH}_4$

Amine or Phosphine	Original Mmoles Phosph. or Amine Mixed	Mmoles $\text{LiAlH}_4$ From Total $\text{H}_2$	Mmoles $\text{H}_2$ Evolved	Mmoles Phosph. Reacted	Heating		Hydrolysis		Observed Experimental Ratios			Principal Solid Products Indicated by Stoichiometry	Expected (b) Ratio $\frac{\text{H}_2\text{PCH}_3}{\text{H}_2\text{FCH}_3}$ (Heat) (Hyd)
					Mmoles Phosph. Recovered	Mmoles $\text{H}_2$ Out	Mmoles Phosph. Recovered	M- moles $\text{H}_2$	$\frac{\text{Initial } \text{H}_2}{\text{Total Phosph.}}$	$\frac{\text{Phosph. (Heat)}}{\text{Phosph. (Hyd)}}$	$\frac{\text{Phosph.}}{\text{LiAlH}_4}$		
$\text{CH}_3\text{PH}_2$	11.09	1.18	4.54	3.91	-----	-----	3.85	0.22	1.16	-----	3.31	65% $\text{LiAl}(\text{MeHP})_4$ and 35% $\text{LiAl}(\text{MeP})_2$	-----
	10.81	1.06	4.14	4.02	1.43 (a)	0.21	2.50	0.09	1.03	0.57	3.90	95% $\text{LiAl}(\text{MeHP})_4$ and 5% $\text{LiAl}(\text{MeP})_2$	0.9
	9.17	1.59	6.32	5.90	2.30 (c)	0	3.36	0.07	1.07	0.69	3.71	86% $\text{LiAl}(\text{MeHP})_4$ and 14% $\text{LiAl}(\text{MeP})_2$	0.75
$(\text{CH}_3)_2\text{PH}$	11.54 (d)	about 1.43	5.5	6.28 (d)	-----	-----	4.37	0.21	0.88 (d)	-----	4.3	$\text{LiAl}(\text{PMe}_2)_4$	-----
	11.72 (e)	0.94	3.26	3.24	-----	-----	2.82	0.51	1.00 (e)	-----	3.4	$\text{LiAl}(\text{PMe}_2)_4$ and $\text{LiAlH}_2(\text{PMe})$	-----
$\text{CH}_3\text{NH}_2$	11.63	1.92	7.62	7.16	0.83 (f) 1.51 (g)	0.01 0.06	1.2 + x (h)		1.06	0.49	3.7	85% $\text{LiAl}(\text{HNMe})_4$ and 15% $\text{LiAl}(\text{NR})_2$	0.74

(a) Heated 40 min at 50° to 60°C.

(b) Based on assumption that reaction  $\text{LiAl}(\text{HPC}_3)_4 \rightarrow \text{LiAl}(\text{PC}_3)_2 + 2\text{H}_2\text{PCH}_3$  goes to completion.

(c) Heated to 100°C for 2.5 hr.

(d) Original  $\text{R}_2\text{HP}$  contained some  $\text{NH}_3$  as impurity.

(e) Pure sample.

(f) 100°C for 1 hr.

(g) 225°C for 1.5 hr.

(h) Remainder of methyl amine was not separated from  $\text{H}_2\text{O}$  in recovery. More present.

action mixture through a Widmer column gave a 46% yield (26.8 g) of  $\text{EtPCl}_2$ ; bp 111-112°C, uncorrected, and density 1.19 g/cc.

In an unsuccessful attempt at Grignard synthesis, 0.5 mole of  $\text{EtMgBr}$  in 100 cc of diethyl ether was added dropwise with stirring under an  $\text{N}_2$  atmosphere to 68.7 g  $\text{PCl}_3$  in 100 cc ether at 0°C. No  $\text{C}_2\text{H}_5\text{P}(\text{OH})_2$  or  $\text{C}_2\text{H}_5\text{PO}(\text{OH})_2$  could be isolated by ether extraction of the hydrolyzed reaction mixture, hence no  $\text{EtPCl}_2$  was formed.

n-Propyl dichlorophosphine was prepared when 9.5 g (0.025 mole)  $(\text{n-C}_3\text{H}_7)_4\text{Pb}$  and 6.55 cc (0.075 mole)  $\text{PCl}_3$  were refluxed for 36 hours in a nitrogen atmosphere. The volatile material was fractionated in the vacuum system. A 60.9% yield of  $\text{n-C}_3\text{H}_7\text{PCl}_2$  was obtained.

