

THE REACTIONS OF TETRAMETHYLDIBORANE WITH
AMMONIA AND TRIMETHYLAMINE

A Thesis
Presented to
the Faculty of the Department of Chemistry
University of Houston

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

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by
Louis Andrew Martincheck

June 1957

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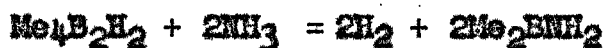
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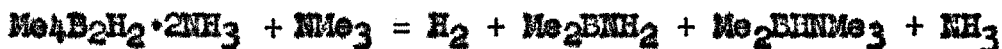
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ABSTRACT

The high vacuum technique was used to study the reactions of tetramethyldiborane with the Lewis bases ammonia and trimethylamine. These reactions have been confirmed to proceed at ambient temperatures as follows:



The reaction of the diammoniate of tetramethyldiborane with trimethylamine displaces ammonia at -80° in amounts greater than one mole of ammonia per mole of the diammoniate. The first mole of ammonia is readily displaced and the remainder is slowly displaced with trimethylamine. The data indicates that the net stoichiometric reaction at room temperature for the displacement of one mole of ammonia is



Comparisons are made for the structure of the diammoniate of tetramethyldiborane with the three proposed structures for the diammoniate of diborane. The results of the trimethylamine displacement studies are best correlated with the structure $(\text{Me}_2\text{B}(\text{NH}_3)_2^+)(\text{H}_2\text{BMe}_2^-)$ which is comparable to that proposed by Parry and coworkers for the diammoniate of diborane.

Two unsuccessful attempts to prepare aminotetramethyldiborane from the products of the tetramethyldiborane-ammonia system are discussed.

The hydrolysis of the methyl derivatives of boric acid to produce methane is shown to be appreciable at temperatures above 110° .

A vapor pressure-composition curve is given for the ammonia-trimethylamine system.

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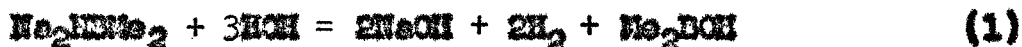
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CHAPTER I

INTRODUCTION

Upon contact with sodium in liquid ammonia at -78° , tetramethyldiborane is split equally into dimethylborine-amine and the salt Na_2BMe_2 .¹ With the sodium in excess the products of this system are quantitatively formed and can be verified by analysis. The dimethylborineamine is recognized by its decomposition at 25° to yield hydrogen and the volatile compound aminodimethylborane. After the removal of the ammonia solvent, followed by displacement with trimethylamine in order to protect it from aminolysis, the salt Na_2BMe_2 may be analyzed by hydrolysis, according to the equation



However, if an excess of tetramethyldiborane is employed for this same preparation, analysis of the solid residue by hydrolysis does not indicate the presence of Na_2BMe_2 . In terms of Na_2BMe_2 , hydrolysis yields insufficient dimethylboric acid and more than the expected amount of hydrogen and a fair amount of trimethylboron.¹ The appearance of trimethylboron at this point is quite interesting

¹ A. B. Burg and G. V. Campbell, Jr., J. Am. Chem. Soc., **74**, 3744 (1952).

since this compound is rarely recognized at this analogous step whenever Na_2HBMe_2 is prepared by utilizing a large excess of sodium.

It is then apparent in the latter case that some correlation exists between an excess of tetramethyldiborane and the subsequent appearance of trimethylboron. An explanation has been advanced which is based upon a reaction between Na_2HBMe_2 and the excess of tetramethyldiborane.² During the early stages of the formulation of this explanation, it was felt that there was still a need for more information regarding the tetramethyldiborane-ammonia and the tetramethyldiborane-trimethylamine systems.

The preparation of Na_2HBMe_2 demonstrates that the reaction of tetramethyldiborane with sodium is much faster than the reaction of tetramethyldiborane with ammonia. However, when tetramethyldiborane is present in an amount greater than that required to prepare Na_2HBMe_2 , the reaction of tetramethyldiborane with ammonia then deserves some consideration.

Tetramethyldiborane is known to combine with two molecules of ammonia to give a product similar to that when diborane combines with two molecules of ammonia. The diammonia complex of diborane has received a great deal of attention in regard

²G. W. Campbell, Jr. and L. A. Martincheck, "The Boron Bases", Eighth Status Report to the Office of Ordinance Research under Contract No. DA-23-072-ORD-761 for the period August 1 to October 31, 1955; G. W. Campbell, Jr., "Further Studies of Boron Bases: $\text{CaHB}(\text{CH}_3)_2$ ", In Press.

to the nature of the two nitrogen atoms incorporated within the structure of the complex. Studies have shown that this compound behaves as if it contains reactive groups³ such as NH_4^+ , BH_4^- , BH_2NH_2 , $\text{H}_2\text{B}(\text{NH}_3)_2^+$, or $\text{BH}_3\text{NH}_2\text{BH}_3^-$. If analogous groups are present in the ammonia complex of tetramethyldiborane, it would be interesting to know what effect they have, if any, when an excess of tetramethyldiborane is added to a liquid ammonia solution of sodium metal.

As a step in this direction it was decided to investigate the reactions of tetramethyldiborane towards ammonia and trimethylamine.

³H. I. Schlesinger and A. B. Burg, J. Am. Chem. Soc., 60, 290 (1938); S. Shore and R. W. Parry, J. Am. Chem. Soc., 77, 6084 (1955); G. W. Schaeffer, M. D. Adams, and F. L. Koenig, J. Am. Chem. Soc., 78, 725 (1956).

CHAPTER II

STATEMENT OF PROBLEM

The material comprising this thesis is concerned with the reactions of tetramethyldiborane towards the two Lewis bases, ammonia and trimethylamine. Along this line two literature sources are noteworthy. In 1936, Schlesinger, Horvitz, and Burg⁴ reported that tetramethyldiborane formed a solid, white, salt-like compound at -80° with two moles of ammonia. This "diammoniate"⁵ was very unstable, in that at -30° it quantitatively transformed, by the loss of hydrogen, to aminodimethylborane. In 1939, Burg and Schlesinger⁶ reported the reaction of tetramethyldiborane with trimethylamine to yield a slightly volatile liquid which was stable at room temperature. The reaction was described by the equation.



⁴H. I. Schlesinger, L. Horvitz, and A. B. Burg, J. Am. Chem. Soc., **58**, 409 (1936); H. I. Schlesinger and A. B. Burg, Chem. Revs., **31**, 1 (1942).

⁵The corresponding diammoniate of diborane was found to readily add only one mole of sodium and suggested the presence of only one ammonium ion in the formula. This lead to the formulation of the diammoniate as being $\text{NH}_4^+(\text{BH}_2\text{NH}_2\text{BH}_2^-)$ which "according to the formula is a mono-ammonium salt having a B-H-B skeleton, rather than a direct derivative of diborane", H. I. Schlesinger and A. B. Burg, J. Am. Chem. Soc., **60**, 290 (1938).

⁶A. B. Burg and H. I. Schlesinger, J. Am. Chem. Soc., **61**, 1078 (1939).

The first project of the work discussed in this thesis was to verify these results and determine also whether a "monoammoniate" of tetramethyldiborane was stable. Another objective was to test for a reaction between dimethylaminoborane and tetramethyldiborane as a means of preparing the hypothetical compound aminotetramethyldiborane. And lastly, it was desired to study what effect trimethylamine had upon the "diammoniate" of tetramethyldiborane.

