# THE REACTIONS OF SOME LEWIS ACIDS WITH HYDRAZINE

by

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To Jocelyn

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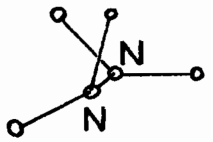
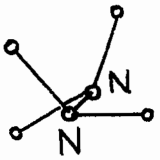
# INTRODUCTION

A large number of addition complexes formed between acceptor molecules containing Group IIIA elements and nitrogen donors are reported in the chemical literature (1-9), and with few exceptions (e.g., ethylenediamine (10)), the donor molecules have contained only one nitrogen atom. It was therefore of particular interest to investigate the reactions of some "electron-deficient" molecules of Group IIIA elements with hydrazine, the simplest substance having two nitrogen atoms which are potential electron donors.

The molecular structure of hydrazine is accepted (11,12) as that shown in the diagram:



or



Since each nitrogen atom will have its bonding electrons distributed in tetrahedral $sp^3$ hybrid orbitals, one of which contains a lone pair of electrons, the above configurations should easily permit the formation of one or two coordinate linkages with suitable acceptor molecules. It is accordingly rather surprising that only one acceptor molecule of a Group IIIA element, diborane, $B_2H_6$, has been used to study the electron donor properties of hydrazine.

In two independent studies (13,14), it was found that diborane reacted with hydrazine to form the addition compound diborane-hydrazine

$2BH_3 \cdot N_2H_4$, or $H_3B \cdot NH_2NH_2 \cdot BH_3$, indicating that both nitrogen atoms in hydrazine are capable of coordinating with borane ($BH_3$) groups. This compound was thermally unstable (14); on heating at 130°C.*, one mole of hydrogen per gram-atom of nitrogen was liberated.

In view of the scarcity of data, it appeared that there was ample scope for the study of the reactions of hydrazine with acceptor molecules other than diborane. It was thought advisable to make a detailed examination of new compounds as they were prepared. This was done in several ways: by measuring their physical properties, by subjecting them to appropriate chemical reactions, and by utilizing the techniques of x-ray diffraction, infrared absorption, and thermal decomposition.

Since boron trifluoride is one of the most active electron acceptors (1,2), its reaction with hydrazine was investigated first. Trimethylborane, $B(CH_3)_3$, was selected for coordination studies to provide a comparison of its complexes with hydrazine with those of boron trifluoride and diborane (13,14). When it was discovered that boron trichloride undergoes a condensation reaction with hydrazine eliminating hydrogen chloride, this particular study was extended to boron tribromide and to aluminum chloride, bromide, and iodide. Some experiments with trimethylaluminum, an extremely reactive material, rounded out the research programme.

In view of the numerous comprehensive reviews which are avail-

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*All temperatures in this thesis are reported in °C.

able (1-9), only a brief outline of the pertinent literature will be given here to provide a basis for the discussion of the new work reported in this thesis.

## Nomenclature

The names of addition compounds (15) are formed by joining the names of the acceptor and the donor by a hyphen, and showing the respective number of molecules with Arabic figures. For example, the compound $AlCl_3 \cdot 3NH_3$ is named aluminum chloride-3-ammonia. However, when one of the components is organic, use is made of the multiplicative terms bis, tris, etc., instead of Arabic numerals. Thus $BF_3 \cdot 2CH_3OH$ is called boron trifluoride-bismethanol.

Compounds of the type $BR_3$ have in recent years been named as substituted boranes ($BH_3$) unless all three substituent groups are halogen atoms (16). For instance, $B(CH_3)_3$ is called trimethylborane.

The term "Lewis acid" used in the title of this thesis refers to those substances which are capable of accepting a pair of electrons to form a coordinate bond (17).

Following the practice of Chemical Abstracts, the radicals $NH_2NH-$ and $NH_2N=$ are called hydrazino and hydrazono, respectively.

## Some Aspects of the Chemistry of the Boron Halides

Boron has a strong tendency to expand its covalence from three to four. According to modern valence theory, the bonding electrons of boron in a $BX_3$ molecule, where X might be an alkyl group or a halogen atom, are arranged in three coplanar $sp^2$ hybrid orbitals at angles of 120° and the $p_\pi$ orbital perpendicular to this plane is left almost vacant. Since atoms normally achieve their most stable configurations by accommodating eight electrons in their outermost valence shell (octet rule), the electronic environment of boron in $BX_3$ molecules is incomplete. The boron atom can therefore accept an electron pair from a suitable donor molecule.

An example of this kind of coordination compound is boron trifluoride-ammonia (18), $BF_3 \cdot NH_3$, in which the lone electron pair on the nitrogen atom, located in an $sp^3$ hybrid orbital, enables the boron atom to attain a stable octet configuration. In this compound, the boron trifluoride component shifts from a planar to a tetrahedral configuration (19,20) (the FBF angle becomes 111° and the FBN angle is 107°), and therefore presumably changes its bonding structure from $sp^2$ to $sp^3$ hybrid orbitals.

More than three hundred coordination compounds of boron trifluoride are mentioned in the literature, and comprehensive surveys of this particular field have appeared in recent years (1,2,3). Although boron trifluoride is a gas with a very low (-101°) boiling point (1), its addition complexes with nitrogen donors are almost invariably solids at room temperature. A representative selection of such compounds is given in Table I.

### TABLE I

### Addition Complexes of Boron Trifluoride with Nitrogen Ligands

| Compound | Melting Point | Reference |
|---|---|---|
| $BF_3 \cdot NH_3$ | 163 ± 1° | 22 |
| $BF_3 \cdot (CH_3)_3N$ | 146 - 146.5° | 23 |
| $BF_3 \cdot CH_3CN$ | 135.5 ± 0.5° | 21 |
| $BF_3 \cdot C_6H_5CN$ | 105 - 121° dec. | 2 |
| $BF_3 \cdot C_5H_5N$ | 48 - 49° | 2 |
| $BF_3 \cdot CH_3CONHC_6H_5$ | 133° | 2 |

In spite of the ease with which boron trifluoride forms addition compounds, most of the latter either decompose or thermally dissociate in the vapour phase. Only one compound, boron trifluoride-trimethylamine, $BF_3 \cdot (CH_3)_3N$, is known to be monomeric and undissociated at the boiling point (24).

Boron trichloride and boron tribromide form far fewer addition compounds than does boron trifluoride. A few representative compounds are listed in Table II.

### TABLE II

### Addition Complexes of Boron Trichloride and Boron Tribromide with Nitrogen Ligands

| Compound | Melting Point | Reference |
|---|---|---|
| $BCl_3 \cdot (CH_3)_3N$ | 243° | 25 |
| $BCl_3 \cdot C_6H_5N(CH_3)_2$* | 146° | 4 |
| $BBr_3 \cdot C_5H_5N$ | 128 - 9° | 26 |
| $BBr_3 \cdot (CH_3)_3N$ | 238 - 40° | 27 |

*N-dimethylaniline.

The small number of known addition compounds is probably due to the fact that the energies of the B-Cl bond (108.5 kcal./mole) and of the B-Br bond (90.2 kcal./mole) in their respective halides are much less than the energy of the B-F bond (154.8 kcal./mole) in boron trifluoride (28). Because of these differences in bond energies, donor molecules containing hydrogen bound to nitrogen usually react differently with $BCl_3$ or $BBr_3$ than with $BF_3$, in that hydrogen halide is eliminated by the two reactants, e.g., (29,30,31)

$$BCl_3 + 6\ NH_3 \longrightarrow 3\ NH_4Cl + B(NH_2)_3$$

$$2\ BBr_3 + 9\ NH_3 \longrightarrow 6\ NH_4Br + B_2(NH)_3$$

The large polarity associated with many molecular addition complexes (e.g., $BF_3 \cdot (CH_3)_3N$ has a dipole moment of 5.76 debyes (23)) also facilitates reactions of this type. Sometimes a complex does form between $BCl_3$ and a compound containing N-H bonds, but such materials usually lose hydrogen chloride easily. Thus the complex boron trichloride-p-toluidine (32), $BCl_3 \cdot p\text{-}CH_3C_6H_4NH_2$, melts at 160° with evolution of hydrogen chloride.

The strength of the coordinate bond in addition compounds is affected by the electronegativity of the groups attached to the donor and acceptor atoms. For instance, the ability of a ligand to donate an electron pair may be markedly reduced by the presence of electron-withdrawing substituents. Thus the compound boron trifluoride-phosphine, $BF_3 \cdot PH_3$, has been prepared (33), whereas the related complexes boron trifluoride-phosphorus trifluoride, $BF_3 \cdot PF_3$, and boron trifluoride-phosphorus trichloride, $BF_3 \cdot PCl_3$, are not known (6).

However, considerations of electronegativity alone can lead to erroneous conclusions. Until recently, it was thought, on the basis of electronegativity values, that the relative acceptor powers of certain boron compounds were in the order $BF_3 > BCl_3 > BBr_3 > \frac{1}{2}B_2H_6 > B(CH_3)_3$. A series of calorimetric experiments by H.C. Brown and his coworkers, which are summarized in Table III, has shown that the actual sequence of acceptor power should be $BBr_3 \sim BCl_3 > BF_3 > \frac{1}{2}B_2H_6 \sim B(CH_3)_3$. This apparently anomalous result for the boron halides was attributed to $\pi$ bonding between B and X in the $BX_3$ molecule, which increases along the series $BBr_3$, $BCl_3$, $BF_3$.

TABLE III

Reactions between $BX_3$ Molecules and Pyridine

| Chemical Reaction (all components in solution) | Heat of Reaction $-\Delta H$, kcal./mole | Reference |
|---|---|---|
| $BBr_3 + C_5H_5N \longrightarrow BBr_3 \cdot C_5H_5N$ | 32.0 | 26 |
| $BCl_3 + C_5H_5N \longrightarrow BCl_3 \cdot C_5H_5N$ | 30.8 | 26 |
| $BF_3 + C_5H_5N \longrightarrow BF_3 \cdot C_5H_5N$ | 25.0 | 26 |
| $\frac{1}{2}B_2H_6 + C_5H_5N \longrightarrow BH_3 \cdot C_5H_5N$ | 14.6 | 34 |
| $B(CH_3)_3 + C_5H_5N \longrightarrow B(CH_3)_3 \cdot C_5H_5N$ | 15.3 | 35 |

Using pyridine as a reference base, the data in Table III indicate that, among the boron halides, boron trifluoride has the lowest heat of reaction with the donor molecule and is therefore the weakest electron acceptor of the three halides studied.

This conclusion is substantiated by recent theoretical calculations by Cotton and Leto (36). They have calculated the energy necessary to reorganize the planar $BX_3$ molecule to the configuration necessary for coordinate bond formation. This process involves two main factors, namely, the breaking of the $\pi$ bonds and the changing of the hybridization of the boron atom. It was found that the reorganization energy (in kcal./mole) is highest for boron trifluoride (48.3) and considerably less for boron trichloride (30.3) and boron tribromide (26.2).

The acceptor order deduced from the data in Table III, i.e., $BBr_3 \sim BCl_3 > BF_3 > \frac{1}{2}B_2H_6 \sim B(CH_3)_3$, is strictly valid only for pyridine as reference base, and exceptions to the rule are known (37). For example, borane-methylthiomethane, $BH_3 \cdot (CH_3)_2S$, is more stable than boron trifluoride-methylthiomethane, $BF_3 \cdot (CH_3)_2S$, which is contrary to the prediction of the series. Further, the compound borane-carbon monoxide, $BH_3 \cdot CO$ (also called borine carbonyl), has been characterized, while the compound boron trifluoride-carbon monoxide, $BF_3 \cdot CO$, is not known. The borane group is able to release electron density to carbon monoxide and to methylthiomethane which have suitable vacant orbitals, whereas with boron trifluoride complexes, supplementary $\pi$ bonding is presumed not to occur.

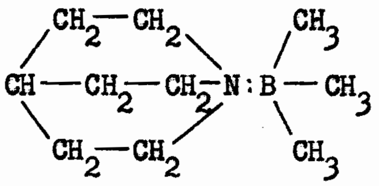
## The Coordination Compounds of Trimethylborane

A large number of addition complexes of trimethylborane have been prepared by H.C. Brown and his coworkers in their study of the influence of steric requirements on the stability of coordination compounds. Brown has reported (38), for instance, that the relative order of base strength $NH_3 <$

$(C_2H_5)_3N < C_2H_5NH_2 < (C_2H_5)_2NH$ observed with hydrogen chloride as reference acid is altered to $(C_2H_5)_3N < NH_3 < (C_2H_5)_2NH < C_2H_5NH_2$ with trimethylborane as reference acid. This was ascribed to the steric interference of the bulky ethyl groups with trimethylborane. The planar configuration (39) of the latter must be converted to a tetrahedral one during the formation of the addition compounds.

The importance of steric hindrance is further illustrated by the contrasting stabilities of the analogous compounds trimethylborane-trimethylamine, $B(CH_3)_3 \cdot (CH_3)_3N$, and trimethylaluminum-trimethylamine, $Al(CH_3)_3 \cdot (CH_3)_3N$. The former compound (40) is 94% dissociated into its components at 104.7°, while the latter substance is a stable solid (41) melting at 105°. Apparently the size (42) of the aluminum atom (radius 1.25 Å), in contrast with that of the boron atom (radius 0.80 Å), is sufficient to preclude steric interactions in the aluminum compound.

Perhaps the most striking demonstration of the influence of steric requirements on coordinate bond strength is the difference in stability between the trimethylborane compounds of triethylamine and quinuclidine (43). The triethylamine complex is so unstable that it is completely dissociated at 100°, due to the steric interaction between the trimethylborane molecule and the bulky ethyl groups. In the quinuclidine molecule, the carbon atoms adjacent to the nitrogen are held back and cannot interfere with the trimethylborane:



This compound is one of the most stable of all those formed by trimethylborane and amines.

## Some Reactions of Aluminum Chloride, Bromide, and Iodide

Although the reactions of boron trichloride and boron tribromide with ammonia result in the formation initially of hydrogen halide and subsequently of ammonium halide, analogous reactions apparently do not occur with the aluminum halides.

More than fifty years ago, Baud (44) reported that aluminum chloride formed stable addition complexes with $1\frac{1}{6}$, 3, 5, 6, and 9 molecules of ammonia, respectively. Franklin (45) extended this work to aluminum iodide and claimed the existence of stable molecules containing 6, 14, and 20 molecules of ammonia per molecule of aluminum iodide, $\mathrm{AlI_3}$. He also postulated such unusual reactions as

$$\begin{tikzcd} 2\,\mathrm{AlI_3} + 3\,\mathrm{KNH_2} \arrow[r] & \mathrm{Al(NH_2)_3 \cdot AlI_3} + 3\,\mathrm{KI} \arrow[d, "\text{crystallization}"] \\ & \mathrm{Al(NH_2)_3 \cdot AlI_3 \cdot 6\,NH_3} \end{tikzcd}$$

At least twenty different addition compounds ranging in composition from $\mathrm{AlX_3 \cdot NH_3}$ to $\mathrm{AlX_3 \cdot 20NH_3}$ were listed by Klemm and his coworkers (46,47). The most stable compounds produced were the mono- and triammonia complexes. The former compounds are covalent; they boil without decomposition above 400°, and the vapour density near the boiling point corresponds to the undissociated complex, $\mathrm{AlX_3 \cdot NH_3}$. The covalence of these compounds is suggested by the similarity of their melting points as compared with those of the simple halides:

Melting Points of $AlX_3$ and $AlX_3 \cdot NH_3$ Compounds

| | X=Cl | X=Br | X=I |
|---|---|---|---|
| m.p. $AlX_3$ | 192° | 98° | 191° |
| m.p. $AlX_3 \cdot NH_3$ | 125° | 124° | 126° |

More recently, the Raman spectrum of $AlCl_3 \cdot NH_3$ has been measured (48) and the data clearly indicate a monomeric molecule with symmetry properties like those of $BF_3 \cdot NH_3$.