#### g. Reaction of Aluminum Hydride with Ethylphosphine.

A solution of  $\text{AlH}_3$  in ether was prepared in the reaction vessel of the earlier system by following the method of Wiberg, Graf, and Uson<sup>6</sup> in which stoichiometric amounts of standard solutions of  $\text{AlCl}_3$  and  $\text{LiAlH}_4$  were mixed. An excess of  $\text{C}_2\text{H}_5\text{PH}_2$  was distilled into the flask by chilling it and its contents with liquid nitrogen. The temperature of the system was allowed to rise gradually to room temperature. No  $\text{H}_2$  was evolved and all the added  $\text{C}_2\text{H}_5\text{PH}_2$  could be recovered. No protonic-hydric hydrogen interaction or complex formation occurred under the conditions of this experiment.

#### Acknowledgement

We wish to thank the Ethyl Corporation of Detroit, Michigan, for the samples of  $\text{Pb}(\text{n-C}_3\text{H}_7)_4$  and  $\text{Pb}(\text{CH}_3)_4$  which were generously provided for this study.

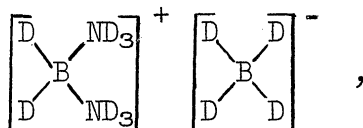
6. E. Wiberg, H. Graft, and R. Uson, Z. anorg. und allgem. Chem., 272, 221 (1953).

APPENDIX

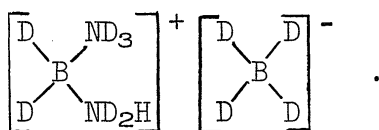
THE ISOTOPE EFFECT IN THE TRACER STUDIES OF THE  
"DIAMMONIATE OF DIBORANE"

The original intent of the tracer studies was to re-examine Girardot's work concerning nitrogen-hydrogen, boron-hydrogen bond rupture. This has been accomplished. Because of the now apparent complexities of the systems which employed ammonia-d<sub>3</sub>, the data obtained do not necessarily lend themselves to a quantitative treatment of the isotope effect involved. However, the available information does make it possible to present a reasonable description of the events occurring in these systems.

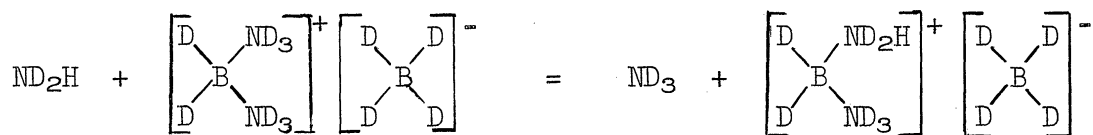
Consider the distribution of protium when B<sub>2</sub>D<sub>6</sub>·2ND<sub>3</sub><sup>1</sup> was prepared from and dissolved in ammonia-d<sub>3</sub>. Since the solvent was about 96% deuterated, the principal species in solution were ND<sub>3</sub>, ND<sub>2</sub>H,



and



H-D exchange occurred through only those hydrogens which were bound to nitrogen; equilibration was rapid.<sup>2</sup>



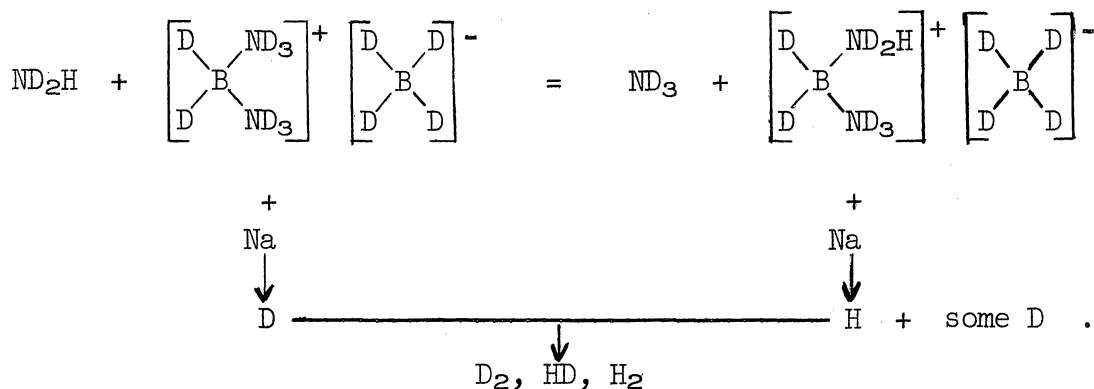
Furthermore, Burg's work<sup>2</sup> indicates that the isotopic separation factor  $\alpha$ , which is a distribution coefficient<sup>3</sup> for the exchange reaction, should be about unity. Therefore, prior to the addition of sodium, this system had reached or approached equilibrium and the nitrogen-hydrogen bonds of the "diammoniate" probably contained protium and deuterium in the ratio of about 4H to 96D.