CHAPTER III

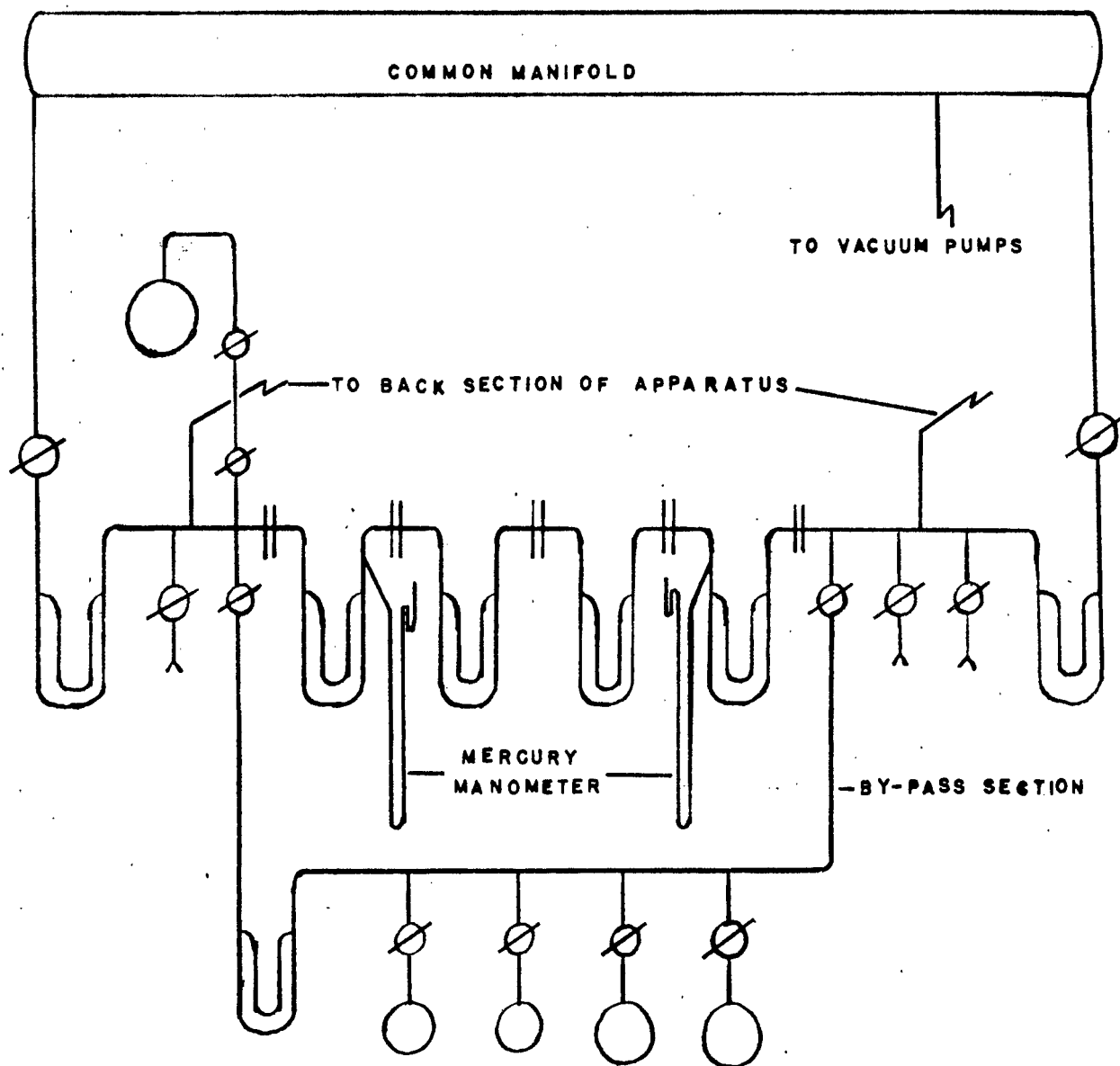
EXPERIMENTAL APPARATUS

The apparatus used in this work was that originally described by Stock⁷ for the manipulation of small amounts of volatile materials which were unstable towards air or moisture. In brief, it was constructed as one piece of Pyrex glass containing a common manifold with branching sections comprised of U-tube traps, mercury float valves, stopcocks, a Topley pump, a McLeod gauge, take-off arms, and storage bulbs.

The manifold and any section of the vacuum line open to the manifold was evacuated by a series of two pumps, a mechanical fore pump and a mercury diffusion pump. Such a pumping system was capable of attaining a low pressure to the order of 10^{-7} mm Hg (this pressure is exclusive of the vapor of mercury) as measured by the McLeod low pressure gauge.

The arrangement of the apparatus used for the work described in this paper is illustrated diagrammatically in Figure 1, page 7, and Figure 2, page 8. In Figure 1, the front section of the vacuum line is shown. A series of six U-tubes were connected to the extreme ends of the manifold. The four inner U-tubes alternated with mercury float valves

⁷A. Stock, *Ber.*, 47, 154 (1914); A. Stock, "Hydrides of Boron and Silicon", Cornell University Press, Ithaca, New York, 1933, pp. 173-207.



LEGEND



U-TUBES



PYREX TUBING



STOPCOCKS



GROUND GLASS JOINT



STORAGE
BULBS



MERCURY FLOAT VALVE

FIGURE 1. FRONT SECTION OF VACUUM APPARATUS.

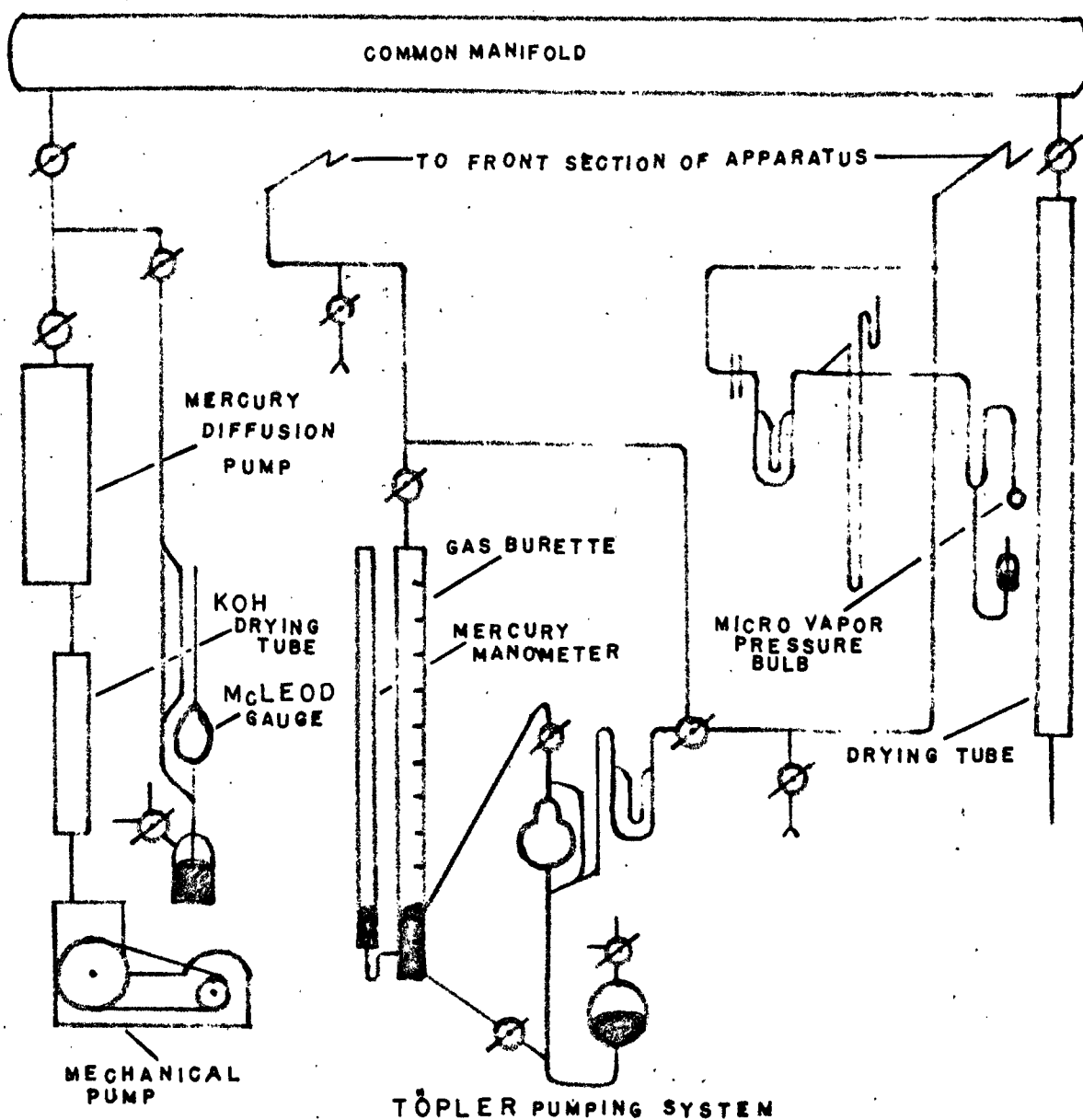


FIGURE 2. BACK SECTION OF VACUUM APPARATUS.

and were connected to two mercury manometers. Across these same four U-tubes was a by-pass section from which storage bulbs were located.

The take-off arms functioned as places of entry or removal of materials by the connection of suitable auxiliary pieces of apparatus.

Figure 2 shows the back section of the same vacuum apparatus. It shows the series arrangement of the mechanical fore pump and the mercury diffusion pump. The potassium hydroxide drying tube immediately ahead of the mechanical fore pump was simply an extra precaution against passing water vapor or acids into the oil of the mechanical pump.

The McLeod low pressure gauge was placed on the back side of the vacuum apparatus for convenience.

The Töpler pump on the back of the apparatus functioned to transfer noncondensable gases into the calibrated gas burette fitted with a mercury manometer. In the studies for this paper, hydrogen and methane were encountered as noncondensable gases⁸.

The back U-tube was used for temporary storage and the micro vapor tension bulb was used to determine the vapor pressure of very small amounts (2 to 5 cc of gas) of volatile materials.

Whenever it was desired to admit atmospheric pressure

⁸The word noncondensable is used relative to the vapor pressure exerted at the temperature of liquid nitrogen (b. p. -196°), which was employed as a refrigerant.

into the vacuum apparatus, moisture-free air could be introduced through the drying tube connected to the manifold.

This drying tube contained the various drying agents, Ascarite, phosphorus pentoxide (supported on glass beads), calcium sulphate, potassium hydroxide, and calcium chloride.

With this description of the vacuum apparatus there is lacking only an explanation of the principle which makes such an apparatus a practical tool for the chemist. This has aptly been described by R. T. Sanderson⁹.

Vapors diffuse rapidly through a vacuum. This fact is the basis of the high vacuum technique for handling volatile, condensable substances. If a volatile substance is introduced into a closed system from which almost all air and other noncondensable gases have been removed (pressure 10^{-3} mm Hg or lower), its vapor will diffuse rapidly throughout the entire system. It may then be moved quantitatively to any part of that system by cooling that part to a temperature at which the substance exerts a negligible vapor pressure. In other words, the kinetic energy of the molecules of vapor provides the motive power for the transfer, which is made irreversible by removing the kinetic energy at the point of cooling."

⁹R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds", John Wiley & Sons, Inc., New York, New York, 1943, p. 1.

CHAPTER IV

EXPERIMENTAL TECHNIQUES

Before a newly constructed vacuum apparatus can be used, it must be checked for leaks, annealed, and thoroughly degassed. The techniques for preparing the apparatus in its final form are discussed here along with some of the more common techniques of high vacuum work.

Detecting leaks. Whenever two pieces of glass are sealed together there is always the possibility of a leak occurring. This may result from microscopic cracks caused by strain having been introduced into the structure of the glass when the seal was made and not having been removed by proper annealing, or, it may be incomplete fusion of the two pieces connected caused by the presence of small particles of dirt.