The above evidence supports the reality of the compounds $AlX_3 \cdot nNH_3$, where n is a small number, but the validity of such compounds as $AlI_3 \cdot 20NH_3$ should be viewed with caution in the absence of unequivocal data. It is unfortunate that some of the compounds were inferred only from physico-chemical measurements.

## Addition Compounds of Trimethylaluminum

In contrast with monomeric trimethylborane, trimethylaluminum has a dimeric bridge structure analogous to that of diborane (49,50). This tendency to dimerization is a consequence of the strong electron acceptor properties of the aluminum atom.

Trimethylaluminum appears to behave as a stronger electron acceptor than trimethylborane, which is doubtless due in part to steric hindrance in the addition compounds of the latter. Some comparisons are given in Table IV.

## TABLE IV

Addition Compounds of Trimethylaluminum and of Trimethylborane

| Compound | Boiling Point* | Reference | Compound | Comment | Reference |
|---|---|---|---|---|---|
| $Al(CH_3)_3 \cdot (CH_3)_2O$ | 159° | 41 | $B(CH_3)_3 \cdot (CH_3)_2O$ | does not form | 51 |
| $Al(CH_3)_3 \cdot (CH_3)_3N$ | 177° | 41 | $B(CH_3)_3 \cdot (CH_3)_3N$ | Note 1 | 40,52,53 |
| $Al(CH_3)_3 \cdot (CH_3)_2NH$ | 186° | 41 | $B(CH_3)_3 \cdot (CH_3)_2NH$ | Note 2 | 40,52 |
| $Al(CH_3)_3 \cdot (CH_3)_3P$ | 189° | 41 | $B(CH_3)_3 \cdot (CH_3)_3P$ | Note 1 | 52 |

*By extrapolation of the vapour pressure equation.

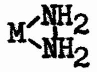
Note 1. Extensively dissociated at 100°.

Note 2. Moderately dissociated at 100°.

## Some Aspects of the Chemistry of Hydrazine

The chemical literature on hydrazine and its derivatives is vast (54). In the following, some coordination and condensation reactions of hydrazine are considered briefly.

Coordination reactions. The ability of hydrazine to serve as an electron pair donor is well recognized. Many acids form salts with hydrazine, such as $N_2H_4 \cdot HCl$, $N_2H_4 \cdot 2HCl$, $N_2H_4 \cdot H_2SO_4$, $N_2H_4 \cdot HBF_4$, etc. Although salts in which hydrogen ions are attached to both nitrogen atoms exist only in the solid state, it is interesting that hydrazine, when coordinated with metallic ions, appears to form a bidentate linkage. The number of attached hydrazine molecules is usually one-half the normal coordination number of that ion. Examples (54) of these complexes are dihydrazinezinc chloride,

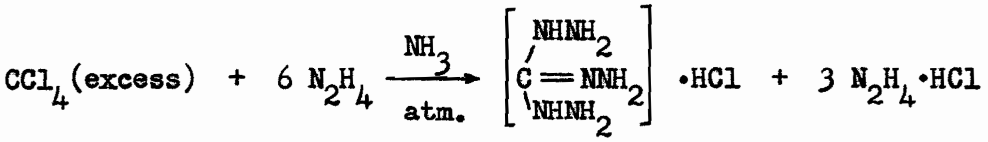
$[Zn(N_2H_4)_2]Cl_2$, and dihydrazinecadmium sulphate, $[Cd(N_2H_4)_2]SO_4$. A three-membered metallic ion-hydrazine ring  $M\begin{smallmatrix}\diagup NH_2\\ \diagdown NH_2\end{smallmatrix}$ is indicated by these compounds, but detailed studies have not been made to verify this point.

Condensation reactions. This term comprises those reactions of hydrazine in which one or more N-H bonds are broken, resulting in the elimination of a small molecule such as hydrogen chloride. Few reactions of this type with inorganic compounds are known, although they are very common in organic chemistry.

The reaction in vacuo of anhydrous hydrazine with phosgene, $COCl_2$, was reported recently to yield mainly hydrazine dihydrochloride and carbohydrazide (55):

$$COCl_2 + 3\ N_2H_4 \longrightarrow N_2H_4{\cdot}2\ HCl + CO(NHNH_2)_2$$

Carbon tetrachloride was stated to undergo solvolysis by hydrazine when refluxed in an atmosphere of ammonia to form triaminoguanidine (56),



$$CCl_4(\text{excess}) + 6\ N_2H_4 \xrightarrow[\text{atm.}]{NH_3} \left[\begin{smallmatrix} & NHNH_2\\ \diagup & \\ C{=}NNH_2 & \\ \diagdown & \\ & NHNH_2\end{smallmatrix}\right]{\cdot}HCl + 3\ N_2H_4{\cdot}HCl$$

but, more recently (57), attempts to duplicate these results ended in failure. It was found that hydrazine hydrochloride and hydrazine hydrobromide were the only solid products in the reactions of carbon tetrachloride and carbon tetrabromide with hydrazine:

$$\underset{(\text{excess})}{2\ CX_4(X{=}Cl,Br)} + 3\ N_2H_4 \xrightarrow[\text{atm.}]{NH_3} 2\ CHX_3 + N_2 + 2\ N_2H_4{\cdot}HX$$

In these reactions, hydrazine appears to function solely as a reducing agent. Similarly, the reaction of carbon tetraiodide with hydrazine in liquid ammonia (58) yielded iodoform, $CHI_3$, as one of the products.

# EXPERIMENTAL

## Introduction

Since most of the materials used in this work react instantly with moisture or oxygen, it is imperative to handle them in a vacuum system. To this end a standard high vacuum apparatus was constructed. The pioneers of this experimental technique were Stock and his coworkers (59); extended developments of their methods are summarized in excellent reviews (60,61,62).

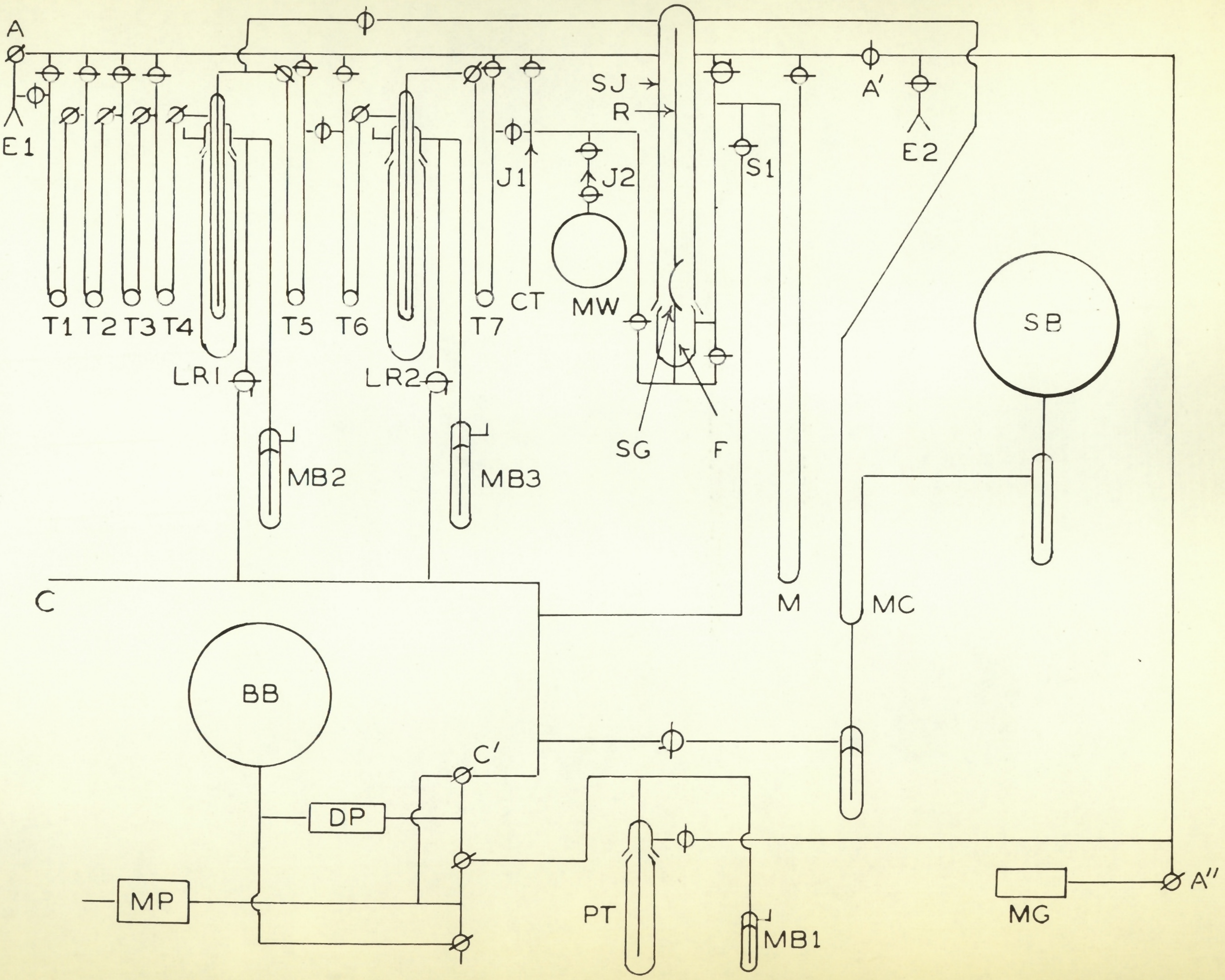
It was found that certain substances, hydrazine in particular, attacked stopcock greases rapidly. Consequently, experiments were usually carried out in sealed, all-glass reaction vessels equipped with magnetically operated "break-seals" for reattachment to the main system. Materials stored in the vacuum apparatus were kept condensed as non-volatile solids by a suitable refrigerant.

## Apparatus

The apparatus was constructed of Pyrex glass and is shown schematically in Figure 1. It consisted of three main sections: (1) a pumping system for the production and maintenance of a high vacuum, (2) a central section for the measurement of pressure, molecular weight, and other properties, and for the transfer of substances to and from the vacuum apparatus, and (3) a distillation line for the separation and purification of volatile compounds.

FIGURE 1

Schematic Diagram of Apparatus


A
SJ
R
A′
E1
E2
J1
J2
S1
T1 T2 T3 T4
T5
T6
T7
CT
MW
SB
LR1
LR2
SG
F
MB2
MB3
C
M
MC
BB
C′
DP
MP
PT
MB1
MG
A″

Each component and its function are described below under separate headings. The stopcocks of the apparatus were lubricated with Kel-F fluorocarbon grease and regreased periodically. After every lubrication, the grease was thoroughly degassed by repeated turning under continuous pumping.

Pumping system. A continuous high vacuum was maintained by a single-stage mercury diffusion pump DP backed by a Welch Duo-Seal rotary oil pump MP. This combination produced a vacuum of approximately $10^{-4}$ mm. of mercury as measured with a tilting McLeod gauge MG. Volatile material was prevented from entering the pumps by condensing it in a large removable trap PT. The pumping system was equipped with three-way stopcocks arranged so that air could be pumped from the apparatus without passing through the diffusion pump; this device prevented the contamination of the latter with mercuric oxide. A five liter ballast flask BB, connected to the diffusion pump outlet, minimized the backing pressure. A mercury escape valve MB1 allowed excess noncondensable gases to escape from the system without admitting air.

Central section. The central section consisted of a mirror-backed mercury manometer M for the measurement of pressure; a sensitive spoon gauge SG served as a null-point indicator. A condensation tube CT was attached to the apparatus at the ground glass joint J1. Another standard joint J2 held a molecular weight bulb MW of accurately known volume (342.75 ± 0.02 ml., calibrated with distilled water). The spoon gauge was fitted with a stopcock S1 leading to a vacuum line CC'. With this arrangement, it was possible to pump out of the spoon gauge jacket SJ the air which had been admitted for pressure measurement, while maintaining at the same time a high vacuum in the remainder of the system.

Distillation line. The high vacuum line AA'A" had several attachments. Two standard joints, E1 and E2, provided a convenient means whereby materials could be introduced into or removed from the system. Seven distillation traps, T1-T7, each of 20-25 ml. capacity, were included in the apparatus, and their interconnections are indicated in the diagram. Two modified LeRoy low temperature fractionation columns (63), LR1 and LR2, were incorporated as shown. A four liter bulb SB, isolated from the system by a mercury cutoff MC, was used occasionally for the temporary storage of volatile materials.

## Techniques

1. The measurement of pressure. It is difficult to predict that occasion when it will be necessary to measure the pressure of a gas which attacks mercury. Accordingly, all pressure measurements were made in the absence of mercury with the aid of delicate glass spoon gauges (60). These were made of soft glass; attachment to the apparatus was effected by a graded seal F. A very thin rigid glass rod R with a fine black pointer surmounted the spoon. The null position of the pointer was recorded by two thin lines on the front and back of the spoon gauge jacket SJ. As the pressure of any gas varied within the spoon gauge, air was admitted into or withdrawn from the outer jacket SJ in order to restore the pointer to its rest position. The pressure was then read directly from the manometer with an accuracy of ± 0.4 mm.

For the measurement of vapour pressure at elevated temperatures, a sample of pure material was sealed up in vacuo in a detachable all-glass spoon gauge apparatus which fitted on the main system at ground glass joints J1 and J2. This instrument was surrounded by a thermostat the temperature of which could be regulated between room temperature and 250°. The thermostatic fluid was di-n-butyl phthalate. Temperatures were measured with a mercury-in-glass thermometer and pressures were determined as previously described.

2. The production and measurement of low temperatures. Liquid air was used for the transfer of volatile compounds. Constant temperature baths in the range -160° to -23° were prepared by cooling a suitable fluid with liquid air in a Dewar vessel. These are the so-called "slush" baths; appropriate tables are given in the literature (61,62). Constant temperatures between -23° and room temperature were obtained by the proper mixture of ice, salt, and water.

The low temperature fractionation columns LR1 and LR2 were successfully employed for the separation of reaction mixtures. With this simple apparatus, any temperature in the range from room temperature to -196° (liquid nitrogen) could be produced and maintained. Frequent adjustment of the heating element ensured a constant temperature within ± 1°.

Copper-constantan thermocouples, with an ice-water mixture as a reference junction, provided accurate measurement of the temperature of the column. A Rubicon Model 2733 potentiometer was used to measure precisely the e.m.f. generated across the junctions of the two metals at different temperatures. Comparison with a high quality mercury-in-glass thermometer, as well as with standard low temperature baths (62), indicated that temperatures could be measured within ± 0.1°. A separate thermocouple was incorporated in this measuring system so that the temperature of a bath used at any point in the apparatus could be determined.