1. B<sub>2</sub>D<sub>6</sub>·2ND<sub>3</sub> was used for the purpose of illustration. Since the boron-hydrogen bonds are apparently inert, with respect to hydrogen exchange, the above illustration applies to B<sub>2</sub>H<sub>6</sub>·2ND<sub>3</sub>.

2. A. B. Burg, J. Am. Chem. Soc., 69, 747 (1947).

3.  $\alpha = \frac{\text{H/D}(B_2D_6 \cdot 2ND_3)}{\text{H/D}(ND_3)}$  .

Nitrogen-hydrogen bonds were ruptured when sodium was allowed to react with the solution at  $-78^{\circ}$ . The principal isotope effect probably occurred at this point. It is believed that the rate-determining step of the reaction involved the rupture of the nitrogen-hydrogen bonds and that the N-H bond took preference over the N-D bond.<sup>4</sup> Since only a small fraction of the total number of nitrogen-hydrogen bonds in the system were ruptured, the evolved gas was considerably enriched in protium; it contained more than 4H to 96D. Because of this, the unreacted "diammoniate" should have been enriched in deuterium as the reaction progressed; however, since the solvent ammonia-d<sub>3</sub> was in large excess (solution ca. 0.01 M), and since the system establishes equilibrium readily, there was a tendency for the unreacted "diammoniate" to contain a constant, or nearly constant, protium-deuterium distribution in the nitrogen-hydrogen bonds. The reaction with sodium may be represented as



Because the gas which is evolved is so greatly enriched in protium, an estimation of the instantaneous separation factor  $\alpha_0$ <sup>5</sup> seemed to be attractive. However, there were several points to consider. First of all, although the deuterium content of the hydrogen evolved in the tracer reactions and the deuterium content of the ammonia-d<sub>3</sub> were known to a degree of accuracy which was certainly sufficient for the principal purpose of the tracer investigation, the isotopic ratios of protium to deuterium were not known to a comparable degree of accuracy. Thus, for example, the ammonia-d<sub>3</sub> was considered to be about 96% deuterated, and most likely was 96-97% deuterated. It can be seen that the H/D ratio for 96% deuterated ammonia-d<sub>3</sub> is 35% greater than that for 97% deuterated ammonia-d<sub>3</sub>.

$$\frac{4/96}{3/97} = 1.35$$

Also, although the instantaneous separation factor is most accurately determined from data which are obtained after a small extent of reaction, in this investigation tracer data were obtained after an appreciable extent of reaction. In spite of these difficulties it seemed that an estimate of the order of magnitude of  $\alpha_0$  would still be worthwhile.

4. Owing to the mass difference between H and D, the zero-point energy of the N-D bond is lower than that of the N-H bond. From a simple, qualitative consideration of the vibrational stretching frequencies of these bonds it is seen that the N-H bond is more readily broken than the N-D bond. Also, from a similar type of consideration it is not unreasonable to expect that an N-H bond would be more reactive than an N-D bond.

5.  $\alpha_0 = \frac{\text{H/D}(\text{gas})}{\text{H/D}(\text{B}_2\text{D}_6 \cdot 2\text{ND}_3)}$  at zero extent of reaction.

The instantaneous separation factor for the reaction of  $B_2D_6 \cdot 2ND_3$  with sodium in liquid ammonia- $d_3$  was approximated from the data of the tracer reactions (see p. 70 of this report). Assuming that the protium-to-deuterium distribution in the nitrogen-hydrogen bonds of the "diammoniate" was  $4H/96D$ , an apparent separation factor was calculated and plotted for a given fraction reacted. This process was repeated, assuming a ratio of  $3H/97D$ . Then the apparent separation factors were extrapolated to zero extent of reaction (Fig. 1). The solid-line extrapolations are drawn through the points of two individual experiments and are intended to give the maximum and minimum values possible for  $\alpha_0$ . In carrying out these extrapolations greater significance was given to those points representing smaller fraction reacted. The dotted-line extrapolation is drawn through the data from both experiments and represents the best estimate of  $\alpha_0$ , which appears to be  $17 \pm 4$ .