These tiny holes can be detected with a Tesla coil when the apparatus is evacuated. The principle involved is quite simple. A Tesla coil is a high-frequency spark discharge coil. At a high voltage the coil emits sparks of high frequency electrons into the air in all directions from the tip of a pointed metallic probe. The sparks are diffuse and subject to deflection by air currents. When the tip of the probe approaches a hole in the evacuated glassware where

there is a current of air rushing towards the hole, the sparks are converged into a single beam which is pulled directly to the hole so that its exact location can be seen. Since metals attract the spark strongly, it is useless to employ a Tesla coil within a half inch or so of a metal clamp for the purpose of detecting leaks in glassware. Leaks in such places were then detected by determining if the apparatus could maintain a constant low pressure over an extended period of time.

Strain. Strain within the glassware was detected by the use of polarized lenses and a flashlight. The polarizer lens was taped to the glass lens of the flashlight and the analyzer lens was actually a pair of polarized sun glasses. The dark polarized light from the flashlight was viewed as it passed through the glassware. The presence of strain bends or depolarizes the light and it then appears bright through the glassware amid non-affected areas.

This method is capable of detecting the more pronounced strain and is dependent upon the quality of the polarized lenses. Strain was then removed by heating the glassware to the annealing temperature. For the Pyrex brand chemical glass No. 774 used, the annealing temperature is 560° C. The appearance of the sodium flame is a good indicator of this temperature.

Evacuation and degassing of the apparatus. In order to obtain as high a vacuum as desired it was necessary to "bake out" the new apparatus by heating it, while pumping, with a gas-oxygen "brush" type of flame to the order of 300° . This procedure liberates enough of the sorbed gases on or beneath the surface of the glass so that a good vacuum was thereafter readily obtained.

Calibration of U-tubes. A sample of a known gas (HCl , CO_2 , NH_3 , or Me_3N) was introduced into the vacuum line and checked for purity by the vapor pressure it exerted at a specific reference temperature. The gas sample was then allowed to expand at room temperature within the U-tube whose volume was to be found. It was necessary that a Hg manometer be part of the volume system. The pressure and temperature were noted. The gas was then condensed in an evacuated weighing bulb of predetermined tare and weighed on a balance. The ideal gas law was assumed to be valid and the volume of the U-tube-Hg manometer system calculated as $V = \frac{PRT}{P}$. A volume correction was made for the added volume due to displaced mercury in the manometer. The actual volumes of the U-tubes recorded were the averages of several similar calibrations.

From this calibration, the volume for standard conditions of any gas could then be determined by noting its

temperature, pressure, and U-tube volume. If the weight of the gas sample were determined also, the molecular weight could be calculated again assuming the ideal gas law to be valid. Because of the error inherent in the calibration of the U-tubes and determining standard volumes by assuming ideality of the gases encountered, molecular weight determinations from gas densities are valid only within approximately 5% of the true molecular weight. For example, an observed molecular weight of 56 for trimethylamine (calculated 59) is considered good enough to identify trimethylamine by this method provided that this identity is supported also by vapor pressure measurements and chemical behavior.

Molecular weight of a noncondensable gas. The total amount of the noncondensable gas was pumped into the gas burette by means of the Töpler pump and the volume was calculated. The gas in the burette was then allowed to expand into a weighing bulb and slightly compressed by pumping mercury into the burette by use of a hand syringe. The amount of gas in the weighing bulb was trapped by closing the stopcock to the bulb while the remainder of the gas was again pumped into the gas burette and the volume was measured. In this manner, the volume of gas to be weighed in the bulb was measured.

Of course, the smaller the quantity of gas or the

the lighter the gas, the greater will be the percent error for the observed molecular weight. One sample of methane gave an observed molecular weight of 12.2 (calc. 16) but reproduced the vapor pressure recorded in the literature (12 mm at -196°) for methane. Again, a sample of hydrogen with an observed molecular weight of 3.0 (50% error) was found to undergo only gas contraction at -196° . Further distinction between hydrogen and methane is possible by igniting the gas as it escapes from a bulb which has been pressurized by blowing into it; hydrogen will "snap" while methane burns with a blue flame. Small traces of volatile boron compounds usually gave a green flash on the first ignition tests.

Separation of a mixture of volatile compounds. R. T. Sanderson adequately describes the technique used to effect the separation of a gaseous mixture at low temperatures and low pressures as follows¹⁰

"If a mixture is condensed and then allowed to warm to a temperature at which only one component has an appreciable vapor pressure and the volatility of the other compounds is still negligible, it should be possible to distill that component quantitatively away from the mixture. This may be thought of as fractional distillation in its simplest form. Similarly, if the whole mixture is allowed to flow as a vapor into a trap held at the above temperature, the most volatile component should flow through the trap, leaving the rest of the mixture behind in a condensed phase. This is fractional condensation."

¹⁰ Ibid., p. 86.

In the high vacuum technique it is possible to combine these two phenomena into fractional distillation-condensation by simply allowing a condensed mixture to slowly warm and flow through a series of U-tubes cooled to successively lower temperatures. The temperatures are, of course, adjusted to the volatilities of the compounds comprising the mixture. The refractionation is effected by displacing the temperature baths one U-tube further along the U-tube series or by replacing a fraction in the original tube and again allowing it to flow through the same series of U-tubes.

For example, an hydrolysis mixture containing H_2 , HCl , Me_2BOH , H_2O , and $Me_3N \cdot HCl$ was separated as follows. All of the contents of the sealed hydrolysis tube were condensed except the hydrogen with liquid nitrogen. The tube was then opened in vacuo and the hydrogen removed by the pumping action of the Töpler pump. The remaining mixture was then warmed slowly and allowed to pass through a series of U-tube traps held at the following temperatures, -25° which held back the major portion of water, -35° which trapped an azeotropic mixture of $HCl-H_2O$, -60° which stopped all of the Me_2BOH , and finally -196° which collected any excess amount of HCl . Only the solid $Me_3N \cdot HCl$ was left behind in the hydrolysis tube. Refractionation of the Me_2BOH fraction was effected by allowing it alone to warm and pass through the same temperature series.

Separating a mixture of two gases is difficult if their

vapor pressures do not differ greatly especially in their low pressure ranges. This is the case for ammonia and trimethylamine. Trimethylamine has an extrapolated vapor pressure of 0.0 mm Hg at -114° while ammonia will pass through a trap held at this temperature with a pressure of 0.5 mm Hg. The temperature at which the vapor pressure of ammonia takes on a value of 0.0 mm Hg is -126° . Temperature control is of paramount importance in this case; if the temperature were greater than -114° , the trimethylamine would not be held back, and if the temperature were much below -114° , there would be the chance that ammonia and trimethylamine both would be held back. It was found rather difficult to control the temperature of a cooled petroleum ether bath by the use of an uncalibrated, full-immersion, pentane thermometer. Consequently, a different method of analyzing mixtures of ammonia and trimethylamine was devised and appears in Chapter X.

Criterion of purity. A simple test for purity of a volatile compound is to measure its vapor pressure when it has been both warmed and cooled to the same temperature. If the compound is pure, the vapor pressures will be promptly reproduced. If impurities are present the attainment of vapor pressure equilibrium is slowed greatly and the vapor pressure will not be promptly reproduced when both warmed and cooled to the same temperature. This method is not entirely conclusive

evidence for purity and should be tested by other methods such as a molecular weight determination or analysis by hydrolysis or reaction.

Sources of errors in observed vapor pressures are due to the surface effects of mercury in the glass manometer and an accuracy of reading a meter stick to the nearest 0.2 mm. Observed vapor pressures within one or two millimeters (depending upon the total pressure being read) of the literature values were considered within a reasonable range for identification purposes. Identifications by vapor pressures for ammonia, trimethylamine, and trimethylboron were based upon three vapor pressure measurements at temperatures differing by at least five degrees centigrade. For this purpose, it was found useful to have graphs of the vapor pressure curves for ammonia, trimethylamine, and trimethylboron.

Analysis of hydrolysis residues. These analyses were performed without the vacuum apparatus. The residue remaining in an hydrolysis tube was dried in vacuo and its weight determined from the gross and tare weights of the tube and residue. The residue was dissolved in water and the chloride precipitated and weighed as AgCl . The filtrate was then treated in a micro-Kjeldahl apparatus and the amine nitrogen determined by the usual distillation and titration.

CHAPTER V

PREPARATION OF REAGENTS

The high vacuum technique affords a convenient method of preparing and storing unstable, volatile compounds, or purifying commercial reagents.

Diborane. Diborane was prepared by the reaction of boron trifluoride etherate with an ether slurry of pulverized lithium hydride.¹¹ A semi-diagrammatic sketch of the apparatus used is shown in Figure 3 on page 20. For this preparation the upright condenser was a bath of ether and dry ice. This type of a condenser led directly to two traps, each fitted with stopcocks at both ends and held respectively at -80° and -196° . The second trap led to a mercury safety bubbler. The apparatus was therefore a closed system.

Before the addition of the etherate, the apparatus was thoroughly flushed with gaseous nitrogen. About 3.7 grams of lithium hydride were allowed to react with an excess of the boron trifluoride etherate. The reaction was smooth; The major part of the diborane was condensed in the -80° trap along with some ether and then finally in the -196° trap.

¹¹J. R. Elliot, E. M. Boldebeck and G. F. Roedel, J. Am. Chem. Soc., 74, 5047 (1952).