3. Weighing procedure. Liquids with boiling points above room temperature were pipetted in an atmosphere of dry nitrogen into a vessel of small (10-12 ml.) capacity equipped with a stopcock and another standard joint for attachment to the vacuum system; the weight was obtained by difference. The liquid and its vapour were condensed to a non-volatile solid in the vessel by liquid air, the nitrogen in the vessel was evacuated, and the substance was then distilled in vacuo to the desired part of the apparatus.

The weights of gaseous materials were determined by the difference in weight of a bulb MW of accurately known volume when filled with the gas and when evacuated. The attack on stopcock grease was insignificant during these operations.

4. Purification of volatile substances. The separation and purification of the components of volatile mixtures were effected by repeated fractional volatilization and condensation in the LeRoy columns and their adjacent traps, all of which were maintained at desired temperatures by suitable coolants. Excellent results were achieved except when the boiling points of the components differed by less than about 30°, and then only partial separations could be obtained.

5. *Determination of purity and molecular weight measurements.* The purity of volatile materials was ascertained by the measurement of the vapour pressure of successive fractions. If these values were almost identical, the compound was considered to be tensiometrically pure. The constancy of the vapour pressures of successive fractions of any material is one of the most sensitive tests of its purity.

Vapour purity was also determined from the value of the molecular weight, which was measured by the direct weighing of a sample in a bulb MW of known volume at a known pressure and temperature and by subsequent application of the Ideal Gas Equation. Accuracy was generally better than 1%.

Vapour pressure measurements together with molecular weight determinations assisted greatly in the identification of materials which were thought to be known, well-characterized compounds.

6. *Analysis.* Chlorine, bromine, iodine, boron, and aluminum were determined by standard gravimetric and volumetric methods (64).

In the presence of aqueous hydrogen chloride, hydrazine may be titrated with standard iodate solution (54). A few milliliters of chloroform and of concentrated hydrochloric acid were added to a solution of a weighed sample of the unknown, and titration with standard iodate solution was continued until the iodine colour was discharged from the organic layer. The initial reaction involves reduction of iodate to iodine; the latter is subsequently oxidized to iodine monochloride, resulting in the disappearance of the iodine colour:

$$N_2H_4 + KIO_3 + 2\,HCl \longrightarrow KCl + ICl + N_2 + 3\,H_2O$$

7. Infrared spectra. Infrared spectra were recorded on a Perkin-Elmer Model 21 double beam spectrophotometer fitted with sodium chloride optics. Gaseous samples were contained at known pressures in a cylindrical cell (5 cm. x 10 cm.), at either end of which sodium chloride windows were affixed with Kel-F grease and Apiezon Q black wax. The spectra of solids were taken using potassium bromide pellets or a mull of "Nujol" or "Fluorolube". The sodium chloride plates were repolished occasionally with the aid of an alcoholic suspension of aluminum oxide and a revolving polishing disc.

8. Debye-Scherrer x-ray diagrams. X-ray diffraction patterns of solid compounds were obtained from samples sealed in glass tubes of 0.01 mm. wall thickness. The pictures were taken on a Seifert machine by Dr. R. St. J. Manley of the Pulp and Paper Research Institute of Canada. $CuK_\alpha$ radiation filtered by nickel (wave length 1.54 Å) was used.

9. Melting points. Finely ground samples of solid materials were placed in capillary tubes under an atmosphere of dry nitrogen. The tubes were sealed in a flame and deposited in an aluminum block melting point apparatus for measurement.

## Preparation of Materials

Anhydrous hydrazine. Hydrazine (95+ %) was refluxed over sodium hydroxide flakes and a few "boileezers" in a three-necked flask which was heated by a Glas-Col mantle. The apparatus was continuously flushed by a slow stream of dried nitrogen which was allowed to escape through a mercury bubbler. The flow of water through the reflux condenser was stopped after three hours and distillation commenced: the fraction boiling at 111-113° was collected. Two analyses by the iodate method (54) indicated that the distillate was pure hydrazine (99.8% and 100.2%, respectively).

Trimethylborane. The method of Brown (65) for the preparation of trimethylborane was modified in that boron trichloride and methyl iodide were used in place of boron trifluoride and methyl bromide. The reaction apparatus consisted of a three-necked 500 ml. flask which was fitted with a dropping funnel, a reflux condenser, and an inlet tube through which dry nitrogen gas was passed continuously. The condenser, kept at -80°, was connected via two large traps to the vacuum system. The stream of dry nitrogen escaped through a mercury bubbler which prevented the admission of air or moisture.

Methyl iodide (43 gm.) in dry n-butyl ether (50 ml.) was added dropwise to a magnetically stirred mixture of magnesium turnings (7.5 gm.) and n-butyl ether (25 ml.). After allowing several hours for the Grignard reagent to form, boron trichloride (10.5 gm.) in n-butyl ether (40 ml.) was added dropwise to the mixture. The reaction vessel was heated briefly with a Glas-Col mantle to ensure completeness of reaction. The crude material, collected in the two traps at liquid air temperatures, was purified initially by distillation through a bath at -80°. The yield of trimethylborane was 79%.

The material was further purified by adding it to an excess of triethylamine (to remove $BCl_3$) and then distilling it into a LeRoy column at -150°. Pure trimethylborane was then obtained by raising the column temperature to -120°. (Found: M, 55.6; v.p. 30.7 mm. at -78.3°. Required for $B(CH_3)_3$: M, 55.9; v.p. 31.3 mm. at -78.3°).

Diborane. This compound was prepared by the method of Schlesinger et al. (66). The reaction was done in vacuo at room temperature. Lithium aluminum hydride (0.55 gm.) was dissolved in anhydrous ethyl ether (10 ml.) in a 50 ml. flask equipped with a magnetic stirrer, and boron trichloride (2.62 gm.), purified by distillation at -90°, was added. Volatile products were passed through a bath at -112°; the distillate was separately redistilled at -112°. The yield of diborane was 62% based on the reaction

$$3\ LiAlH_4 + 4\ BCl_3 \longrightarrow 3\ LiCl + 3\ AlCl_3 + 2\ B_2H_6$$

(Found: M, 27.7. Required for $B_2H_6$: M, 27.7).

Ethyl ether, n-butyl ether, and tetrahydrofuran. Reagent grade materials were kept over a large quantity of sodium ribbon for several days. Distillation was then carried out under anhydrous conditions.

Miscellaneous materials. Commercial samples of boron trifluoride, boron trichloride, boron tribromide, trimethylaluminum, hydrogen chloride, ammonia, methylamine, trimethylamine, and triethylamine were purified by fractional condensation and volatilization in the vacuum system. Their purity was ascertained by the measurement of vapour pressure, molecular weight, and infrared spectrum.

Reagent grade samples of the following substances were available commercially and they were used without further purification: aluminum chloride, aluminum bromide, aluminum iodide, lithium aluminum hydride, ethanol, carbon tetrachloride, acetone, dimethyl sulphoxide, and methyl iodide.

# RESULTS

## The Interaction of Boron Trifluoride and Hydrazine

The boron trifluoride used in these experiments was purified by a triple distillation through a LeRoy column at -150° (Found: M, 67.8; v.p. 96.7 mm. at -124.3°. Required for $BF_3$: M, 67.8; v.p. 96.6 mm. at -124.3° (14). The infrared spectrum of the vapour was identical to that reported in the literature (67,68).

Boron trifluoride (7.92 millimoles) and hydrazine (2.87 mmoles) were combined and maintained overnight in vacuo at -80°. An almost quantitative recovery of boron trifluoride (7.69 mmoles) by distillation at -80° indicated that no appreciable reaction had taken place at this temperature.

A different result was obtained by raising the temperature. In a typical experiment, boron trifluoride (11.63 mmoles) and anhydrous hydrazine (5.89 mmoles) were brought together and kept at room temperature for thirty minutes before freezing the mixture with liquid air. A vigorous exothermic reaction yielded a white solid which was involatile at room temperature and which contained boron trifluoride and hydrazine in a ratio of 1:1, corresponding to a new compound, boron trifluoride-hydrazine, $BF_3 \cdot N_2H_4$ (Found: $N_2H_4$, 32.3%. Required for $BF_3N_2H_4$: $N_2H_4$, 32.1%.). The amount of unchanged boron trifluoride (5.81 mmoles; M, 67.8. Required for $BF_3$: M, 67.8.), recovered by distillation at -80°, also indicated that boron trifluoride (5.82 mmoles) had reacted with hydrazine (5.89 mmoles) in a ratio of 1:1.

Using identical procedures and longer reaction times, the following complex mixtures with higher $BF_3/N_2H_4$ ratios were obtained:

| Composition Ratio $BF_3/N_2H_4$ | Reaction Time (hours) | Analysis: % $N_2H_4$ Found | Calc. |
|---|---|---|---|
| 1.09 | 2 | 30.4 | 30.2 |
| 1.16 | 3 | 28.3 | 28.8 |

The 1:1 compound could not readily be obtained if the reaction was done with an excess of hydrazine rather than of boron trifluoride. Hydrazine (9.68 mmoles) and boron trifluoride (3.26 mmoles) were left in contact for thirty minutes; during this time, a colourless, very viscous syrup was formed. No material distilled out of the reaction vessel at -80°. A volatile substance (shown by analysis to be hydrazine) distilled at a very slow rate from the reaction mixture at room temperature. After seventy-two hours, 5.48 mmoles of hydrazine had been recovered (distillation still incomplete), leaving a clear jelly containing 4.20 mmoles hydrazine and 3.26 mmoles boron trifluoride.

The data cited thus far suggested that hydrazine and excess boron trifluoride reacted to form initially a 1:1 compound which gradually absorbed additional boron trifluoride. One would accordingly expect that the proper experimental conditions should yield a compound of the formula $2BF_3 \cdot N_2H_4$, since hydrazine is thought to have two centres of donor activity. The following series of experiments was undertaken with this goal in mind.

The reaction of boron trifluoride with hydrazine above room temperature. Boron trifluoride (11.77 mmoles) and hydrazine (3.87 mmoles) were sealed in an all-glass reaction vessel and allowed to react for four hours at 140°. A white nonvolatile solid was produced in the reaction. The amount of boron trifluoride (4.67 mmoles; M, 67.5. Required for $BF_3$: M, 67.8.) recovered by distillation at room temperature showed that the solid reaction product contained boron trifluoride and hydrazine in a ratio of 1.84:1 (Found: $N_2H_4$, 20.9%. Required for $(BF_3)_{1.84}\ N_2H_4$: $N_2H_4$, 19.8%.). There were no other reaction products.

In another experiment, boron trifluoride (6.85 mmoles) and hydrazine (2.30 mmoles) were heated to 200° for four hours and then left overnight at 110°. The only products of the reaction were a white nonvolatile solid and boron trifluoride (3.10 mmoles; M, 69.7). The residue therefore contained boron trifluoride and hydrazine in a ratio of 1.63:1.

When boron trifluoride (11.24 mmoles) and hydrazine (3.60 mmoles) were heated for one hour at 300°, a large amount of noncondensable gases among the reaction products suggested that extensive decomposition had occurred. This aspect was investigated in considerable detail and is discussed under the heading "Pyrolysis of boron trifluoride-hydrazine".

The reaction of boron trifluoride-hydrazine with liquid boron trifluoride. Boron trifluoride (3.91 mmoles) was condensed onto a sample of boron trifluoride-hydrazine, $BF_3 \cdot N_2H_4$, (0.433 mmole), and the two materials were left for one hour at -130°. The quantity of boron trifluoride (3.86 mmoles; M, 67.8. Required for $BF_3$: M, 67.8.) recovered by distillation between -130° and -80° proved that no appreciable reaction had occurred.

The reaction of boron trifluoride with hydrazine in diethyl ether. Complex mixtures ranging in composition from $(BF_3)_{1.40}N_2H_4$ to $(BF_3)_{1.88}N_2H_4$ were obtained through the reaction in vacuo of boron trifluoride with hydrazine in anhydrous diethyl ether. Factors such as efficiency of mixing, reaction time, and temperature appeared to influence the composition of the product isolated.

In one experiment, boron trifluoride (12.52 mmoles), hydrazine (3.91 mmoles), and diethyl ether (10 ml.) were sealed in vacuo in an all-glass apparatus and permitted to react for ten days. The solvent and the unreacted boron trifluoride were removed by distillation at room temperature, leaving a white solid residue of empirical composition $(BF_3)_{1.88}N_2H_4$ (Found: $N_2H_4$, 20.1%.).

The other experiments of this type involved much shorter reaction times, and substances were obtained with boron trifluoride to hydrazine ratios in the range 1.40 to 1.84, but unfortunately the ratio was never 2. Some representative mixtures are given in the table.

| Composition Ratio $BF_3/N_2H_4$ | Analysis: % $N_2H_4$ |
|---|---|
| 1.40 | 25.2 |
| 1.70 | 21.8 |
| 1.84 | 20.4 |
| 1.88 | 20.1 |

Lastly, 0.237 gm. of the solid mixture $(BF_3)_{1.16}N_2H_4$, described on p. 27, was treated with additional boron trifluoride (15.3 mmoles) in diethyl ether (15 ml.) in vacuo for eleven hours. A substance of empirical composition $(BF_3)_{1.72}N_2H_4$ (Found: $N_2H_4$, 21.6%) was recovered after distillation of the diethyl ether and excess boron trifluoride at room temperature.

<u>The reaction of boron trifluoride with hydrazine in tetrahydrofuran.</u> An all-glass reaction apparatus was charged with anhydrous tetrahydrofuran (25 gm.), and to this solvent, boron trifluoride (34.52 mmoles) and hydrazine (10.07 mmoles) were added by distillation in vacuo. The reactants were sealed off and stirred (magnetically) overnight at room temperature; a clear solution resulted. The solvent and the excess boron trifluoride were distilled away under low pressure at room temperature, leaving a white crystalline deposit of a new compound, 2-boron trifluoride-hydrazine, $2BF_3 \cdot N_2H_4$ (Found: $N_2H_4$, 19.25, 19.43%. Required for $B_2F_6N_2H_4$: $N_2H_4$, 19.12%.).

These experiments showed that at least two compounds were formed between boron trifluoride and hydrazine, namely, boron trifluoride-hydrazine, $BF_3 \cdot N_2H_4$, and 2-boron trifluoride-hydrazine, $2BF_3 \cdot N_2H_4$. However, it was not possible to rule out the existence of compounds of intermediate stoichiometry such as 3-boron trifluoride-2-hydrazine, $3BF_3 \cdot 2N_2H_4$. In order to decide this point, a portion of the phase diagram of the system boron trifluoride - hydrazine was determined. A series of mixtures of boron trifluoride and hydrazine was prepared and their melting points in sealed capillary tubes (nitrogen atmosphere) were determined. The data are summarized in Table V and a plot of composition vs. melting point is shown in Figure 2. The mixtures were nonvolatile at room temperature.

The positions of maxima in solid-liquid equilibrium diagrams occur at the compositions of solid compounds (69). The portion of the phase diagram shown in Figure 2 clearly indicates only one maximum, at 50 mole % boron trifluoride. It may therefore be concluded that boron trifluoride-hydrazine, $BF_3 \cdot N_2H_4$, is the only compound formed by the two components in the region of composition 45-65 mole % boron trifluoride. There remains the possibility of an incongruently melting compound, but no indication of a peritectic point was apparent from the curve in Figure 2.

At the extreme right of the complete phase diagram, the curve must eventually drop to the melting point of pure boron trifluoride, which is -127° (1). Hence the steeply rising portion of Figure 2 must pass through a maximum, probably at 66 2/3 mole % boron trifluoride, corresponding to the composition of 2-boron trifluoride-hydrazine. In fact, the melting point of this compound, the preparation of which is described on p. 30, was found to be 260°.