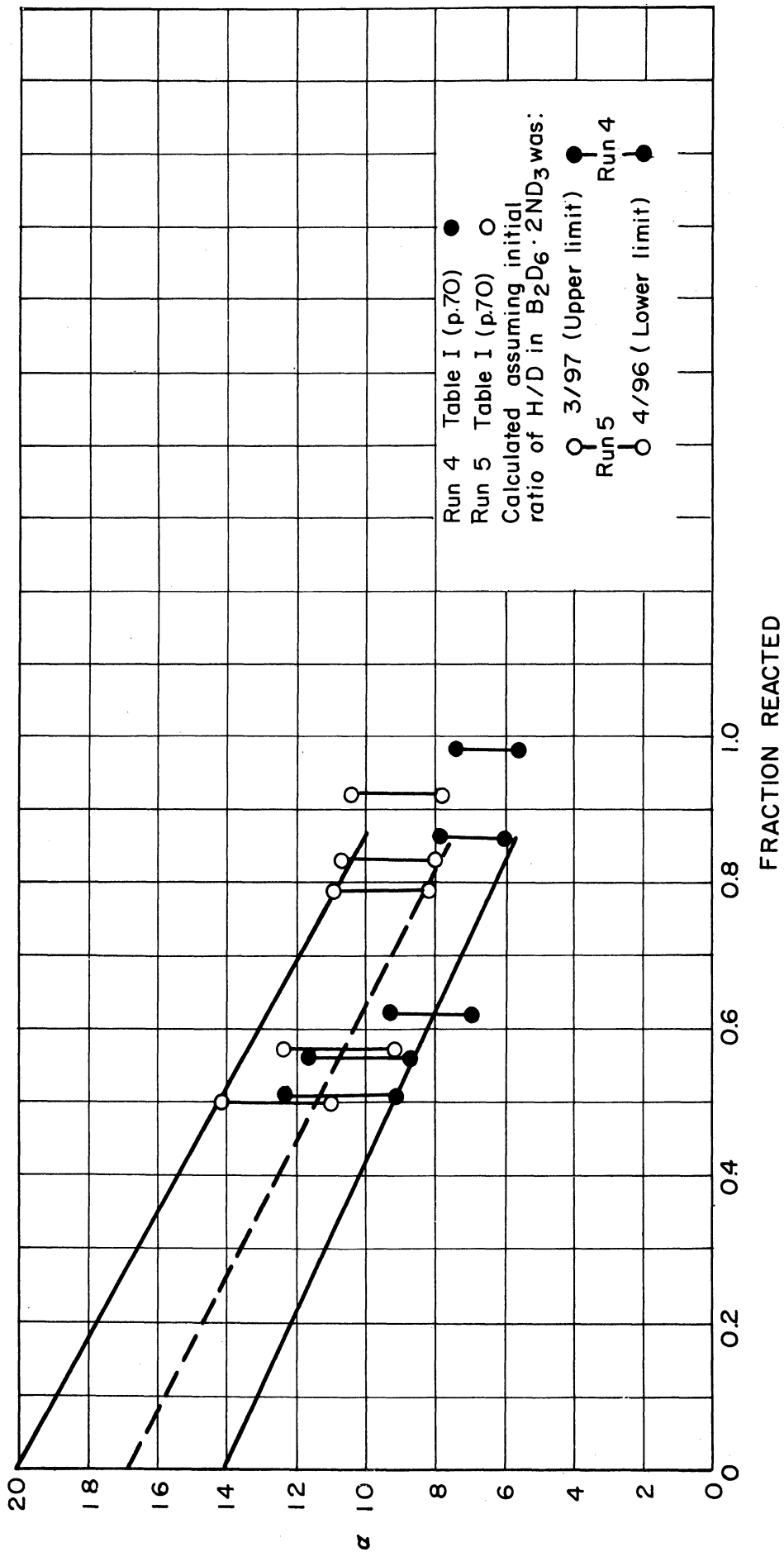


Fig. 1. An approximation of  $\alpha_0$  for the reaction of B<sub>2</sub>D<sub>6</sub> · 2ND<sub>3</sub> with sodium in ammonia-d<sub>3</sub>.





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