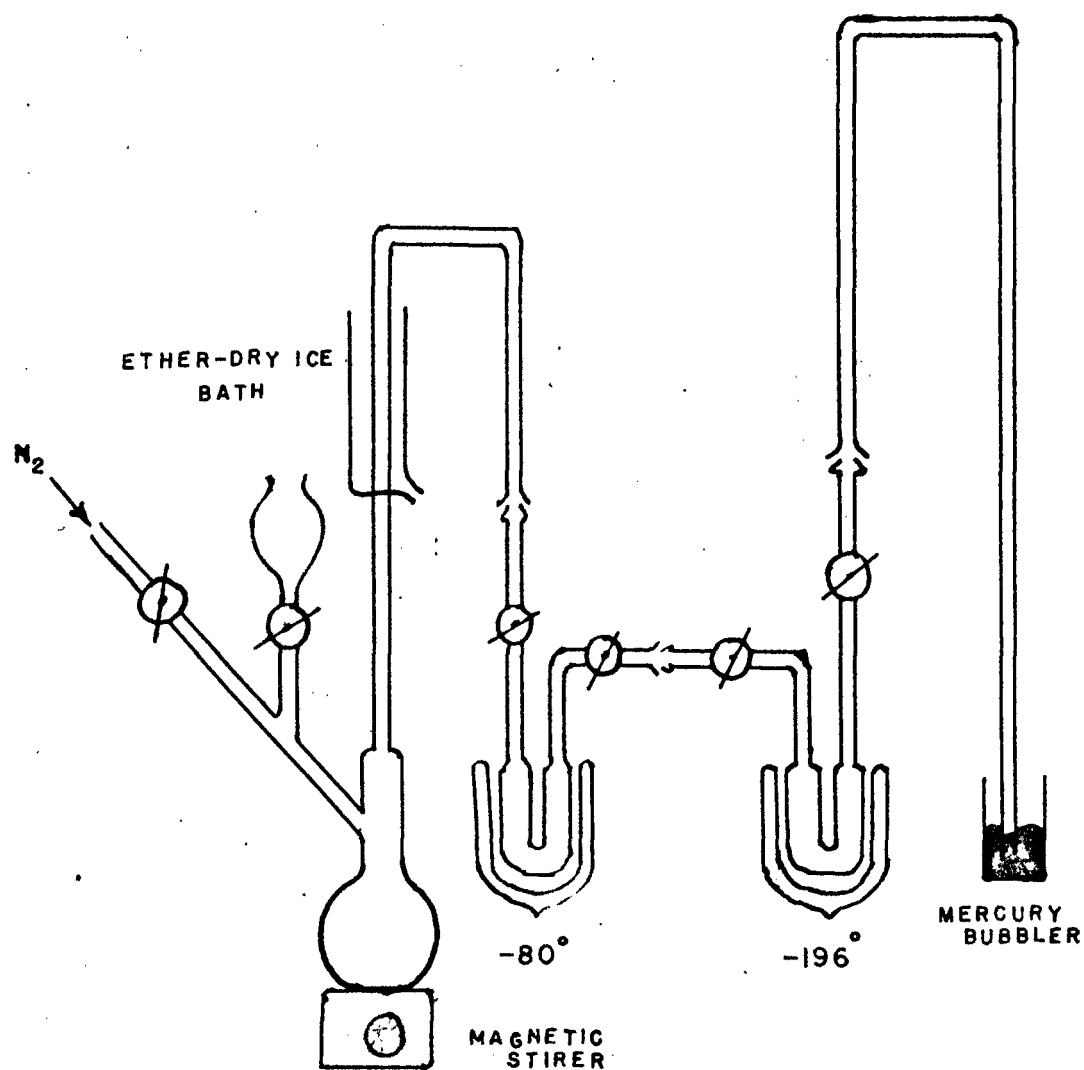


FIGURE 3. APPARATUS USED TO PREPARE DIBORANE AND TRIMETHYLBORON.

After the reaction was complete, the -80° and -196° traps were connected to the vacuum line. The diborane was separated from the ether mixture by the fractionation procedure previously mentioned. The yield was about one liter of diborane at room temperature and pressure, and of high purity.

Trimethylboron. Trimethylboron was prepared by the reaction of the Grignard reagent, methyl magnesium iodide, with an ether solution of the etherate of boron trifluoride. The apparatus employed was the same as that which was used to prepare diborane. In this manner about 5 cc of liquid trimethylboron were prepared.

Tetramethyldiborane. Tetramethyldiborane was prepared by the reaction of diborane with trimethylboron.¹² A large excess of trimethylboron was added to diborane in a glass tube which was then sealed in vacuo and allowed to stand at room temperature for about a week. The tube was then opened in vacuo to the vacuum line and the contents fractionated through two U-tubes held at -80° and -196° . The portion retained at -80° was mainly tetramethyldiborane. This fraction was then stored on the vacuum line at -80° . Each quantity of tetra-

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

methyldiborane used in experimentation was purified by fractional condensation at -80° until the vapor tension at 0° was 48.0 mm (literature value 48.0 mm).

Ammonia. The source of ammonia came from a cylinder of anhydrous ammonia purchased from the Matheson Company. Ammonia from the cylinder was condensed into a storage bulb on the vacuum line which contained small chunks of sodium metal. About 80 cc of liquid ammonia was stored as its sodium solution at -80° in order to remove the last traces of water. Pure ammonia was then available after the removal of any hydrogen which was produced upon standing.

Trimethylamine. Trimethylamine was purchased also from the Matheson Company. About 250 cc of liquid trimethylamine were condensed from a cylinder into a pyrex bomb tube which contained about 10 grams of phosphorus pentoxide. The tube was sealed and allowed to stand at room temperature for a week with occasional shaking. The tube was later opened and the dry trimethylamine was distilled into a small metal cylinder until needed.

Water. The water used for hydrolysis was distilled water that was redistilled in the vacuum line and stored in the same apparatus.

Hydrogen Chloride. The hydrogen chloride used for acid hydrolysis was obtained by distilling technical grade concentrated hydrochloric acid solution through a trap held at -80° in order to remove water and collecting the gaseous hydrogen chloride by condensation at -196° . The hydrogen chloride was also stored in the vacuum apparatus.

CHAPTER VI

THE REACTIONS OF TETRAMETHYLDIBORANE WITH AMMONIA AND TRIMETHYLAMINE

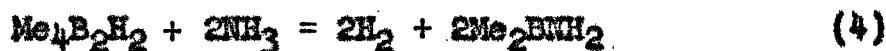
The work shown here is in confirmation with the literature. The separate studies of the reaction of tetramethyldiborane with ammonia and the reaction of tetramethyldiborane with trimethylamine not only afforded good experience at the high vacuum work but also set a sounder background for the study of the reaction of the diammonia complex of tetramethyldiborane with trimethylamine.

From this point on, the formulas quite frequently will be substituted for the names of compounds because of the bulkiness of nomenclature, especially for boron compounds, for which there is a lack of a standard simple nomenclature.

The reaction of $\text{Me}_4\text{B}_2\text{H}_2$ with NH_3 . When ammonia was added to tetramethyldiborane at -30° a solid, white, salt-like compound was formed which was stable and nonvolatile up to a temperature of about -50° . If ammonia or tetramethyldiborane was present in excess, it was possible to distill away the excess amount by warming from -30° to -60° . The amount retained was always in the stoichiometric ratio shown by the equation



When the complex or "diammoniate"¹³ was warmed to -50° , decomposition was apparent from the appearance of hydrogen being slowly evolved. At -30° hydrogen was given off in appreciable quantities. The decomposition went to completion at room temperature to give H_2 and Me_2BNH_2 . The net reaction at room temperature was in agreement with the equation



The details of four experiments are tabulated in Table I on page 26. These results are in complete agreement with those reported in the literature.¹⁴

It should be noted in Table I that in experiments 1 and 2 an excess of NH_3 was used whereas in experiments 3 and 4 an excess of $Me_4B_2H_2$ was present and could be recovered. The existence of a "monoammoniate" is not supported by the data.

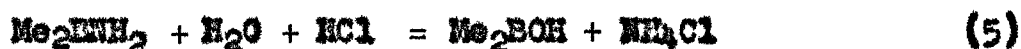
Of the two products obtained from the $Me_4B_2H_2-NH_3$ system the hydrogen was the simplest to readily identify and measure. The physical nature of Me_2BNH_2 too often lead to inaccurate identification or measure of the yield of Me_2BNH_2 when based upon its vapor density. At room temperature it may exist not only as a monomeric vapor but also as a sub-

¹³vide n. 5, p. 4.

¹⁴H. I. Schlessinger, Horvitz and Burg, loc. cit.

linable polymeric solid.¹⁵ Observed molecular weights taken from vapor densities ranged from 52 to 90 (Me_2BNH_2 calculated 56.8).

A convenient way to determine the amount of Me_2BNH_2 was hydrolysis in an acid medium which goes according to the equation



From this mixture the volatile dimethylboric acid could be isolated and it was an indirect measure of the yield of Me_2BNH_2 .

TABLE I

THE REACTION OF NH_3 WITH $\text{Me}_4\text{B}_2\text{H}_2$ AT 25° C.

Experiment		1	2	3	4
NH_3 added	(mmoles)	2.25	4.19	2.32	0.58
$\text{Me}_4\text{B}_2\text{H}_2$ added	"	1.00	1.03	2.19	1.93
H_2 produced	"	1.91	2.03	1.95	0.51
Me_2BNH_2 isolated	"	1.67	1.85	1.67	0.44
NH_3 recovered	"	-	2.03	-	-
$\text{Me}_4\text{B}_2\text{H}_2$ recovered	"	-	-	0.79	1.39
Ratio $\text{H}_2/\text{Me}_4\text{B}_2\text{H}_2$		1.91	2.01	-	-
Ratio $\text{Me}_2\text{BNH}_2/\text{Me}_4\text{B}_2\text{H}_2$		1.67	1.80	-	-

*No attempt to recover NH_3 was made in this experiment.

¹⁵H. I. Schlesinger, G. W. Schaeffer and others, Final Report to the Naval Research Laboratory for the year 1947-48 of Contract N6ori-20, T. O. X., pp. 14-19.