The compound boron trifluoride-hydrazine was insoluble in benzene, slightly soluble in diethyl ether, and moderately soluble in acetone. The compound 2-boron trifluoride-hydrazine was soluble in tetrahydrofuran. Both new compounds were hygroscopic and dissolved readily in water to yield acidic solutions. Both retained the reducing characteristics of

## TABLE V

### Melting Points of Boron Trifluoride-Hydrazine Mixtures

| Mole % $BF_3$ in mixture | Method of Preparation | Melting Point |
|---|---|---|
| 46.5 | Footnote A | 72° |
| 47.6 | " | 81 |
| 50.0 | $BF_3 \cdot N_2H_4$ (p. 26) | 87 |
| 52.2 | Footnote B | 74 |
| 55.4 | " | ~ 70 |
| 56.9 | " | 112 |
| 58.4 | " | 146 |
| 59.2 | " | 190 |
| 59.8 | " | 206 |
| 60.2 | " | 209 |
| 60.8 | " | 225 |
| 61.8 | " | 232 |
| 62.0 | Footnote C | 235 |
| 62.4 | Footnote B | 245 |
| 63.2 | " | 249 |
| 63.5 | " | 248 |
| 66.6 | $2BF_3 \cdot N_2H_4$ (p. 30) | 260 |

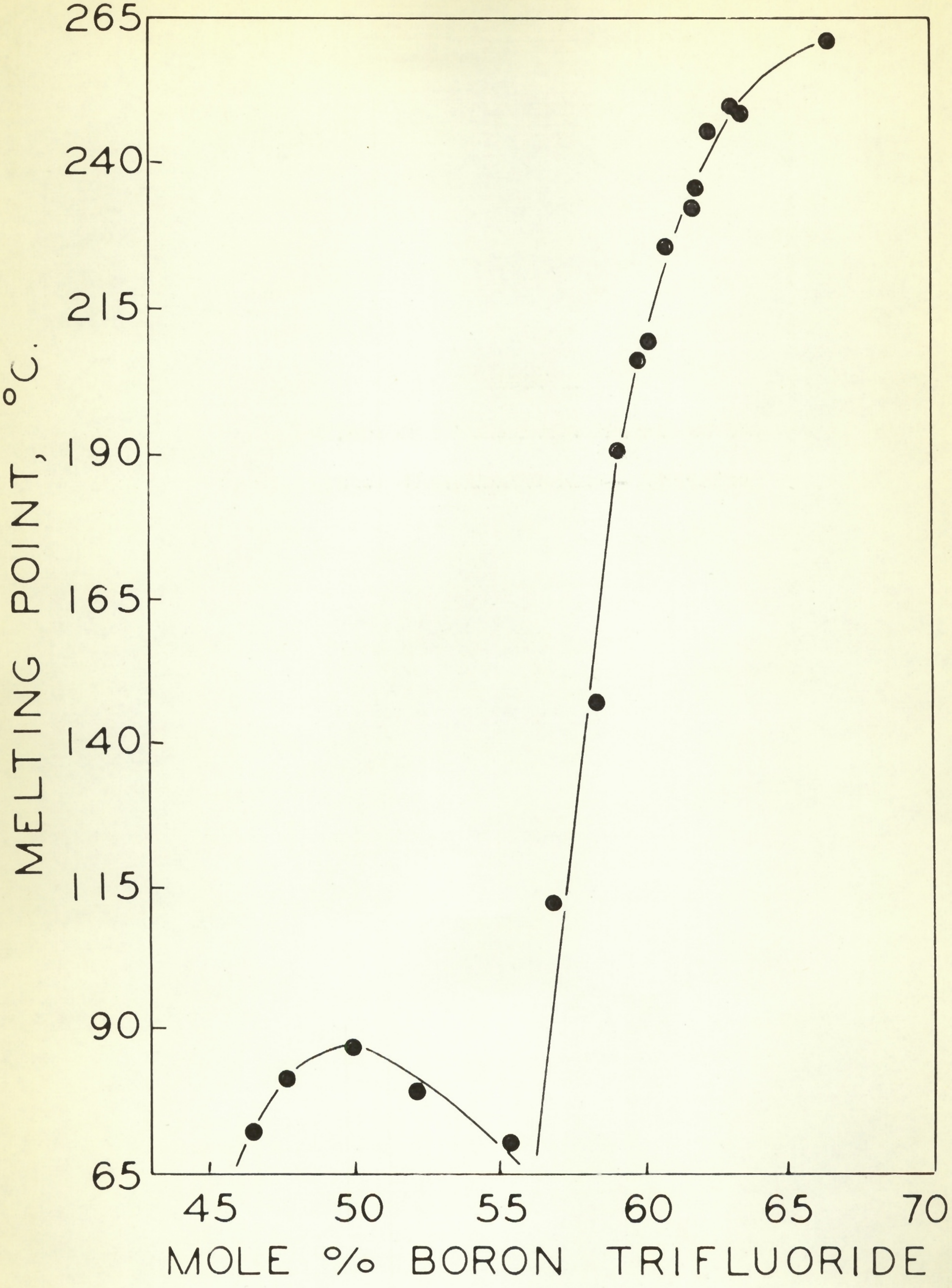
Footnote A. Stoichiometric amounts of the two components were allowed to react at room temperature for one hour. There were no volatile products.

Footnote B. Stoichiometric amounts of the two components were sealed in an all-glass reaction apparatus and left overnight at 110°. There were no volatile products.

Footnote C. The preparation of this mixture, $(BF_3)_{1.63}N_2H_4$, is described on p. 28.

FIGURE 2

A Portion of the Phase Diagram of the System Boron Trifluoride - Hydrazine



265
240
215
190
165
140
115
90
65
45
50
55
60
65
70
MELTING POINT, °C.
MOLE % BORON TRIFLUORIDE

hydrazine in that their aqueous solutions decolourized instantly an aqueous solution of potassium permanganate.

## Characterization of Boron Trifluoride-Hydrazine

Infrared spectra. The infrared spectra of boron trifluoride-hydrazine and of 2-boron trifluoride-hydrazine are shown in Figure 3, and their characteristic vibration frequencies are listed in Tables VI and VII, respectively. Both spectra were obtained using the potassium bromide pellet technique.

Crystal structure of boron trifluoride-hydrazine. The x-ray powder diffraction pattern of boron trifluoride-hydrazine was obtained and twenty-eight lines were indexed according to Bragg's equation (69):

$$\lambda = 2d \sin \theta$$

From these measurements, the dimensions of the crystallographic unit cell can be calculated (70). The data for boron trifluoride-hydrazine, presented in Table VIII, were consistent with a regular unit cell of dimensions

$$a = 6.93\ \text{Å} \qquad \alpha = 111.5°$$
$$b = 5.50\ \text{Å} \qquad \beta = 64.0°$$
$$c = 6.78\ \text{Å} \qquad \gamma = 88.3°$$

which indicates triclinic symmetry.

The pyrolysis of boron trifluoride-hydrazine. Considerable interest is associated with the pyrolysis of boron trifluoride-hydrazine since numerous examples are known in which interesting boron-nitrogen polymers have been prepared by the pyrolysis of addition compounds containing boron-nitrogen

TABLE VI

<u>Infrared Vibration Frequencies of Boron Trifluoride-Hydrazine</u>

| Frequency $\text{cm}^{-1}$ | Intensity | | Assignment |
|---|---|---|---|
| 3500-3650 | mb | | $H_2O$? |
| 3400 | s | | N-H stretching (asym.) |
| 3305 | s | | N-H stretching (sym.) |
| 3050 | sb | | N-H intermolecular? |
| 2710 | wsh | | - |
| 1620 | s | | $NH_2$ deformation (asym.) |
| 1495 | vw | | - |
| 1440 | s | | $NH_2$ deformation (sym.) |
| 1355 | s | | $NH_2$ rocking (asym.) |
| 1260 | s | | $NH_2$ rocking (sym.)? |
| 1100 | vsvb | u | B-F stretching (asym.) and |
| 1035 | ssh | | B-N stretching |
| 965 | vs | | N-N stretching |
| 725 | w | | $NH_2$ wagging (sym.)? |

s = strong m = medium w = weak v = very b = broad sh = shoulder

u = unresolved asym = asymmetric sym = symmetric

## TABLE VII

### Infrared Vibration Frequencies of 2-Boron Trifluoride-Hydrazine

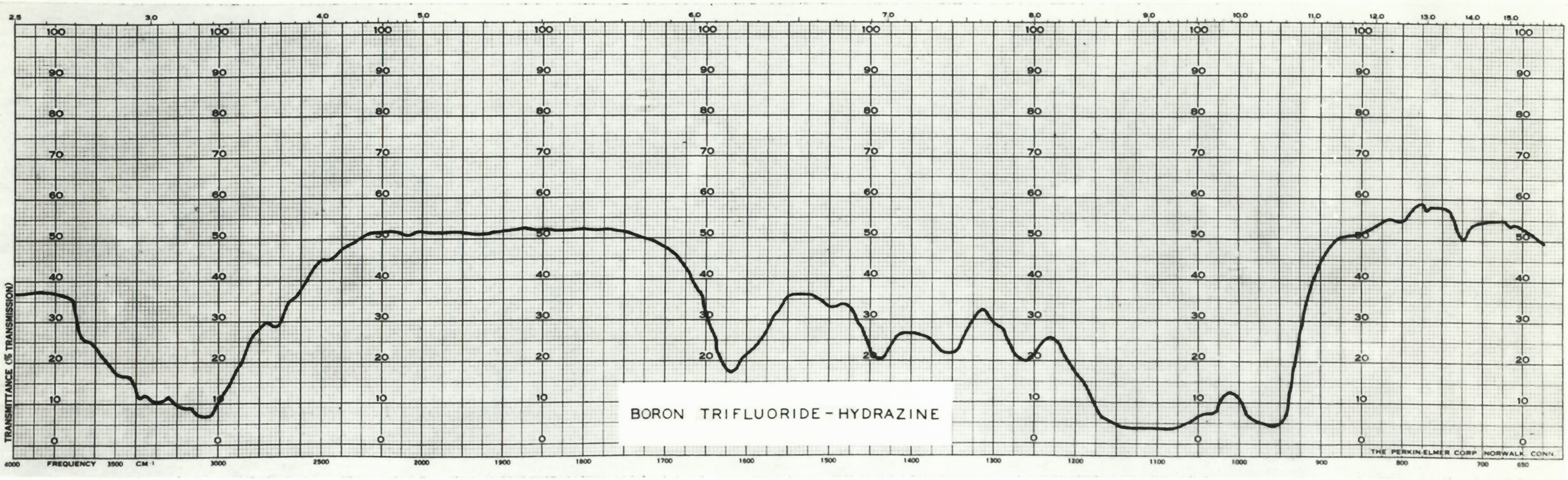
| Frequency, cm$^{-1}$ | Intensity | Assignment |
|---|---|---|
| 3390 | vwsh | N-H stretching (asym.) |
| 3240 | w | N-H stretching (sym.) |
| 2900 | w | combination or overtone |
| 2710 | w | " |
| 2635 | w | " |
| 2550 | m | " |
| 2350 | w | " |
| 2030 | w | " |
| 1900 | w | " |
| 1600 | m | $NH_2$ deformation (asym.) |
| 1535 | wsh | |
| 1475 | sb | $NH_2$ deformation (sym.) |
| 1302 | m | $NH_2$ rocking (asym.) |
| ~ 1100 | sbsh u | B-F stretching (asym.) and |
| 1040 | vs | B-N stretching |
| 970 | m | N-N stretching |
| 883 | w | - |
| 795 | mb | $NH_2$ wagging (sym.)? |
| 771 | m | |
| 645 | w | - |

s = strong m = medium w = weak v = very b = broad sh = shoulder

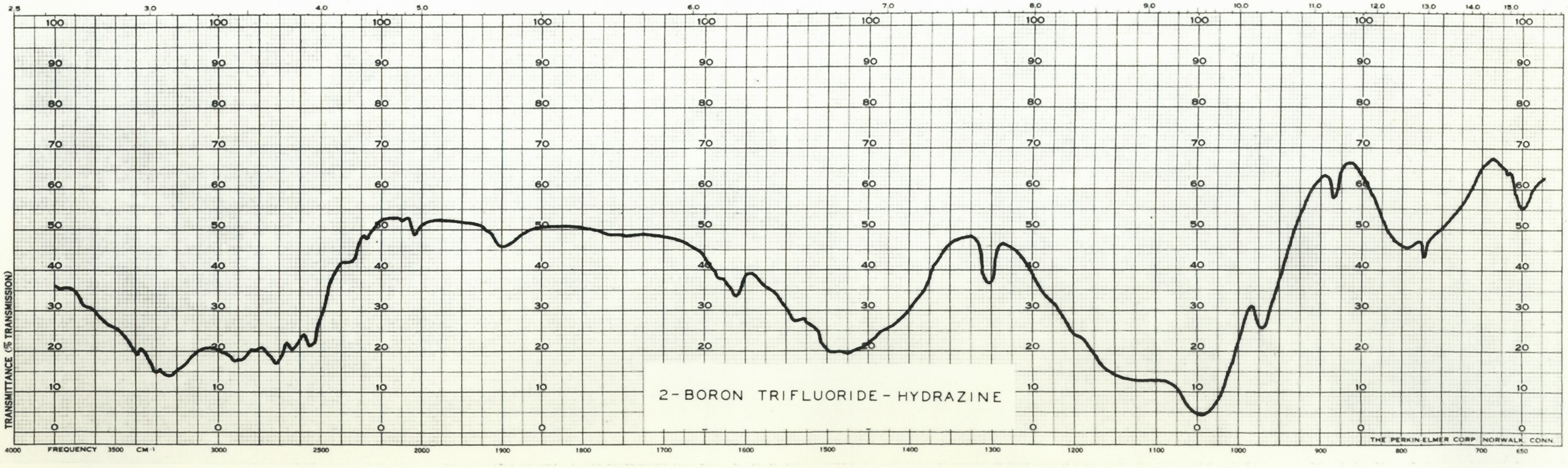
u = unresolved asym = asymmetric sym = symmetric

FIGURE 3

Infrared Spectra of Boron Trifluoride-Hydrazine and 2-Boron Trifluoride-Hydrazine (Potassium Bromide Pellet Technique)



BORON TRIFLUORIDE - HYDRAZINE



2-BORON TRIFLUORIDE - HYDRAZINE

## TABLE VIII

### X-ray Powder Diffraction Data for Boron Trifluoride-Hydrazine*

| Line | Intensity | $d_{obs.}$ (Å) | $d_{calc.}$ (Å) | hkl |
|---|---|---|---|---|
| 1 | vvw | 5.50 | 5.52 | 100 |
| 2 | vvw | 4.87 | 4.87 | 010 |
| 3 | vs | 4.27 | 4.23 | 001 |
| 4 | vs | 3.47 | 3.47 | $\bar{1}01$ |
| 5 | vw | 3.25 | 3.25 | 101 |
| 6 | vw | 3.11 | 3.10 | $2\bar{1}0$ |
| 7 | vvw | 2.96 | 2.99 | 110 |
| 8 | s | 2.78 | 2.76 | 200 |
| 9 | s | 2.43 | 2.43 | 011,020 |
| 10 | m | 2.31 | 2.31 | $3\bar{2}1$ |
| 11 | vw | 2.22 | 2.24 | $1\bar{2}\bar{2}$ |
| 12 | w | 2.11 | 2.11 | 002 |
| 13 | w | 2.03 | 2.03 | 210,111 |
| 14 | w | 1.93 | 1.93 | 102 |
| 15 | vvw | 1.80 | 1.80 | $1\bar{3}0$ |
| 16 | vvw | 1.76 | 1.76 | $\bar{1}21$ |
| 17 | vvw | 1.65 | 1.65 | 021 |
| 18 | w | 1.57 | 1.56 | 012 |
| 19 | vvw | 1.48 | 1.49 | $04\bar{1}$ |
| 20 | vvw | 1.44 | 1.44 | $\bar{3}02$ |
| 21 | vvw | 1.39 | 1.39 | 130 |
| 22 | vvw | 1.34 | 1.34 | 103,302 |
| 23 | vvw | 1.26 | 1.26 | 212 |
| 24 | vvw | 1.23 | 1.24 | $01\bar{4}$ |
| 25 | vvw | 1.19 | 1.19 | 410 |
| 26 | vvw | 1.16 | 1.16 | $\bar{3}03$ |
| 27 | vvw | 1.13 | 1.13 | $\bar{2}13$ |
| 28 | vvw | 1.11 | 1.10 | 500 |

*A 57.30 mm. camera was used.
s = strong m = medium w = weak v = very

coordinate bonds (6).

Vapour pressure measurements in the range 140° to 230° had shown that boron trifluoride-hydrazine underwent irreversible thermal decomposition at sufficiently high temperatures. There was no detectable decomposition of the compound after it had been heated for twelve hours at 105°. When four millimoles of $BF_3 \cdot N_2H_4$ were heated for ten days at 185-190°, somewhat less than one millimole of noncondensable gases was produced.

Boron trifluoride-hydrazine (5.65 mmoles) was pyrolyzed in an all-glass reaction vessel for 4 1/2 hours at 275-300°. The volatile products were nitrogen (1.72 mmoles; M, 27.8. Required for $N_2$: M, 28.0.), ammonia (0.486 mmole; M, 17.4; v.p. 40.9 mm. at -79.0°. Required for $NH_3$: M, 17.0; v.p. 40.0 mm. at -79.2° (76). Positive identification also obtained from the infrared spectrum (71,72).), and a small trace of a third unidentified material. Analysis of the solid residue for hydrazine indicated that 0.52 mmole boron trifluoride-hydrazine remained unchanged. The pyrolysis was therefore more than 90% complete.

An x-ray powder diffraction pattern showed that ammonium fluoborate, $NH_4BF_4$, and boron nitride, BN, were the major components of the solid residue with the former present in much larger amounts (its lines were much more intense). At least one other solid compound (unidentified) was in the residue in smaller amounts. The data supporting these conclusions are given in Table IX.

The first three columns contain the data for the pyrolysis residue.

## TABLE IX

### X-ray Data for Pyrolysis Residue*

| Line No. | Intensity (residue) | d (Å) (residue) | d (Å) ($NH_4BF_4$) | Intensity ($NH_4BF_4$) | d (Å) (BN) |
|---|---|---|---|---|---|
| 1 | mw | 5.75 | 5.7 | 15 | - |
| 2 | mw | 5.00 | - | - | - |
| 3 | ms | 4.50 | 4.50 | 100 | - |
| 4 | vvw | 3.93 | 3.84 | 20 | - |
| 5 | w | 3.75 | 3.65 | 63 | - |
| 6 | ms | 3.54 | 3.55 | 75 | - |
| - | - | - | 3.35 | 3 | - |
| 7 | s | 3.21 | 3.18 | 75 | 3.33 |
| 8 | s | 2.89 | 2.89 | 50 | - |
| - | - | - | 2.84 | 38 | - |
| 9 | m | 2.53 | 2.53 | 75 | - |
| - | - | - | 2.40 | 15 | - |
| 10 | m | 2.32 | 2.33 | 25 | - |
| - | - | - | 2.28 | 25 | - |
| 11 | w | 2.24 | 2.22 | 15 | - |
| 12 | s | 2.16 | 2.16 | 75 | 2.17 |
| 13 | vvw | 2.09 | 2.09 | 15 | 2.06 |
| 14 | vvw | 1.99 | - | - | - |
| 15 | w | 1.81 | 1.81 | 13 | 1.82 |
| 16 | vvw | 1.72 | 1.72 | 5 | - |
| 17 | w | 1.65 | 1.65 | 38 | 1.67 |
| 18 | vvw | 1.57 | - | - | 1.55 |
| 19 | vvw | 1.43 | 1.45 | 15 | - |
| 20 | vvw | 1.37 | - | - | 1.32 |
| 21 | vvw | 1.29 | - | - | 1.25 |

*A 57.30 mm. camera was used.

s = strong m = medium w = weak v = very

Listed in the next two columns are the data for ammonium fluoborate, copied from the American Society for Testing Materials (ASTM) Diffraction Data Cards. ASTM methods assign the number 100 for the intensity of the darkest line and the intensities of the other lines are graded relative to this arbitrary standard. Thus a line with an intensity of 15 is very faint. The last column contains the "d" values for boron nitride, which were not available in the literature. They were computed from equation (1); the reflection indices hkl of the strongest lines and the unit cell dimensions "a" and "c" (hexagonal system) have been published (73,74):

$$\frac{1}{d^2_{hkl}} = \frac{4}{3a^2}\left(h^2 + hk + k^2\right) + \frac{l^2}{c^2} \qquad (1)$$

Although reproducible analytical results were obtained for $BF_4^-$, they were judged unreliable in view of the fact that the hydrolysis of the unchanged boron trifluoride-hydrazine would result in equilibria involving $BF_4^-$ (See next section, "Hydrolysis of boron trifluoride-hydrazine"). Accurate analysis for BN is almost impossible because of the inertness of this material.

The hydrolysis of boron trifluoride-hydrazine. The following observations were made of the action of water on boron trifluoride-hydrazine. Two aqueous freezing point depression measurements indicated apparent molecular weights in solution of 49.5 and 54.5, or approximately one-half the formula weight of $BF_3 \cdot N_2H_4$ which is 99.9. Potassium chloride (1), cesium sulphate (1), and nitron acetate (75) solutions all gave precipitates with an aqueous solution of the addition complex, thus confirming the presence of fluoborate ion, $BF_4^-$. It was further noted that the initial acidity (pH = 4.35) of a dilute aqueous solution decreased slightly (pH = 4.65) on standing for thirty-five minutes.

A number of other studies were undertaken for the further characterization of boron trifluoride-hydrazine. The object of these investigations was to determine the effect of strong Lewis acids and bases such as hydrogen chloride and ammonia on the addition complex, $BF_3 \cdot N_2H_4$.

The reaction of boron trifluoride-hydrazine with liquid hydrogen chloride. Boron trifluoride-hydrazine (0.667 mmole) and anhydrous hydrogen chloride (6.73 mmoles; M, 36.7. Required for HCl: M, 36.5) remained in contact for one hour at -96°. The amount of hydrogen chloride (6.72 mmoles; M, 36.7) recovered by distillation at -96° indicated that no appreciable reaction had occurred.

The reaction of boron trifluoride-hydrazine with gaseous hydrogen chloride. Anhydrous hydrogen chloride (9.70 mmoles; M, 36.5. Required for HCl: M, 36.5) was added to boron trifluoride-hydrazine (3.86 mmoles) and kept for one hour at room temperature. Unchanged hydrogen chloride (9.58 mmoles; M, 36.5) was recovered almost completely, proving that no significant reaction had taken place.

In a second experiment, boron trifluoride-hydrazine (3.73 mmoles) and anhydrous hydrogen chloride (8.05 mmoles; M, 37.0) were sealed in an all-glass apparatus and left overnight at 110°. The products of the reaction were a nonvolatile solid and a gas recovered by distillation at -80° (4.97 mmoles; M, 40.3. Required for HCl: M, 36.5. Required for $BF_3$: M, 67.8). The infrared spectrum of the gas showed clearly that it was a mixture of boron trifluoride and hydrogen chloride (67,68,72). From the molecular weight value (40.3), it was calculated that the volatile product consisted of 4.36 mmoles hydrogen chloride and 0.61 mmole boron trifluoride. Thus 3.69 mmoles hydrogen chloride reacted with 3.73 mmoles boron trifluoride-hydrazine to yield a solid residue and 0.61 mmole boron trifluoride.

In an attempt to prepare the addition compound $BF_3 \cdot N_2H_4 \cdot HCl$, boron trifluoride-hydrazine and hydrogen chloride were combined in exactly equimolar quantities. Boron trifluoride-hydrazine (2.71 mmoles) and anhydrous hydrogen chloride (2.73 mmoles; M, 36.7) were maintained overnight at 110° in an all-glass reaction vessel. Again the reaction products were a nonvolatile solid and a gaseous substance (0.835 mmole; M, 45.2. Required for HCl: M, 36.5. Required for $BF_3$: M, 67.8.). This gas was also shown by its infrared spectrum to be a mixture of boron trifluoride and hydrogen chloride. The composition of this volatile material was calculated to be 0.604 mmole hydrogen chloride and 0.232 mmole boron trifluoride. Therefore 2.13 mmoles hydrogen chloride reacted with 2.71 mmoles boron trifluoride-hydrazine to yield a solid product and 0.232 mmole boron trifluoride. Thus it appeared that both displacement of $BF_3$ by HCl and absorption of HCl by the addition product $BF_3 \cdot N_2H_4$ occurred simultaneously.

The reaction of boron trifluoride-hydrazine with liquid ammonia. In a typical experiment, boron trifluoride-hydrazine (1.86 mmoles) and anhydrous ammonia (10.38 mmoles; M, 17.2. Required for $NH_3$: M, 17.0.) were left in contact for one hour at -80°. The amount of ammonia (6.66 mmoles; M, 17.0) recovered by distillation at -80° indicated that a new compound, boron trifluoride-hydrazine-2-ammonia, $BF_3 \cdot N_2H_4 \cdot 2NH_3$, had been formed at that temperature. Above -80°, this crystalline compound dissociated irreversibly, evolving ammonia. Measurements of the dissociation pressure were not reproducible and the conventional plot of log p vs. 1/T was always concave to the reference axes.

A sample of boron trifluoride-hydrazine-2-ammonia (1.86 mmoles) was warmed very gradually to room temperature and the following fractions of ammonia were collected:

| Distilling Temperature | Ammonia Recovered (mmoles) | Molecular Weight |
|---|---|---|
| -64° | 0.637 | 17.1 |
| -46 | 0.814 | 17.9 |
| -26 | trace | - |
| 0 | 1.496 | 17.4 |
| +28 | distillation very slow | - |

The data indicate that ammonia was evolved in two distinct stages, but, since no stoichiometric amount could be recovered, it was not possible to isolate the monoammonia compound.

The reaction of boron trifluoride-hydrazine with liquid methylamine. Anhydrous methylamine (8.05 mmoles; M, 31.0. Required for $CH_3NH_2$: M, 31.06.) was condensed onto boron trifluoride-hydrazine (1.296 mmoles) and these materials were left for seventy minutes at -80°. Methylamine (5.56 mmoles; M, 30.8) was removed by distillation (which was very slow) at -45°, leaving a residue consisting of 2.49 mmoles $CH_3NH_2$ and 1.296 mmoles $BF_3 \cdot N_2H_4$. Measurements of the dissociation pressure of this material were not reproducible. Further prolonged distillation at room temperature yielded additional methylamine (1.24 mmoles; M, 31.8), thereby altering the composition of the residue (a syrupy substance) to 1.25 mmoles $CH_3NH_2$ and 1.296 mmoles $BF_3 \cdot N_2H_4$.

These data suggest that boron trifluoride-hydrazine absorbed methylamine to form addition compounds of indefinite composition which, on warming, evolved methylamine very slowly.

The reaction of boron trifluoride-hydrazine with liquid trimethylamine. After boron trifluoride-hydrazine (0.667 mmole) and trimethylamine (3.71 mmoles; M, 58.5; v.p. 217.9 mm. at -25.0°. Required for $(CH_3)_3N$: M, 59.1; v.p. 219.0 mm. at -25.0° (76).) had reacted for one hour at -80°, most of the trimethylamine (3.29 mmoles; M, 58.4) was recovered after four hours' distillation at that temperature. Redistilled trimethylamine (2.78 mmoles; M, 58.9) was then added to the reaction vessel and the reactants were kept at -80° for an additional sixteen hours. After overnight distillation at -80°, the amount of trimethylamine recovered (2.68 mmoles; M, 58.9) showed that during the two reactions described, only 0.52 mmole trimethylamine had been absorbed by the 0.667 mmole boron trifluoride-hydrazine. Thus boron trifluoride-hydrazine appeared to absorb an indefinite amount of trimethylamine at -80°, and, on warming, the latter was released very slowly.

The reaction of boron trifluoride-hydrazine with gaseous trimethylamine. When trimethylamine (12.85 mmoles; M, 59.9) and boron trifluoride-hydrazine (4.53 mmoles) were left together in vacuo at room temperature for twelve hours, 97.3% of the trimethylamine (12.50 mmoles; M, 59.8) was recovered unchanged. A minute amount of an unidentified liquid (hydrazine?) was produced.

Miscellaneous. For assistance in the correlation of infrared data, the compounds boron trifluoride-trimethylamine (23,24,77), $BF_3 \cdot (CH_3)_3N$, and boron trichloride-trimethylamine (25), $BCl_3 \cdot (CH_3)_3N$, were prepared and their infrared spectra were measured using the potassium bromide pellet technique.* The two spectra are shown in Figure 4 and the characteristic vibration frequencies are summarized in Tables X and XI, respectively.

## The Interaction of Trimethylborane and Hydrazine

Trimethylborane, $B(CH_3)_3$, is a much weaker electron acceptor than boron trifluoride. It was chosen for coordination studies to provide a comparison of its hydrazine complexes with those of boron trifluoride (reported in this thesis) and of diborane (13,14).

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* Grateful acknowledgement is made to Mr. Dutton of this laboratory for the preparation and infrared measurements of these compounds.