The reaction of $\text{Me}_4\text{B}_2\text{H}_2$ with Me_3N . When Me_3N was added to $\text{Me}_4\text{B}_2\text{H}_2$ at -80° a solid, white, salt-like compound was formed which upon warming to room temperature yielded a clear, colorless, slightly volatile liquid (vapor pressure of 23 mm at 28°) which slowly produced H_2 by decomposition. The stoichiometry for the reaction was in agreement with the equation



which is in confirmation of the literature.¹⁶ The $\text{Me}_2\text{BHNMe}_3$ was recognized from its hydrolysis products according to the equation



In one experiment (experiment 3, Table II, page 28) the amine complex produced by the reaction was indicated to be $\text{Me}_2\text{BHNMe}_3$ from the analysis of a weighed sample. The sample weight of 32.0 mg represented 0.32 mmoles of $\text{Me}_2\text{BHNMe}_3$. Room temperature hydrolysis with an HCl - H_2O mixture produced 0.29 mmoles of H_2 and 0.29 mmoles of Me_2BOH . The residue from hydrolysis after drying in vacuo weighed 30.3 mg and represented 0.32 mmoles of $\text{Me}_3\text{N} \cdot \text{HCl}$. This is in complete agreement for the above equation describing the hydrolysis of $\text{Me}_2\text{BHNMe}_3$.

The details of three experiments appear in Table II

¹⁶Burg and Schlesinger, 61, loc. cit.

below.

TABLE II
THE REACTION OF Me_3N WITH $\text{Me}_4\text{B}_2\text{H}_2$

Experiment		1	2	3
Me_3N added	(mmoles)	1.46	2.05	0.67
$\text{Me}_4\text{B}_2\text{H}_2$ added	"	0.35	0.90	0.20
Me_3N recovered (excess)	"	0.74	0.24	0.23
Me_3N in product (Kjeldahl)	"	0.69	-	-
Ratio of Me_3N in product/ $\text{Me}_4\text{B}_2\text{H}_2$		1.97	2.02	1.95

In these studies Me_3N was condensed with the $\text{Me}_4\text{B}_2\text{H}_2$ with liquid nitrogen and the mixture was stored at -80° for periods of 10 days, 1 day, and 1 day respectively for experiments 1 to 3, after which the excess Me_3N was removed at -80° by distillation in vacuo.

The decomposition of Me_2BHMe_3 at room temperature.

The room temperature decomposition of Me_2BHMe_3 was noticed to yield H_2 , Me_3N , and the complex Me_3BHMe_3 among its products. In one experiment, a 1.79 mmole sample of Me_2BHMe_3 was kept at room temperature in a 300 cc bulb for one month. In this time 0.03 mmole of H_2 , 0.04 mmole of Me_3B , and 0.11 mmole of Me_3N were produced. An equilibrium seemed to be involved for the decomposition. When the remaining amount of Me_2BHMe_3

stood at room temperature for three hours, another small portion of H_2 was produced. This phenomenon was found to be repetitive and fast enough to make it impossible to determine the vapor pressure of Me_2BHNMe_3 above room temperature as it is recorded in the literature.¹⁷

An insight to the probability of Me_2BHNMe_3 being unstable can be gained by comparison to Me_3BNMe_3 . The three methyl groups each on the boron and nitrogen atoms in Me_3BNMe_3 illustrate the effect of their steric hinderance in that Me_3BNMe_3 is 70% dissociated¹⁷ at -80° . Even at room temperature, Me_3BNMe_3 is dissociated enough that Me_3B and Me_3N may be isolated from Me_3BNMe_3 by fractional condensation in vacuo. The strain of the B-N bond in Me_2BHNMe_3 should be less than that in Me_3BNMe_3 by approximately the amount contributed by one methyl group.

Another factor involved is the relative acid strengths of the Me_2BH group and Me_3B . The B-N bond in Me_3BNMe_3 is further weakened because the three methyl groups on the boron atom displace electrons toward the boron atom; the electron density around boron is increased and hence the acid strength of Me_3B is decreased. Because the effect of a third methyl group is absent, the Me_2BH group should be a stronger acid than Me_3B , but the expected increase in stability could be

¹⁷H. I. Schlesinger and others, J. Am. Chem. Soc., 61, 1078 (1939); H. Brown, J. Am. Chem. Soc., 67, 374 (1945).

overshadowed by the steric interference between the methyl groups attached to the boron and nitrogen atoms resulting in an overall force which tends to separate the two atoms. From the amount of Me_3N produced in the sample discussed above, the indication is that Me_2BHMe_3 is 6% decomposed at room temperature.

A possible explanation of the decomposition of Me_2BHMe_3 may be found through its dissociation to form the compounds from which it is constituted, probably, according to the equation



In this system, the equilibrium lies to the left. This would account for the appearance of HMe_3 . The hydrogen and Me_3B may have their source from the subsequent decomposition of $(\text{Me}_2\text{BH})_2$ which disproportionates to the lower methylated derivatives of diborane, hydrogen, trimethylboron, and higher boranes. The hydrogen produced would serve to stabilize the system against further decomposition of Me_2BHMe_3 .

CHAPTER VII

ATTEMPTS TO PREPARE AMINOTETRAMETHYLDIBORANE

In this chapter a review is made of the significance of the $\text{Me}_4\text{B}_2\text{H}_2\text{-NH}_3$ system when the tetramethyldiborane is in excess. In this case it was then possible to determine if the hypothetical compound aminotetramethyldiborane could be prepared in this manner. The preparation of the same compound was also attempted in another manner by allowing Me_2BNH_2 to be in contact with $\text{Me}_4\text{B}_2\text{H}_2$. Both methods failed to yield aminotetramethyldiborane.

The reaction of $\text{Me}_4\text{B}_2\text{H}_2 \cdot 2\text{NH}_3$ with $\text{Me}_4\text{B}_2\text{H}_2$. The diammoniate of tetramethyldiborane¹⁸ is similar in composition to the diammoniate of diborene¹⁹ in that each readily evolve one equivalent of hydrogen upon treatment with sodium in liquid ammonia. This shows the diammoniate of tetramethyldiborane to contain the NH_4^+ ion. It seemed likely that an excess of tetramethyldiborane, with its available Me_2BH groups, would react with the ammonium ion.

Aminodiborane has been prepared by the action of diborene

¹⁸G. V. Campbell, Jr., PhD Dissertation at the University of Southern California.

¹⁹Schlesinger and Burg, 60, 290, ibid.

on the diammoniate of diboreane.²⁰ The analogy to be made at this point is that tetramethyldiboreane has been brought in contact with the diammoniate of tetramethyldiboreane without apparent reaction. Reaction mixtures with tetramethyldiboreane available for reaction with the diammoniate of tetramethyldiboreane have been described previously as experiments 3 and 4 in Table I on page 26, in which $\text{Me}_4\text{B}_2\text{H}_2$ was present in an amount greater than that required to form $\text{Me}_4\text{B}_2\text{H}_2 \cdot 2\text{NH}_3$. It was shown that aminotetramethyldiboreane was not produced but instead only Me_2BNH_2 and H_2 and the excess $\text{Me}_4\text{B}_2\text{H}_2$ was recovered from the reaction mixture.

The reaction of Me_2BNH_2 with $\text{Me}_4\text{B}_2\text{H}_2$. In a further attempt to prepare $\text{Me}_2\text{BNH}_2\text{BMe}_2$, Me_2BNH_2 and $\text{Me}_4\text{B}_2\text{H}_2$ were mixed. The anticipated reaction was as follows



Hence, 0.50 moles²¹ of Me_2BNH_2 and 0.27 moles of $\text{Me}_4\text{B}_2\text{H}_2$ were allowed to stand in contact with each other for two weeks at -80° . The mixture was then warmed to -30°

²⁰K. I. Schlesinger and D. M. Ritter, *J. Am. Chem. Soc.*, **60**, 2297 (1938).

²¹This is the amount of Me_2BNH_2 as calculated from the observed molecular weight of 50.2 for a 0.61 mmole mixture of Me_2BNH_2 and NH_3 . The amount of NH_3 present in the mixture was then 0.11 moles.

and 0.12 moles of H_2 was collected.²² The volatile material was then fractionated through a series of U-tubes held respectively at the decreasing temperatures of -60° , -80° , -120° , and -196° . The observed molecular weights of these fractions were 52.5, 68.5, 44.1, 28.4, and 53.4, and do not suggest the presence of $Me_2B(CH_3)_2BMe_2$ which would have a molecular weight of 98.6.

It appears from the standpoint of structure, that Me_2BNH_2 would have a considerably lower tendency to add a borine group than the analogous H_2BNH_2 ²³ due to the presence of the two methyl-groups on boron, each tending to increase the electron density around the boron atom. The presence of the two methyl-groups on boron evidently afford a block to the formation of the hypothetical compound amino-B,B,B',B'-tetramethyldiborane, although the aminodiborane, N-methylaminodiborane, and N,N-dimethylaminodiborane have been prepared by similar methods to those used here.²⁴

²²This is the expected amount of H_2 produced from the reaction of 0.11 moles of KH_3 with $Me_2B_2H_2$. This amount of KH_3 was present in the sample of Me_2BNH_2 taken for this experiment.

²³Schlesinger and Ritter, *ibid.*

²⁴A. B. Burg and C. L. Randolph, Jr., *J. Am. Chem. Soc.*, **71**, 3451 (1949).

CHAPTER VIII

THE REACTION OF THE METHYL BORIC ACIDS WITH AQUEOUS HCl AT ELEVATED TEMPERATURES

This study was carried out in order to interpret the results of the preliminary investigations of the $\text{Me}_4\text{B}_2\text{H}_2\text{-NH}_3$ system and the $\text{Me}_4\text{B}_2\text{H}_2\text{-HMe}_3$ system in which analyses of compounds by hydrolysis data gave results which were difficult to explain. An explanation was suspected to be found in the conditions employed during hydrolysis. The following study shows how this suspicion was confirmed.