## TABLE X

## Infrared Vibration Frequencies of Boron Trifluoride-Trimethylamine

| Frequency $cm^{-1}$ | Intensity | Assignment |
|---|---|---|
| 3600-2800 | several very weak peaks | |
| 1486 | s | $CH_3$ deformation (asym.) |
| 1470 | wsh | |
| 1455 | w | |
| 1270 | w | - |
| 1256 | m | $CH_3$ deformation (sym.) |
| 1210 | wsh | - |
| 1177 | s | $B^{10}$-F stretching (asym.) |
| 1135 | vs | $B^{11}$-F stretching (asym.) |
| 1100 | vs | B-N stretching |
| 990 | m | C-N stretching (asym.) |
| 961 | mw | |
| 922 | vs | $CH_3$ rocking or wagging |
| 839 | vs | $CH_3$ rocking |
| 693 | sn | $CH_3$ wagging? |

s = strong m = medium w = weak v = very n = narrow

sh = shoulder asym = asymmetric sym = symmetric

## TABLE XI

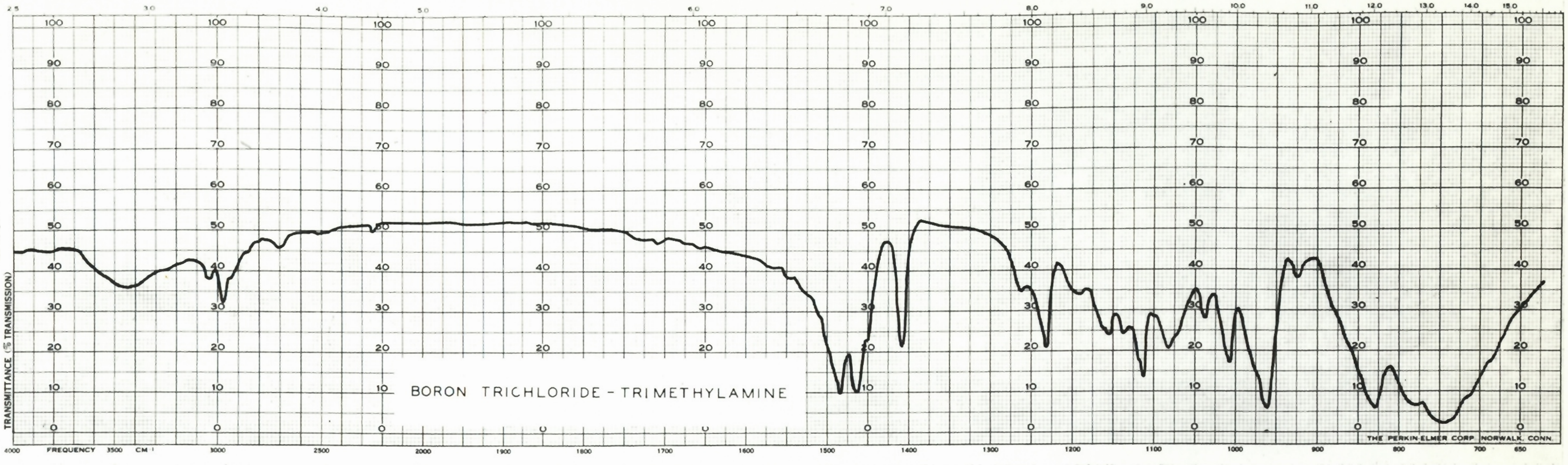
## Infrared Vibration Frequencies of Boron Trichloride-Trimethylamine

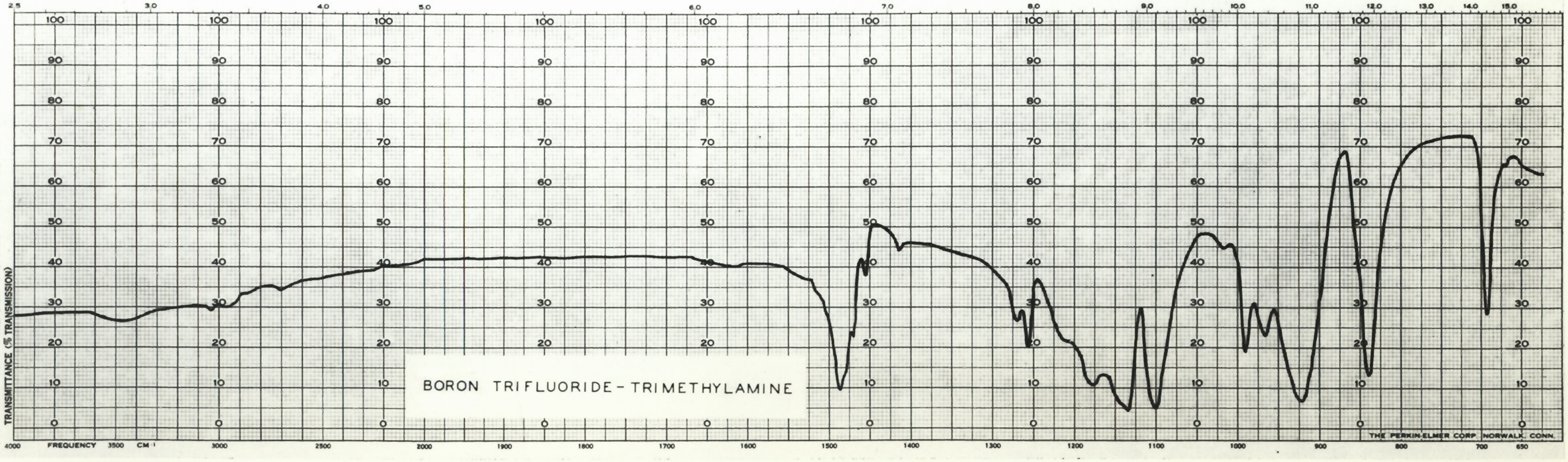
| Frequency $cm^{-1}$ | Intensity | Assignment |
|---|---|---|
| 3650-3250 | vwvb | - |
| 3020 | vw | C-H stretching (asym.) |
| 2965 | w | C-H stretching (sym.) |
| 1487 | s | $CH_3$ deformation (asym.) |
| 1471 | s | |
| 1453 | vwsh | |
| 1409 | mn | unassigned |
| 1265 | wsh | - |
| 1235 | m | $CH_3$ deformation (sym.) |
| 1192 | w | - |
| 1159 | m | $CH_3$ rocking? |
| 1140 | mw | - |
| 1116 | ms | B-N stretching |
| 1085 | m | $CH_3$ wagging? |
| 1042 | w | - |
| 1011 | m | C-N stretching (asym.) |
| 965 | s | $CH_3$ rocking or wagging |
| 927 | w | - |
| 833 | s | $CH_3$ rocking |
| 780 | msh | B-Cl stretching (asym.)? |
| 745 | vsb | |

s = strong m = medium w = weak v = very b = broad sh = shoulder
asym. = asymmetric sym. = symmetric

FIGURE 4

Infrared Spectra of Boron Trifluoride-Trimethylamine and Boron Trichloride-Trimethylamine (Potassium Bromide Pellet Technique)


BORON TRICHLORIDE - TRIMETHYLAMINE


BORON TRIFLUORIDE - TRIMETHYLAMINE

In a typical experiment, trimethylborane (9.69 mmoles) and anhydrous hydrazine (3.26 mmoles) were combined and kept at room temperature overnight. The reaction was initially rapid, but a long time was required for its completion as indicated by a slow decrease in the total pressure. A white crystalline material was formed gradually on the walls of the reaction vessel. The amount of unreacted trimethylborane (3.26 mmoles; M, 55.2. Required for $B(CH_3)_3$: M, 55.9.), recovered by distillation at -80°, showed that trimethylborane (6.43 mmoles) had reacted with hydrazine (3.26 mmoles) in a ratio of 2:1, thus forming the new compound 2-trimethylborane-hydrazine, $2B(CH_3)_3 \cdot N_2H_4$. When this addition complex was warmed, it evolved trimethylborane slowly at -65° to -70°, but at 0°, trimethylborane (3.24 mmoles; M, 56.0) was removed rapidly, leaving a residue containing trimethylborane (3.19 mmoles) and hydrazine (3.26 mmoles) in a ratio of 1:1, corresponding to the new compound trimethylborane-hydrazine, $B(CH_3)_3 \cdot N_2H_4$. The compound 2-trimethylborane-hydrazine did not dissociate reversibly.

When trimethylborane (7.46 mmoles; M, 55.9) was added to a sample of trimethylborane-hydrazine (4.04 mmoles), and the reactants maintained overnight at room temperature, the recovery of trimethylborane (3.40 mmoles; M, 55.8) by distillation at -80° indicated that the compound 2-trimethylborane-hydrazine had been regenerated, since 4.04 mmoles of $B(CH_3)_3 \cdot N_2H_4$ had absorbed an additional 4.06 mmoles of $B(CH_3)_3$.

The 1:1 addition complex did not have a measurable vapour pressure at room temperature. When heated, it melted at 42-43°, and decomposed slowly above 60°. Its aqueous solution, which was alkaline, had strong reducing properties in that it decolourized instantly a solution of potassium permanganate. If the aqueous solution of the compound was strongly acidified with hydrochloric acid, there was an explosion accompanied by a brilliant green flash.

The infrared spectrum of trimethylborane-hydrazine was obtained by the potassium bromide pellet technique and is shown in Figure 5. The principal vibrations and their assignments are summarized in Table XII. For purposes of comparison, the infrared spectrum of trimethylborane-ammonia (40,78,79), $B(CH_3)_3 \cdot NH_3$, was measured by the Nujol mull technique. This compound is so volatile (40,78) that its infrared spectrum cannot be obtained by the more convenient pellet method. The spectrum is shown in Figure 5, and the characteristic vibrations are listed in Table XIII. The compound was prepared as follows: trimethylborane (1.97 mmoles) and ammonia (2.79 mmoles) were allowed to warm slowly from -80° to room temperature over a period of nine hours. Ammonia (0.91 mmole) was recovered by distillation at -80°, indicating that trimethylborane (1.97 mmoles) had reacted with ammonia (1.88 mmoles) in a ratio of 1:1.

Trimethylborane-hydrazine was further characterized by its reactions with ammonia and with diborane, and by its pyrolysis.

<u>The reaction of trimethylborane-hydrazine with ammonia</u>. Trimethylborane-hydrazine (1.80 mmoles) and anhydrous ammonia (3.78 mmoles; M, 17.1. Required for $NH_3$: M, 17.0.) were combined and left at room temperature for two hours. Ammonia (3.62 mmoles; M, 17.1) was recovered by distillation at -80°, and a small amount of unidentified liquid by

## TABLE XII

## Infrared Vibration Frequencies of Trimethylborane-Hydrazine

| Frequency $cm^{-1}$ | Intensity | Assignment |
|---|---|---|
| 3342 | m | N-H stretching (asym.) |
| 3277 | m | N-H stretching (sym.) |
| 3110 | mb | N-H intermolecular? |
| 2908 | m | C-H stretching (asym.) |
| 2812 | msh | C-H stretching (sym.) |
| 2510 | w | - |
| 2350 | wb | - |
| 2090 | w | - |
| 1640 | m | $NH_2$ deformation (asym.) |
| 1602 | s | |
| 1440 | wvb | $CH_3$ deformation (asym.)<br>$NH_2$ deformation (sym.) |
| 1343 | sb | $NH_2$ rocking (asym.) |
| 1282 | vs | $CH_3$ deformation (sym.) |
| 1192 | msh | $NH_2$ rocking (sym.) |
| 1135 | vs | B-C stretching (asym.) |
| 1103 | m | $NH_2$ wagging (asym.) |
| 1075 | vsb | B-N stretching |
| 997 | svb | $CH_3$ rocking |
| 956 | s | N-N stretching |
| 870 | vw | - |
| 851 | w | $CH_3$ rocking |
| 782 | w | $NH_2$ wagging (sym.) |
| 768 | wsh | |
| 679 | s | B-C stretching (sym.) |

s = strong m = medium w = weak v = very b = broad sh = shoulder

asym = asymmetric sym = symmetric

TABLE XIII

Infrared Vibration Frequencies of Trimethylborane-Ammonia*

| Frequency $cm^{-1}$ | Intensity | Assignment |
|---|---|---|
| 3370 | s | N-H stretching (asym.) |
| 3280 | m | N-H stretching (sym.) |
| 3190 | m | N-H intermolecular? |
| 2080 | w | - |
| 1845 | w | - |
| 1787 | w | - |
| 1736 | w | - |
| 1638 | m | $NH_3$ deformation (asym.) |
| 1595 | s | |
| 1283 | vs | $CH_3$ deformation (sym.) |
| 1135 | s | B-C stretching (asym.) |
| 1103 | vs | B-N stretching |
| 985 | sb | $CH_3$ rocking |
| 882 | m | $CH_3$ rocking |
| 780 | w | - |
| 730 | msh | $NH_3$ wagging? |
| 716 | s | |
| 682 | m | B-C stretching (asym.) |

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*The regions 3100-2800 $cm^{-1}$ and 1500-1325 $cm^{-1}$ are omitted due to interference from the Nujol peaks.

s = strong  m = medium  w = weak  v = very  b = broad  sh = shoulder

asym = asymmetric  sym = symmetric

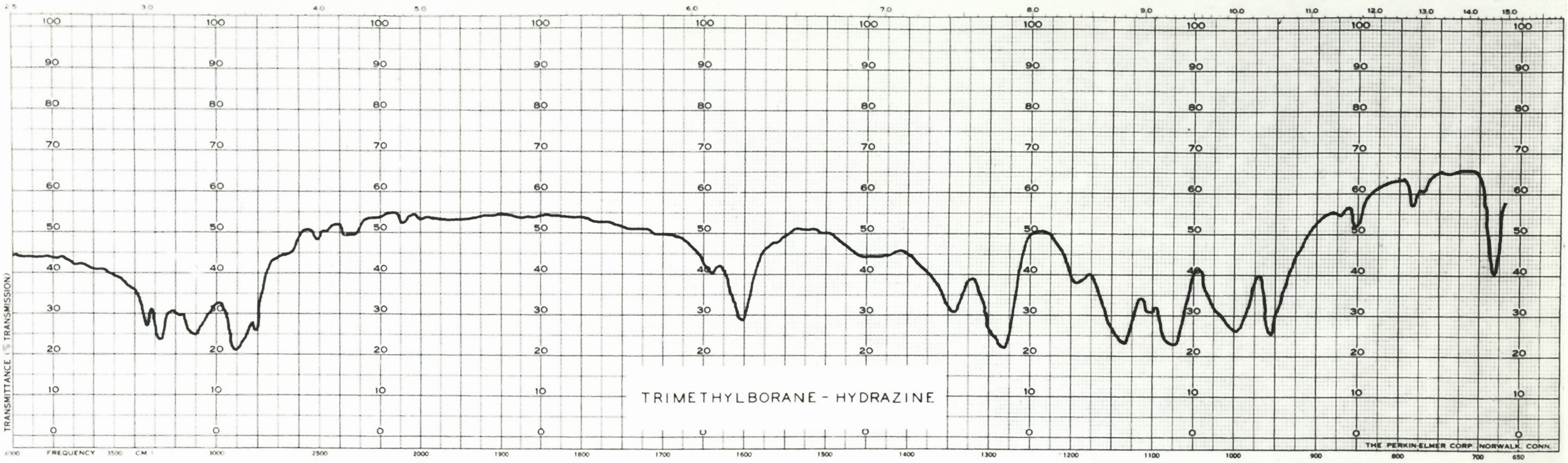
FIGURE 5

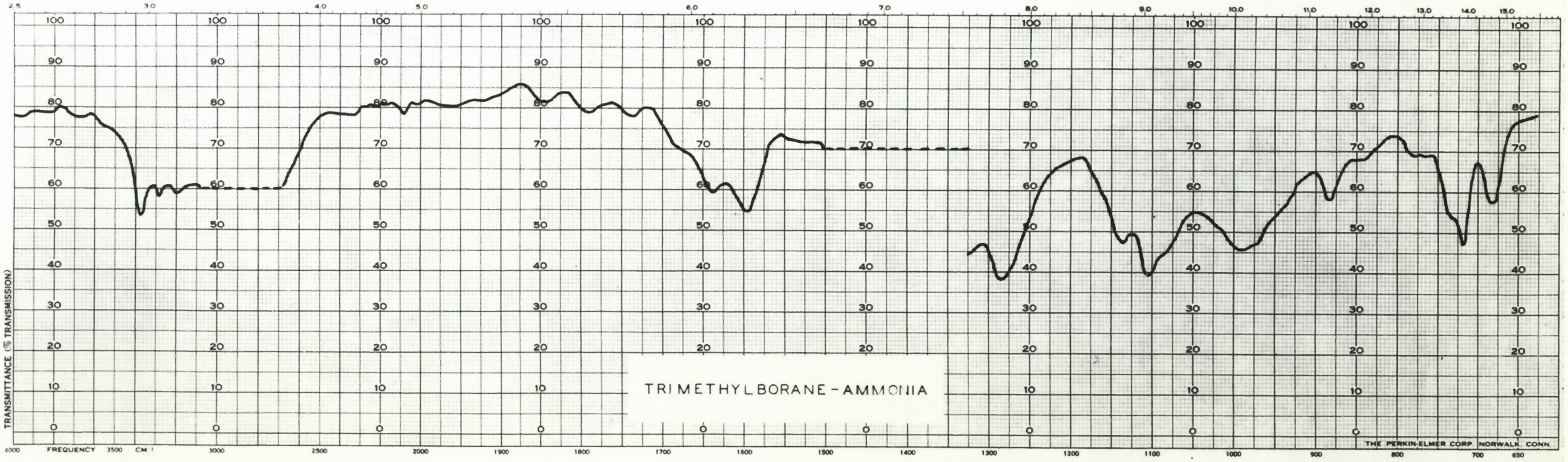
Infrared Spectra of Trimethylborane-Hydrazine

(Potassium Bromide Pellet Technique)

and

Trimethylborane-Ammonia (Nujol Mull Technique)


TRIMETHYLBORANE - HYDRAZINE


TRIMETHYLBORANE - AMMONIA

distillation at room temperature. Therefore the extent of the displacement reaction

$$NH_3 + B(CH_3)_3 \cdot N_2H_4 \longrightarrow B(CH_3)_3 \cdot NH_3 + N_2H_4$$

was not appreciable under these conditions.