Experimental problem and solution. In some of the first reaction studies of the $\text{Me}_4\text{B}_2\text{H}_2\text{-NH}_3$ system, results were obtained which differed from that reported in the literature²⁵ in that (1) the yield of Me_2BNH_2 , as measured by the Me_2BOH yielded upon hydrolysis, was very low and (2) the hydrolysis of the products received from the $\text{Me}_4\text{B}_2\text{H}_2\text{-NH}_3$ system yielded a noncondensable gas indicating the products retained some hydride activity, which would not be true of Me_2BNH_2 . It was difficult to give a reasonable interpretation of these results.

Repeated experiments, which were performed in order to

²⁵Schlesinger and Burg, Chem. Revs., loc. cit.

determine the reproducibility of the hydride activity of the initial reaction products, yielded three significant facts; (1) the amount of hydride activity retained by the reaction products was not reproducible, (2) the noncondensable gas yielded upon hydrolysis was not hydrogen, but rather methane, as identified by vapor pressure, observed molecular weight, and flame tests, and (3) the residue from hydrolysis could be titrated with NaOH in solution with a large excess of Mannitol which indicates the presence of H_3BO_3 or $NaB(OH)_2$.

Thus it appeared that the temperature of 140° , which was maintained during the hydrolysis, was high enough to cause a cleavage of the CH_3-B bond. Therefore, hydrolysis studies at 140° of some methyl derivatives of boric acid were made in order to help clarify the studies of the hydrolyses of Me_2BH_2 and Me_2BHMe_3 obtained from the $Me_4B_2H_2-NH_3$ and the $Me_4B_2H_2-HMe_3$ systems.

Elevated temperature hydrolysis of the methyl boric acids. Samples of Me_2BH_2 , obtained from the thermal decomposition of $Me_2BH \cdot NH_3$, were purified and hydrolyzed with an $HCl-H_2O$ mixture at high temperatures. The amount of Me_2BOH obtained from the hydrolyses of these samples was sealed in a tube along with an $HCl-H_2O$ mixture and heated in the oven for several hours at 110° , 140° , and 160° respectively. A sample of trimethylboron and a sample of trimethylamine were treated similarly. The detailed results of these studies are

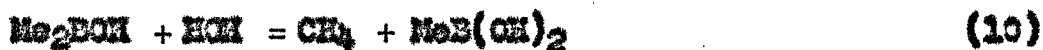
shown in Table III below.

TABLE III
THE REACTION OF METHYL DERIVATIVES OF BORIC ACID WITH
AQUEOUS HCl AT ELEVATED TEMPERATURES

Compound	Quantity (mmoles)	Temp. (°C.)	Time (hrs)	CH ₄ Produced (mmoles)	Me ₂ BOH in prod- uct (mmoles)
Me ₃ B	0.51	140	5	0.29	0.30
Me ₂ BOH	1.73	160	10	0.66	0.90
Me ₂ BHCH ₂	0.91	160	10	0.57	0.36
Me ₂ BHCH ₂	0.80	140	3	0.03	0.75
Me ₂ BHCH ₂	1.03	110	2	0.003	1.04
Me ₃ N	0.76	140	14	< 1/10 cc	-

In a number of further studies, where Me₂BHCH₂ was hydrolyzed at 105° to 110°, the time has been extended to several days without appreciable methane formation. Hence it appears that the production of methane becomes appreciable at temperatures much higher than 110°, but up to 110° the CH₃-B bonds are not ruptured.

It is evident from the data in Table III that the B-C bonds of trimethylboron and dimethylboric acid were hydrolyzed at 140° to 160° according to the equations



with the ultimate hydrolysis perhaps yielding boric acid to a

small extent as



The results of this particular study then helped clarify the hydrolysis data obtained from the first experimental investigations of the $\text{Me}_4\text{B}_2\text{H}_2\text{-NH}_3$ system and the $\text{Me}_4\text{B}_2\text{H}_2\text{-NMe}_3$ system. For example, in one experimental study of the reaction between $\text{Me}_4\text{B}_2\text{H}_2$ and NH_3 , 1.77 mmoles of a volatile substance with a molecular weight of 58.3 (Me_2NHNH_2 calculated 56.8) was hydrolyzed overnight at 140° . Hydrolysis yielded 0.65 mmoles of Me_2BOH and 1.11 mmoles of a noncondensable gas with a molecular weight of 15.8 (CH_4 calculated 16). This gas burned with a bluish flame when ignited. The micro-Kjeldahl determination of ammonia in the hydrolysis residue indicated 1.71 mmoles. If, according to equation (10), 1.11 mmoles of Me_2BOH had undergone hydrolysis and the correct amount of Me_2BOH should be 1.76 mmoles. This then gives very good agreement, together with the nitrogen determination, as what should be expected when 1.77 mmoles of Me_2NHNH_2 is hydrolyzed.

In another case, the slightly volatile liquid obtained from the reaction of 0.94 mmoles of $\text{Me}_4\text{B}_2\text{H}_2$ and 1.96 mmoles of Me_3N was hydrolyzed similarly overnight at 140° . Hydrolysis yielded only 0.14 mmoles of Me_2BOH but 3.62 mmoles of a noncondensable gas with a molecular weight of 10.4. When ignited, the noncondensable gas burned with a green flame, then immediately blue, and "popped" gently back into the weighing bulb

that was being used. A chloride determination of the hydrolysis residue precipitated 1.90 mmoles of AgCl . If the non-condensable gas is considered a mixture of H_2 and CH_4 and 1.83 mmoles is the expected yield of $\text{Me}_2\text{BNEtMe}_3$ in this particular preparation and hydrolyzes according to equation (6) to produce 1.83 mmoles of H_2 , then 1.74 mmoles of CH_4 are present in the mixture. This represents 1.74 mmoles of Me_2BOH hydrolyzed and the total amount of Me_2BOH produced during hydrolysis was then actually 1.83 mmoles which is in excellent agreement with the expected yield and the chloride determination.

CHAPTER IX

THE REACTION OF THE DIAMMONIATE OF TETRAMETHYLDIBORANE WITH TRIMETHYLAMINE

Although both diborane and tetramethyldiborane clearly combine with two molecules of ammonia, it is not a simple matter to write a formula for these diammonia complexes which would accurately indicate their structures or chemical properties. The two nitrogen atoms apparently are not equivalent. Even though it appears that two types of combined nitrogen atoms are observed through chemical reaction, the structural differences are not yet established. For example, the diammonia complexes of both diborane and tetramethyldiborane yield immediately one equivalent of hydrogen when acted upon by sodium in liquid ammonia. Further contact with sodium then liberates slowly up to 40% more hydrogen which indicates the presence of more than just one mole of available protonic hydrogen.

The following study was made in order to obtain more information about the diammoniate of tetramethyldiborane. It was desired to determine if the diammoniate would undergo displacement of NH_3 by the stronger Lewis base Me_3N .

The reaction of $\text{Me}_4\text{B}_2\text{H}_2 \cdot 2\text{NH}_3$ with Me_3N . These experiments were performed by forming the diammoniate of $\text{Me}_4\text{B}_2\text{H}_2$ at low temperatures and allowing it to stand at -30° for at least

3 hours (in most cases over 10 hours) before the removal of the excess NH_3 by distillation away from -80° . The diammoniate was then treated with several successive small portions of Me_3N (approximately 30 cc as a gas) at temperatures up to -30° in an attempt to displace the ammonia. The displacements were thus continued until the Me_3N removed from the system gave a consistent vapor pressure which approached that of pure Me_3N (observed 9 mm at -80° , literature 6.5 mm). The displaced product was a solid, white salt-like substance at -80° .

Trimethylamine was found to displace appreciable amounts of ammonia in the first three displacements as indicated by the large increase in the vapor pressure of the material removed by distillation in vacuo at -80° over that of the pure trimethylamine originally introduced. After the displacements were completed, the product was warmed slowly to 25° , in vacuo, to yield H_2 , Me_2NHNH_2 , and $\text{Me}_2\text{NHNHMe}_3$. The details of five of these experiments appear in Table IV on page 41.

It should be noticed in Table IV that in experiments 2 and 3, the Me_3N displacements were carried out in the usual manner without delay and displaced a little more than one mole of NH_3 while in experiment 5, prolonged standing of the diammoniate in liquid Me_3N shows that the amount of displaced ammonia is 57% more than one mole of NH_3 from the diammoniate. This

then indicates that one mole of NH_3 is readily displaced while the second mole is but slowly displaced. This fact plays an important role in the interpretation of this particular study.

TABLE IV
THE REACTION OF $\text{Me}_4\text{B}_2\text{H}_2 \cdot 2\text{NH}_3$ WITH Me_3N

Experiment	1	2	3	4	5*
$\text{Me}_4\text{B}_2\text{H}_2$ taken (moles)	0.99	0.55	1.03	1.09	1.03
NH_3 taken "	2.01	1.25	2.73	2.97	2.77
H_2 upon warming "	0.35	0.17	0.55	1.04	0.33
NH_3 recovered "	-	0.89	1.87	-	2.33
Me_2BHNH_2 "	0.12	-	0.39	0.51	0.24
$\text{Me}_2\text{BHNMe}_3$ "	1.50	0.60	1.04	1.25	1.44
Ratio $\text{H}_2/\text{Me}_4\text{B}_2\text{H}_2$	0.35	0.31	0.53	0.95	0.03
Ratio $\text{Me}_2\text{BHNMe}_3 / \text{Me}_4\text{B}_2\text{H}_2 \cdot 2\text{NH}_3$	1.55	1.09	1.01	1.15	1.39
Moles NH_3 displaced per mole $\text{Me}_4\text{B}_2\text{H}_2 \cdot 2\text{NH}_3$	-	1.36	1.12	-	1.57

*In this experiment the diazoniates stood in contact with approximately $3/4$ cc of liquid Me_3N at -80° for a period of three weeks before further displacements.