<u>The reactions of 2-trimethylborane-hydrazine and trimethylborane-hydrazine with diborane.</u> 2-Trimethylborane-hydrazine, $2B(CH_3)_3 \cdot N_2H_4$, (3.26 mmoles), and diborane (4.01 mmoles; M, 27.7. Required for $B_2H_6$: M, 27.7.) were maintained overnight at -80°. The quantitative recovery of diborane by distillation at -80° (3.99 mmoles; M, 27.9) proved that no reaction had taken place.

In another experiment, trimethylborane-hydrazine, $B(CH_3)_3 \cdot N_2H_4$, (3.26 mmoles), and diborane (4.49 mmoles; M, 27.6) were combined and left overnight at room temperature. The reaction produced a solid residue and several volatile products: diborane, trimethylborane, unsym-dimethyldiborane, and hydrogen.

The reaction was stopped by surrounding a portion of the apparatus with a liquid air bath. After some time, all the volatile material had condensed, leaving hydrogen (0.75 mmole; M, 1.2. Required for $H_2$: M, 2.0.). The condensable substances were fractionated carefully at -143°, yielding diborane (0.59 mmole; M, 26.6), and repeatedly at -115°, yielding trimethylborane (0.50 mmole; M, 59.4; v.p. 26 mm. at -80°. Required for $B(CH_3)_3$: M, 55.9; v.p. 27.3 mm. at -80° (65).) and unsym-dimethyldiborane (2.46 mmole; M, 58.9; v.p. 11 mm. at -79.5°. Required for unsym-$(CH_3)_2B_2H_4$: M, 55.7; v.p. 13 mm. at -78.5° (62). Positive identification was obtained from its infrared spectrum (80).). The separation of trimethylborane from unsym-dimethyldiborane was difficult owing to the proximity of their vapour pressures.

The solid residue was heated gradually, resulting in the evolution of the following amounts of noncondensable gas:

| Temperature of Residue | Amount of Gas (mmoles) | Molecular Weight |
|---|---|---|
| 100° | 3.94 | 17.6 |
| 170° | 0.75 | 7.21 |
| 250° | 4.13 | 2.46 |

These data suggest that methane, hydrogen, and possibly nitrogen were evolved on heating the residue. The quantity of condensable gas released during these operations was small. The methane was presumed to originate from unreacted trimethylborane-hydrazine, while the evolution of hydrogen is characteristic of diborane-hydrazine, $2BH_3 \cdot N_2H_4$ (13,14).

Only a portion (1500-2850 $cm^{-1}$) of the infrared spectrum of unsym-dimethyldiborane has been published in the chemical literature (80). A more complete spectrum (650-4000 $cm^{-1}$) is presented in Figure 6, and the vibration frequencies are outlined in Table XIV.

<u>The pyrolysis of trimethylborane-hydrazine</u>. Trimethylborane (8.58 mmoles) and hydrazine (8.58 mmoles) were combined in an all-glass apparatus and heated to 150-160° for 16 1/2 hours. The principal products were (a) noncondensable gases ($N_2$, $CH_4$; 0.67 mmole), (b) ammonia (0.42 mmole; M, 18.0; v.p. 35.6 mm. at -79.5°. Required for $NH_3$: M, 17.0; v.p. 40.0 mm. at -79.2°

## TABLE XIV

### Infrared Vibration Frequencies of unsym-Dimethyldiborane

| Frequency $cm^{-1}$ | Intensity | Assignment |
|---|---|---|
| 3680 | vw | - |
| 2970 | m | C-H stretching (asym.) |
| 2840 | wsh | C-H stretching (sym.) |
| 2570 | ssp | $B-H_{terminal}$ stretching (asym.) |
| 2495 | ssp | $B-H_{terminal}$ stretching (sym.) |
| 2140 | wsh | - |
| 2100 | w | - (2 x 1055?) |
| ~ 1990 | vwvb | - (1055+920?) |
| 1755 | wb | - |
| 1686 | m | unidentified |
| 1545 | vsb | $B-H_{bridge}$ stretching |
| 1440 | m | $CH_3$ deformation (asym.) |
| 1317 | s | $CH_3$ deformation (sym.) |
| 1152 | s,u | $BH_2$ "scissors"<br>and |
| 1115 | | B-C stretching (asym.) |
| 1055 | s | $BH_2$ rocking? |
| 920 | w | $BH_2$ wagging |
| 849 | w | $CH_3$ rocking |

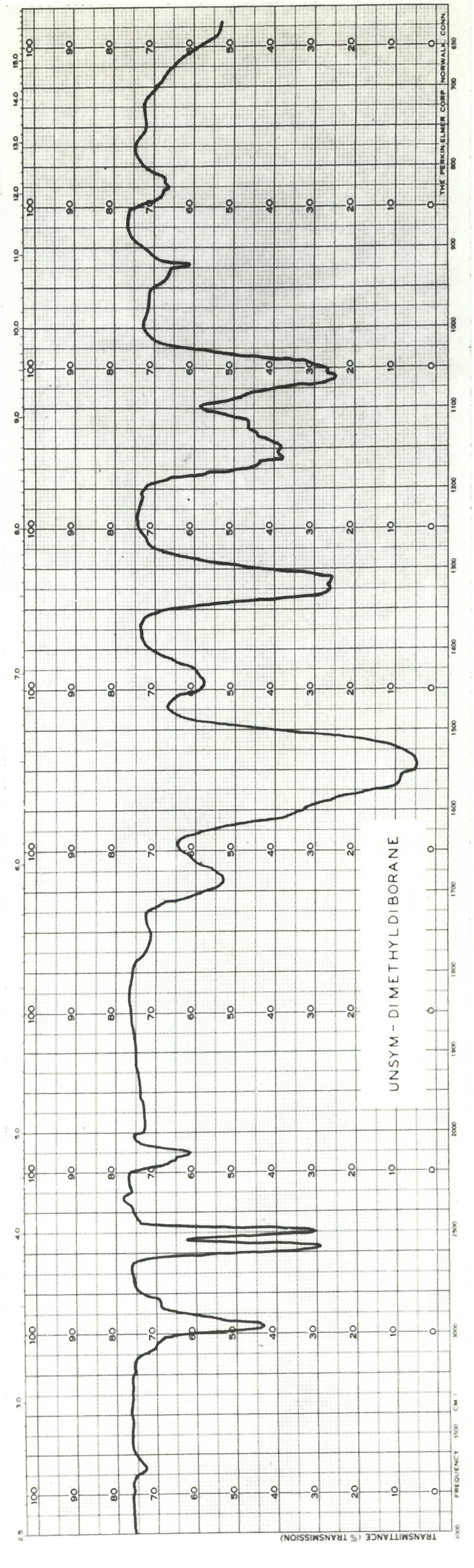
s = strong m = medium w = weak v = very b = broad sp = sharp

sh = shoulder u = unresolved asym = asymmetric sym = symmetric

FIGURE 6

Infrared Spectrum of unsym-Dimethyldiborane

(10 cm. gas cell at pressure of 10.6 mm.)



UNSYM - DIMETHYLDIBORANE

(76).), (c) a mixture of butane and the isomeric butenes (2.44 mmoles; M, 56.3. Required for $C_4H_8$: M, 56.1. Required for $C_4H_{10}$: M, 58.1. Identification was made from the infrared spectrum (72,81) and the mass spectrum*; the latter indicated that the ratio $C_4H_{10}:C_4H_8 \leqslant 1:3$), and (d) an unidentified complex residue.

Both trimethylborane and hydrazine were individually heated under identical reaction conditions, as follows. Trimethylborane (7.75 mmoles) was heated in a sealed all-glass reaction vessel for 16 1/2 hours at 150-160°. Quantitative recovery of the gas (7.75 mmoles; M, 56.7. Required for $B(CH_3)_3$: M, 55.9.) indicated that no decomposition had taken place.

Hydrazine (9.33 mmoles) was heated in an all-glass apparatus to 150-160° for 16 1/2 hours. The reaction products were nitrogen (0.14 mmole; M, 32.8. Required for $N_2$: M, 28.0.), ammonia (0.52 mmole; M, 17.5. Required for $NH_3$: M, 17.0.), and unchanged hydrazine (8.86 mmoles; analysis by the iodate method (54)) in accordance with the decomposition scheme (82, 83,84),

$$3\ N_2H_4 \longrightarrow 4\ NH_3 + N_2$$

The extent of decomposition of hydrazine was only 5%.

Thus hydrazine and trimethylborane are changed very little when they are individually heated to 150-160° for a prolonged period, whereas trimethylborane-hydrazine appears to undergo a complex decomposition reaction. The appearance of butane and butenes among the decomposition products is remarkable.

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*This measurement was very kindly made by Dr. L. Elias of the Physical Chemistry Laboratory, McGill University.

## The Reaction of Trimethylaluminum with Hydrazine

A middle cut of commercial trimethylaluminum was fractionated carefully at 0° and collected in a trap at -80° (v.p. 13.2 mm. at 24.7°. Required for $(Al(CH_3)_3)_2$: v.p. 12.8 mm. at 24.7° (85,86).). The infrared spectrum was identical to that reported in the literature (49,87).

The reaction in vacuo. Anhydrous hydrazine (4.72 mmoles) and trimethylaluminum (20.0 mmoles) were kept at room temperature overnight. The products of the reaction were an inert pale brown solid, which did not change visibly on heating to 300°, a mixture of noncondensable gases (20.0 mmoles (18.58 mmoles $CH_4$ and 1.42 mmoles $H_2$); M, 15.00; 15.08. Required for $CH_4$: M, 16.0; for $H_2$: M, 2.0. Successive vapour pressure measurements on a fraction gradually approached that of $CH_4$), and unreacted trimethylaluminum (12.03 mmoles; v.p. 15.9 mm. at 26.7°. Required for $(Al(CH_3)_3)_2$: v.p. 13.7 mm. at 26.7°. Identification also made by infrared spectrum). The infrared spectrum of the residue had some bands which were similar to those found for aluminum nitride (88). The data suggested that the reaction in vacuo was complex.

The reaction in diethyl ether. In a typical experiment, anhydrous diethyl ether (20 ml.) was thoroughly degassed in vacuo and to it were added hydrazine (10.09 mmoles) and trimethylaluminum (27.9 mmoles). The apparatus was sealed and the reactants were stirred overnight at room temperature. A white suspension formed in the ether.

Methane (20.1 mmoles; M, 16.3; v.p. 21.5 mm. at -191°. Required for $CH_4$: M, 16.0; v.p. 20.0 mm. at -191.8° (76).) was the only noncondensable gas produced. The solvent and unreacted trimethylaluminum were distilled at room temperature, leaving a white crystalline deposit. Analyses of the latter for aluminum were not reproducible, but the weight of the crude reaction product (1.57 gm.) corresponded approximately to that required (1.46 gm.) for the formation of the substance sym-disbimethylaluminohydrazine, $(CH_3)_2AlNHNHAl(CH_3)_2$. The evolution of exactly two moles of methane per mole of hydrazine consumed was supporting evidence. The substance was extremely unstable: it reacted violently with water or ethanol and it decomposed violently when subjected to mechanical shock. Consequently no further effort was made to purify and characterize the compound.

## The Reactions of Boron Trichloride and Boron Tribromide with Hydrazine

Although boron trifluoride reacts with hydrazine to form two stable addition complexes, $BF_3 \cdot N_2H_4$ and $2BF_3 \cdot N_2H_4$, the reaction of boron trichloride or boron tribromide with hydrazine results in the elimination of hydrogen halide by the two reactants, yielding hydrazine hydrohalide, $N_2H_4 \cdot HX$, and a new substance with boron-nitrogen linkages.

The purification of boron trichloride was effected by passing it into a LeRoy distillation column at -120° and removing it from the column at -90° (Found: M, 117.6; v.p. 478.5 mm. at 0°. Required for $BCl_3$: M, 117.2; v.p. 477 mm. at 0° (89,90).). Boron tribromide was distilled from mercury through a bath at -23° and trapped at -80° (Found: v.p. 58.9 mm. at 21.4°. Required for $BBr_3$: v.p. 58 mm. at 21.4° (62,76).).

The reaction of boron trichloride with hydrazine. Boron trichloride (11.90 mmoles) and anhydrous hydrazine (94 mmoles) were distilled into the side arm of a one liter flask. After sealing the apparatus, the reactants were stirred overnight at room temperature. An extremely vigorous reaction produced a white solid which almost redissolved in the excess hydrazine. The direct reaction of the two materials should be done with small quantities, otherwise there is a considerable risk of explosion. Unreacted hydrazine (analyzed by the iodate method (54)) and a trace of ammonia (0.32 mmole; M, 16.8. Required for $NH_3$: M, 17.0.) were recovered by distillation at room temperature. The white solid appeared to contain boron trichloride and hydrazine in a ratio of 1:4 (Found: $N_2H_4$, 51.4, 52.5%. Required for $BCl_3N_8H_{16}$:$N_2H_4$, 52.3%.).

The reaction of boron trichloride with hydrazine in tetrahydrofuran led to a different reaction product. Boron trichloride (46.8 mmoles) was dissolved in anhydrous tetrahydrofuran (50 ml.) at -64°. The solution was diluted to 200 ml. with tetrahydrofuran, and hydrazine (310 mmoles) was added dropwise with stirring in an atmosphere of dry nitrogen. A precipitate formed immediately. After decantation of the solvent, volatile impurities were removed by vacuum distillation at room temperature, leaving a tacky, pale yellow material. The latter was washed several times with anhydrous diethyl ether, and the resulting white crystalline material seemed to contain boron trichloride and hydrazine in a ratio of 1:6 (Found: Cl, 38.7, 38.6%. Required for $BCl_3N_{12}H_{24}$: Cl, 38.9%.). This substance was soluble in water, giving a neutral solution, but was insoluble in boiling pyridine. A comparison of the infrared spectra of the complex material $BCl_3N_{12}H_{24}$ and hydrazine hydrochloride (91), $N_2H_4 \cdot HCl$, is given in Table

XV. The data in Table XV suggest that hydrazine hydrochloride was one of the principal constituents of the reaction mixture.