Hydrogen was indicated to be a product of the thermal decomposition of the displaced product in that a noncondensable gas could be pumped into the gas burette by the Töpler pump where it exerted a high pressure (over 200 mm Hg) even when cooled to the temperature of liquid nitrogen. Were the gas

methane, the vapor pressure at this temperature would have dropped to 12 mm Hg.

Aminodimethylborane was indicated to be a product also, when volatile samples trapped at -110° hydrolyzed to yield Me_2BOH but not any hydrogen. Molecular weight determinations of the -110° fractions were not used for identification because of the possible presence of Me_3N which has a similar molecular weight.

The $\text{Me}_2\text{BNEtMe}_3$ was identified by an observed melting point range of -20° to -17° (literature value -13°) and vapor pressures of 3.8 mm and 9.9 mm respectively at 23.5° and 45.5° (literature values 3.7 mm and 10.2 mm). Confirmatory identification was obtained by the analysis of hydrolysis data. The hydrolysis of $\text{Me}_2\text{BNEtMe}_3$ has been previously described as proceeding according to the following equation.



The details of the hydrolysis of samples of $\text{Me}_2\text{BNEtMe}_3$ appear in Table V on page 43.

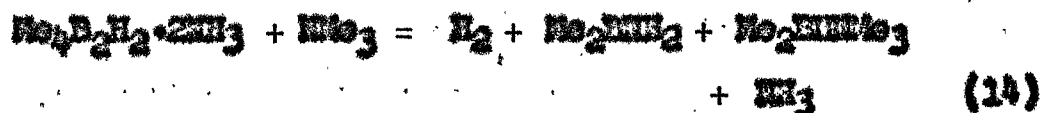
The data in Table V indicates that one mole of ammonia is readily displaced and is in agreement with the following equation.



Upon warming, the complex $\text{Me}_4\text{B}_2\text{H}_2 \cdot \text{NH}_3 \cdot \text{NEt}_3$ decomposes probably according to the equation



The sum of these two equations would then give the net reaction as being



This is similar to that for the reaction of Me_3H with B_2H_6 reported by Schaeffer.²⁶



TABLE V

HYDROLYSIS OF Me_2BHNO_3 OBTAINED FROM THE
 $\text{Me}_4\text{B}_2\text{H}_2 \cdot 2\text{NH}_3$ - HNO_3 SYSTEM

Experiment*	2	3	4	5
Me_2BHNO_3 sample (mg)	60.5	112.6	135.6	144.4
Me_2BHNO_3 calculated (mmoles)	0.60	1.04	1.34	1.44
H_2^{**} "	0.91	1.18	1.56	1.43
$\text{Me}_2\text{BOH}^{**}$ "	0.31	0.97	0.93	1.36
Hydrolysis residue (mg)	40.1	102.0	123.4	134.7
$\text{Me}_3\text{H} \cdot \text{HCl}$ calculated (mmoles)	0.42	1.07	1.23	1.41
AgCl precipitated "	0.42	1.08	1.25	1.66
Micro-Kjeldahl nitrogen "	6.47	1.09	1.27	1.44

*These experiments stem from those tabulated in Table IV.

**A high H_2 value and a low Me_2BOH value result from the reaction $\text{Me}_2\text{BOH} + \text{HCl} = \text{CH}_4 + \text{MeB}(\text{OH})_2$. See Chapter III.

²⁶G. W. Schaeffer, et al., paper read at the national meeting of the American Chemical Society at Dallas, Texas (1956).

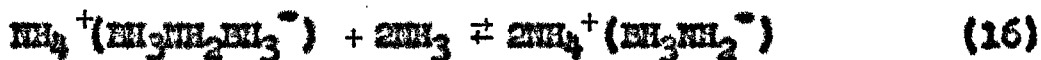
Equation (13) points out that the yield of Me_2BHNH_2 and H_2 should always be the same. Though the data does not show this very well, it is interesting to note that the amount of Me_2BHNH_2 detected never exceeded the amount of hydrogen yielded. The amount of hydrogen is probably the more accurate value since hydrogen can be so easily and completely removed and measured. It was difficult to isolate Me_2BHNH_2 from large amounts of Me_3N and traces of NH_3 by fractional distillation condensation because of the similarities of these three compounds in their very low vapor pressure ranges. Consequently, large amounts of Me_3N discarded during experimentation probably contained small amounts of Me_2BHNH_2 .

When more than one equivalent of NH_3 was displaced, (possibly by further reaction between Me_3N and $\text{Me}_4\text{B}_2\text{H}_2 \cdot 2\text{NH}_3 \cdot \text{Me}_3\text{N}$) the following was observed; (1), more than one equivalent of NH_3 was recovered (2), more than one equivalent of $\text{Me}_2\text{BHNHMe}_3$ was produced (3), less than one equivalent of H_2 was evolved upon warming, and (4), less than one equivalent of Me_2BHNH_2 was produced. All this is obvious in Table IV.

The constitution of $\text{Me}_4\text{B}_2\text{H}_2 \cdot 2\text{NH}_3$. The structure of the diammoniate of diborane has been the subject of much controversy. Formulas based upon chemical properties, which give some insight to structure, still leave much to be desired. However, the diammoniate of tetramethyldiborane should have

the same basic structure as the diammoniate of diborane, so a comparison of the results of the present work will be made with similar studies concerned with the unmethylated parent compound, and the interpretations of structure which have been made.

Three structural formulas have been proposed for the analogous diammoniate of diborane. The formula $\text{NH}_4^+(\text{BH}_3\text{NH}_2\text{BH}_3^-)$ has been advanced to account for the one equivalent of H_2 readily given off when the diammoniate is treated with sodium in liquid ammonia.²⁷ A slow secondary reaction producing 40% more hydrogen, which suggested the availability of more than just one equivalent of NH_4^+ ions, lead to the postulation that the following equilibrium was involved between the diammoniate of diborane and the ammonia solvent.

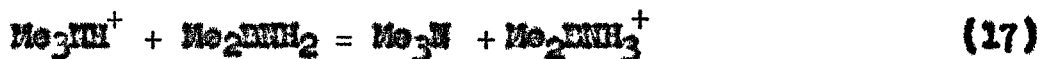


If the diammoniate of tetramethyldiborane were written similarly, it would be $\text{NH}_4^+(\text{Me}_2\text{BH}(\text{NH}_2)\text{BHMe}_2^-)$. In order to account for more than one mole of replaceable NH_3 , an equilibrium analogous to equation (16) cannot be written because (1) the ammonia solvent is absent and (2) a reaction between displaced ammonia and $\text{NH}_4^+(\text{Me}_2\text{BH}(\text{NH}_2)\text{BHMe}_2^-)$, thus retaining the ammonia, is unlikely since it has been found that the displaced NH_3 was removed along with the excess Me_3N by distillation.

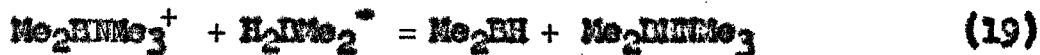
²⁷Schlesinger and Burg, 60, 290, loc. cit.

However, the above formulation, though satisfying the condition of one readily replaceable NH_3 , disregards another property of the diammoniate, namely that the diammoniate of diborane appears to contain the borohydride group²⁸ BH_4^- .

With both the NH_4^+ ion and the BH_4^- ion in mind, the diammoniate of diborane has been formulated²⁸ as $\text{NH}_4^+(\text{H}_2\text{BNH}_2-\text{BH}_4^-)$. The diammoniate of tetramethyldiborane can be written similarly as $\text{NH}_4^+(\text{Me}_2\text{BNH}_2\text{H}_2\text{BMe}_2^-)$. After replacing one mole of NH_3 with Me_3N , the resulting complex would be written as $\text{Me}_3\text{NH}^+(\text{Me}_2\text{BNH}_2\text{H}_2\text{BMe}_2^-)$. In order to account for more replaceable ammonia a reaction sequence can be formulated for the reaction of the structural units of $\text{Me}_3\text{NH}^+(\text{Me}_2\text{BNH}_2\text{H}_2\text{BMe}_2^-)$ and Me_3N as follows.



The formation of subsequent $\text{Me}_2\text{BNHMe}_3$ may then follow as



The net equation would be

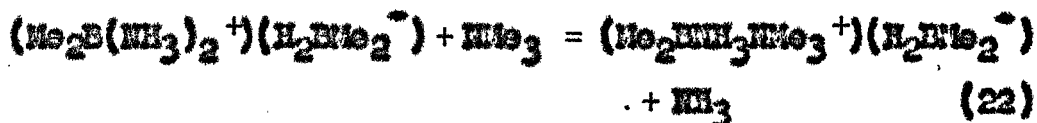


However, verification of this reaction sequence would not be a simple matter and it is even questionable in view of the observation that Me_2BNH_2 apparently did not react with an

²⁸Schaeffer, Adams and Koenig, loc. cit.

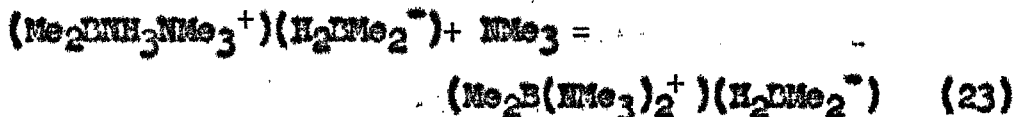
ion containing a protonic hydrogen, similar to equation (17), when a sample of $\text{Me}_2\text{B}(\text{NH}_2)_2$ containing ammonia was mixed with $\text{Me}_4\text{B}_2\text{H}_2$ as described in Chapter VII. The only reaction observed was that between the ammonia and tetramethyldiborane.

A third formulation for the diammoniate of diborane which indicates the borohydride ion and a positive ion containing NH_3 groups has been suggested²⁹ as $(\text{H}_2\text{B}(\text{NH}_3)_2^+)(\text{BH}_4^-)$. Writing the diammoniate of $\text{Me}_4\text{B}_2\text{H}_2$ similarly would yield $(\text{Me}_2\text{B}(\text{NH}_3)_2^+)(\text{H}_2\text{BMe}_2^-)$. Because the observations of the displacement studies indicate that one ammonia molecule is readily displaced and that the further displacement of any ammonia is done slowly, the formula $(\text{Me}_2\text{B}(\text{NH}_3)_2^+)(\text{H}_2\text{BMe}_2^-)$ may not seem likely because both NH_3 groups are written as being equivalent and indicates that one NH_3 group is just as replaceable as the other. This need not be the case, however. The replacement of one NH_3 molecule by a NMe_3 molecule would probably go as follows.



The introduction of the one bulky trimethylamine molecule may well serve as a partial block for the approach of a second bulky trimethylamine molecule, such that the following reaction is greatly retarded.

²⁹Shore and Parry, *ibid.*



A statistical treatment could also be considered in this case. The first NMe_3 molecule must have a given number of paths by which it may approach $(\text{Me}_2\text{B}(\text{NH}_3)_2^+)(\text{H}_2\text{BMe}_2^-)$ and displace either one of the ammonia molecules. Once it assumes the relative position previously occupied by the displaced NH_3 group it has then by its mere presence placed an unique limit to the number of paths by which a second NMe_3 molecule may approach $(\text{Me}_2\text{BNH}_3\text{NMe}_3^+)(\text{H}_2\text{BMe}_2^-)$ and displace the remaining NH_3 molecule. The first NMe_3 molecule then has a choice of two NH_3 molecules to act upon; the second NMe_3 molecule has no such choice. Statistically speaking, the second mole of ammonia would then be expected to come off at approximately half the rate of the first one, neglecting other factors. Any steric effects afforded by the presence of the first NMe_3 group would further decrease the rate.

Of the three structural formulas proposed for the diammoniate of diborane and if similar formulas are assumed for the diammoniate of tetramethyldiborane, the displacement studies favor a formulation of $(\text{Me}_2\text{B}(\text{NH}_3)_2^+)(\text{H}_2\text{BMe}_2^-)$ for the following reasons (1) both the borohydride and ammonium ion characters are indicated (2), more than one mole of replaceable ammonia is indicated and (3), a simple treatment based upon commonly accepted chemical principles can explain the difference in the

ease of displacing a second ammonia molecule from the compound
 $(Me_2B(NH_3)_2)^+(H_2BMe_2^-)$.

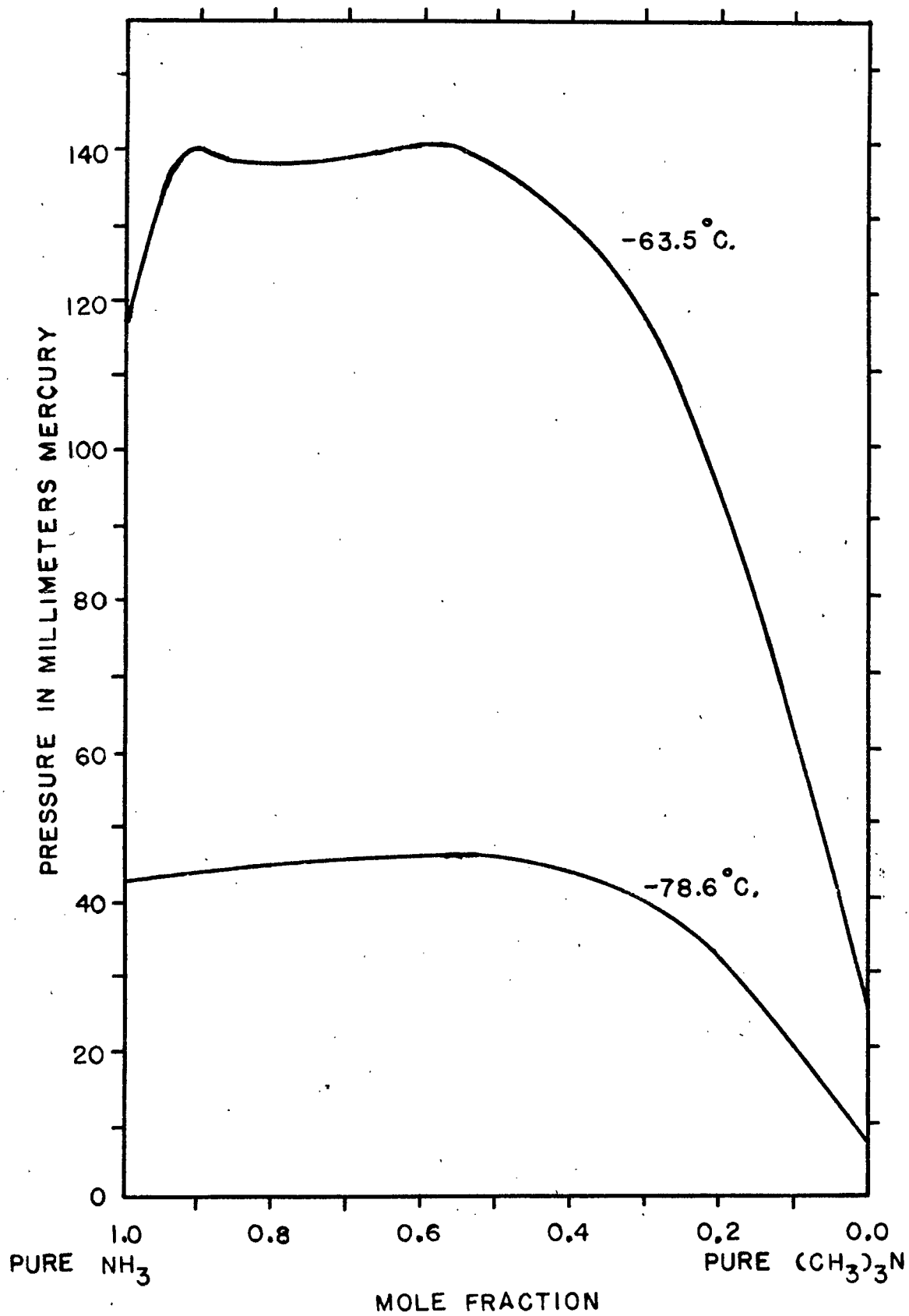
CHAPTER X

THE ANALYSIS OF ARNONIA-TRIMETHYLAMINE MIXTURES

In order to determine the effectiveness of Me_3N displacements from ammoniated $\text{Me}_4\text{B}_2\text{H}_2$, it was necessary to devise a rapid method of analyzing a sample of Me_3N for NH_3 content. This was accomplished by determining the vapor pressure-composition curves for this two component system, at the two different temperatures -73.6° (sublimation point of dry ice) and -63.5° (melting point of chloroform). There was a positive deviation from Raoult's law, with a maximum at a NH_3 -mole-fraction of 0.6, which limited the applicability of the method to the NH_3 -mole-fraction range of 0.0 to 0.40. Analysis based upon these data gave reproducible results, with an accuracy of approximately 5%. (see Figure 4, page 51)

The technique employed was to successively dilute a known amount of NH_3 with known amounts of Me_3N after each vapor pressure measurement until the mole fraction of NH_3 changed from 1.00 to 0.10. For each measurement a constant sample size was taken and the vapor pressure was read for a system of constant volume. Thus, for each known gas mixture the vapor pressure was determined for a constant number of moles in a constant volume. Five minutes were allowed in each case for the mixture to reach equilibrium before recording the vapor pressure.

FIGURE 4. VAPOR PRESSURE - COMPOSITION DIAGRAMS FOR AMMONIA AND TRIMETHYLAMINE



CHAPTER XI

SUMMARY AND CONCLUSIONS

From the results of the work discussed in this thesis the following conclusions may be made.

The reaction of tetramethyldiborane and ammonia has been confirmed as reported in the literature to proceed at room temperature as follows:



The reaction of tetramethyldiborane and trimethylamine has been confirmed as reported in the literature to proceed at room temperature as follows.



The compound Me_2BNMe_3 is approximately 6% decomposed at room temperature. Among the decomposition products appear hydrogen, trimethylamine, and the trimethylamine addition complex with trimethylboron.

Dimethylaminoborane is stable towards tetramethyldiborane. Tetramethyldiborane is stable towards the diammoniate of tetramethyldiborane. Simple mixtures of either pair of reagents cited do not yield the hypothetical compound amino-tetramethyldiborane.

Both trimethylboron and hydroxydimethylborane undergo acid hydrolysis to produce methane at temperatures above 110° . In a similar environment, trimethylammonium chloride is stable.

At low temperatures ammonia may be displaced from the diammoniate of tetramethyldiborane by the stronger Lewis base trimethylamine. When the resulting complex is warmed to room temperature, thermal decomposition yields H_2 , Me_2BHNH_2 , and Me_2BNHMe_3 . The net reaction when one mole of ammonia is replaced with trimethylamine may well be as follows:



However, more than just one mole of ammonia can be displaced from the diammoniate of tetramethyldiborane. This may be accomplished by the repeated addition and removal of Me_3N or by allowing the diammoniate to stand in contact with Me_3N at -30° for several days.

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