An unsuccessful attempt was made to separate the substance $BCl_3N_8H_{16}$ into its components by fractional sublimation. A sample of the material, heated at 160-165° in vacuo, yielded hydrazine (analyzed by the iodate method), hydrazine hydrochloride (white needles containing hydrazine and chlorine but no boron; m.p. 91°; $N_2H_4$, 50.1%. Required for $N_2H_5Cl$: white needles; m.p. 89° (92); $N_2H_4$, 47.1%.), and a nonvolatile residue containing hydrazine (50.6, 50.7%), chlorine (13.2, 13.6%), and boron.

The reaction product $BCl_3N_{12}H_{24}$ was extracted twenty-one times with anhydrous hydrazine in a nitrogen-filled "dry box". The extracts were separated from the solid each time by centrifugation. The residual material, a white solid, was small in amount due to its appreciable solubility in hydrazine. After being dried in vacuo at room temperature, it was found to contain 15.61% boron and no chlorine. These analytical data suggested that the substance contained four gram-atoms of nitrogen per gram-atom of boron, i.e., 80.8% nitrogen. The remaining few per cent were presumed to be hydrogen. On the basis of the reaction scheme to be proposed in the Discussion, the most reasonable empirical formula appeared to be $BN_4H_5$ (Required: B, 15.05%). This substance did not melt when heated to 300°. It was soluble in water, giving an alkaline solution. Its infrared spectrum, obtained by the potassium bromide pellet method, is shown in Figure 7, and the vibration frequencies are summarized in Table XVI.

## TABLE XV

### Infrared Vibration Frequencies of $BCl_3N_{12}H_{24}$ and $N_2H_4 \cdot HCl$

| $N_2H_4 \cdot HCl$ |  | $BCl_3N_{12}H_{24}$ |  |
|---|---|---|---|
| Frequency $cm^{-1}$ | Intensity | Frequency $cm^{-1}$ | Intensity |
| 3261 | sn | 3260 | ssh |
| 3150 | sn |  | bu |
| 3034 | sn |  |  |
| 2950 | s? | 2950? |  |
| 2903 | s? |  |  |
| 2716 | sb | 2700? |  |
| 2602 | sn | 2580? |  |
| 2350 | w | 2340? |  |
| 1970 | mb |  |  |
| 1745 | wb |  |  |
| 1638 | mb | 1630 | sbu |
| 1584 | mb | 1570 |  |
| 1500 | sn | 1497 | sn |
| 1417 | mn | 1410 | s |
|  |  | 1350 | svb |
| 1246 | sn | 1238 | m |
| 1124 | sb | ~ 1100 | vsbu |
| 1101 | sb |  |  |
| 973 | sn | 982 | sn |

s = strong  m = medium  w = weak  v = very  b = broad  n = narrow

sh = shoulder  u = unresolved

## TABLE XVI

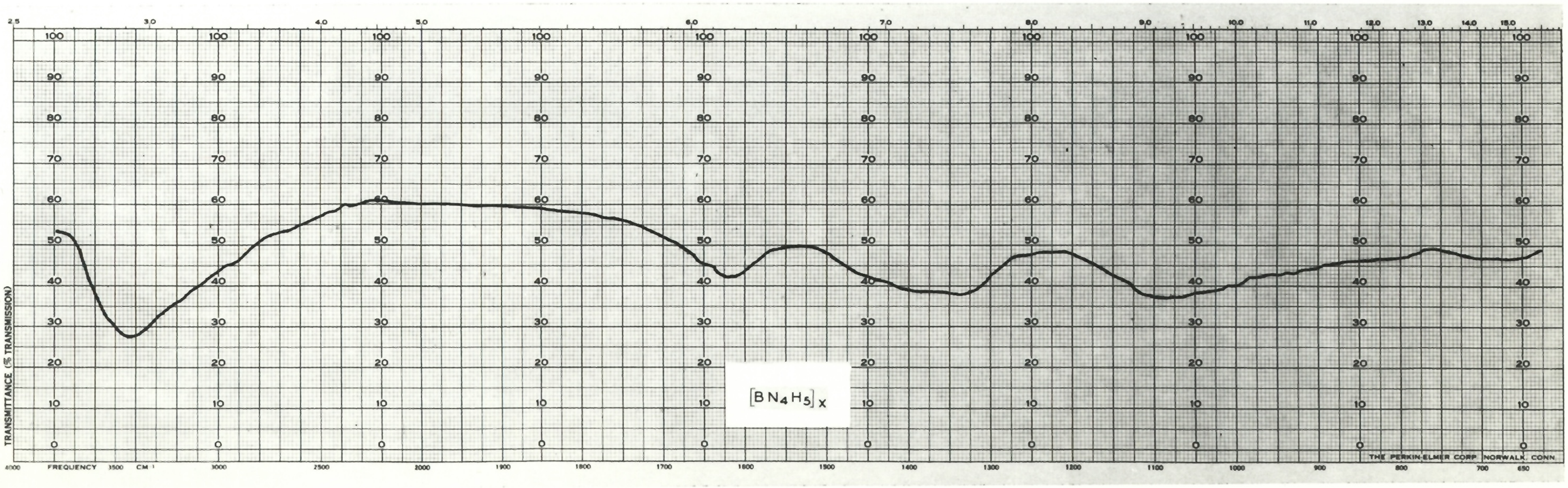
### Infrared Vibration Frequencies of $(BN_4H_5)_X$

| Frequency cm$^{-1}$ | Intensity | Assignment |
|---|---|---|
| 3350 | svb | N-H stretching and BN vibrations |
| 1620 | sb | N-H deformation (asym.) |
| ~ 1330 | svb | B-N stretching |
| ~ 1050 | svb | N-H wagging? |
| ~ 700 | mvb | unassigned |

s = strong m = medium v = very b = broad asym = asymmetric

FIGURE 7

Infrared Spectrum of $(BN_4H_5)_X$ (Potassium Bromide Pellet Technique)


$[BN_4H_5]_x$
TRANSMITTANCE (% TRANSMISSION)
FREQUENCY CM⁻¹
2.5
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
4000
3500
3000
2500
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
650
100
90
80
70
60
50
40
30
20
10
0
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The reaction of boron tribromide with hydrazine. Boron tribromide (104 mmoles) was cautiously dissolved in tetrahydrofuran (250 ml.) at -80° in an atmosphere of dry nitrogen. The dropwise addition of anhydrous hydrazine (1250 mmoles) to the solution at room temperature immediately produced a white precipitate which almost redissolved in the excess hydrazine. After the removal of the tetrahydrofuran, the hydrazine layer was evaporated to dryness in the vacuum system. The residue, a sticky pale brown solid, was washed several times with absolute ethanol in the "dry box", yielding a white solid that seemed to contain boron tribromide and hydrazine in a ratio of 1:6 (Found: Br, 53.9%. Required for $BBr_3N_{12}H_{24}$: Br, 54.2%.). A comparison of the infrared spectrum of the complex substance $BBr_3N_{12}H_{24}$ with that of hydrazine hydrobromide (91), $N_2H_4 \cdot HBr$, is given in Table XVII. It is evident from the data in Table XVII that one of the components of the reaction mixture was hydrazine hydrobromide.

The material $BBr_3N_{12}H_{24}$ was extracted twelve times with hydrazine under anhydrous conditions; the extracts were separated from the residue each time by centrifugation. The residual white solid, dried at room temperature in the vacuum system, contained 15.31% boron and a small trace of bromine. By analogy with the reaction of boron trichloride with hydrazine, the empirical formula of the residue was again thought to be $BN_4H_5$ (Required: B, 15.05%). This substance was soluble in water, did not melt when heated to 300°, and its infrared spectrum was the same as that shown in Figure 7 and summarized in Table XVI.

## TABLE XVII

## Infrared Vibration Frequencies of $BBr_3N_{12}H_{24}$ and $N_2H_4 \cdot HBr$

| $N_2H_4 \cdot HBr$ | | $BBr_3N_{12}H_{24}$ | |
|---|---|---|---|
| Frequency $cm^{-1}$ | Intensity | Frequency $cm^{-1}$ | Intensity |
| 3250–2690 | su | 3245 | sn |
| | | 3140 | ssh |
| | | 2940 | s |
| 2575 | sn | 2560 | sn |
| 2330 | w | 2320 | msh |
| 1930 | mb | ~ 1950 | wb |
| 1725 | wb | 1720 | wb |
| 1615 | mb | 1620 | mn |
| | | 1593 | w |
| 1568 | mb | 1565 | mn |
| 1491 | sn | 1488 | sn |
| 1410 | sn | 1402 | mn |
| 1243 | sn | 1221 | sn |
| 1100 | sb | 1090 | vs |
| 1095 | sb | 1072 | vs |
| 965 | sn | 955 | sn |
| 495 | sb | | |

s = strong  m = medium  w = weak  v = very  n = narrow  b = broad  sh = shoulder
u = unresolved

## The Reactions of the Aluminum Halides with Hydrazine

Although the reactions of the boron halides (except $BF_3$) with ammonia (29,30,31,93) result in the elimination of hydrogen halide by the two reactants and the formation of boron amide or boron imide,

$$BCl_3 + 6\ NH_3 \longrightarrow B(NH_2)_3 + 3\ NH_4Cl$$

$$2\ BBr_3 + 9\ NH_3 \longrightarrow B_2(NH)_3 + 6\ NH_4Br$$

$$2\ BI_3 + 9\ NH_3 \longrightarrow B_2(NH)_3 + 6\ NH_4I$$

analogous reactions with the aluminum halides do not occur. Rather, addition compounds such as $AlCl_3 \cdot NH_3$ are formed (46,47,48). It is of interest, therefore, to investigate the reactions of the aluminum halides with hydrazine and to contrast its behaviour with that of ammonia in this respect.

The reaction of aluminum chloride with hydrazine. Under anhydrous conditions, a 50 ml. flask with a ground glass neck was charged with aluminum chloride (16.5 mmoles) and attached to the side-arm of a one liter flask. Anhydrous hydrazine (150 mmoles) was condensed onto the aluminum chloride by distillation in vacuo. On warming to room temperature, a rapid reaction occurred, leaving a white solid in the reaction bulb. After 1 3/4 hours, unreacted hydrazine (analyzed by the iodate method) was recovered by distillation at room temperature. The solid residue appeared to contain aluminum chloride and hydrazine in a ratio of 1:4 (Found: $N_2H_4$, 51.8%; Cl, 39.2%. Required for $AlCl_3N_8H_{16}$: $N_2H_4$, 49.1%; Cl, 40.7%.).

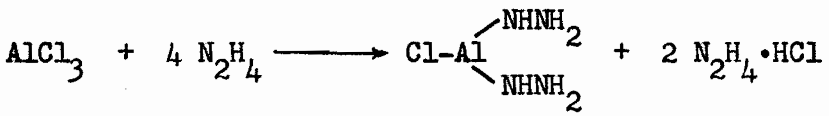
When the aluminum chloride was diluted by suspending it in carbon tetrachloride, its reaction with hydrazine yielded the same product. In a typical experiment, aluminum chloride (25.4 mmoles) and carbon tetrachloride (250 ml.) were placed in a three-necked flask. Anhydrous hydrazine was added dropwise with stirring in an atmosphere of dry nitrogen; a white precipitate formed immediately. After filtration, the precipitate was dried at room temperature in the vacuum system. A portion of the carbon tetrachloride filtrate, evaporated to dryness on a steam bath, left no residue. The empirical formula of the solid material again seemed to be $AlCl_3N_8H_{16}$ (Found: Al, 10.09, 10.14%; Cl, 39.8, 39.2%. Required for $AlCl_3N_8H_{16}$: Al, 10.33%; Cl, 40.7%.).

However, when anhydrous diethyl ether was used as a solvent, the reaction between aluminum chloride (16.5 mmoles) and hydrazine (141 mmoles) yielded a white solid that was considered to contain aluminum chloride and hydrazine in a ratio of 1:5.25 (Found: Al, 8.96%; Cl, 34.8%; $N_2H_4$, 55.9%. Required for $AlCl_3N_{10.5}H_{21.0}$: Al, 8.95%; Cl, 35.3%; $N_2H_4$, 55.8%.).

Lastly, using absolute ethanol as a solvent, the reaction between hydrazine (219 mmoles) and aluminum chloride (24.8 mmoles) gave a precipitate of pure hydrazine hydrochloride, $N_2H_4 \cdot HCl$ (Found: Cl, 50.9%; m.p. 90-100° (gradual). Required for $N_2H_5Cl$: Cl, 51.7%; m.p. 89° (92). Positive identification was made from the infrared spectrum (91).). All the aluminum remained in solution.

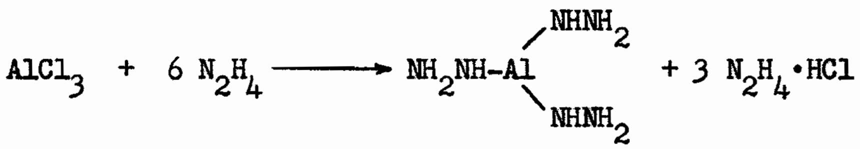
The complex reaction product $AlCl_3N_8H_{16}$ was partially soluble in water producing an alkaline solution which (a) possessed strong reducing properties in that it instantly decolourized a solution of potassium permanganate, and (b) gave a positive test for chloride ion. The product dissolved readily in aqueous solutions of HCl, $HNO_3$, and NaOH, but it was not soluble in aqueous ammonia or in pyridine. A comparison of the infrared spectra of $AlCl_3N_8H_{16}$ and $AlCl_3N_{10.5}H_{21.0}$ (both obtained by the potassium bromide technique) with that of hydrazine hydrochloride, $N_2H_4\cdot HCl$ (91), is given in Table XVIII. It is apparent from this table that the spectra of all three substances were similar.

The data cited suggested that the reaction of aluminum chloride with hydrazine was characterized by the elimination of hydrogen chloride, which appeared among the products as hydrazine hydrochloride. The 4:1 stoichiometry of the reaction both in vacuo and in carbon tetrachloride might be represented by



$$AlCl_3 + 4\ N_2H_4 \longrightarrow Cl\text{-}Al\begin{matrix}\diagup NHNH_2\\ \diagdown NHNH_2\end{matrix} + 2\ N_2H_4\cdot HCl$$

Stoichiometric ratios higher than 4:1 could arise if all three atoms of chlorine in aluminum chloride reacted with hydrazine:



$$AlCl_3 + 6\ N_2H_4 \longrightarrow NH_2NH\text{-}Al\begin{matrix}\diagup NHNH_2\\ \diagdown NHNH_2\end{matrix} + 3\ N_2H_4\cdot HCl$$

The separation of hydrazine hydrochloride from the remainder of the reaction product was attempted (unsuccessfully) by the technique of fractional sublimation. $AlCl_3N_8H_{16}$ (1.002 gm.) was heated in vacuo at 160-170° until the evolution of volatile material had ceased. Hydrazine

## TABLE XVIII

## Infrared Vibration Frequencies of $AlCl_3N_8H_{16}$, $AlCl_3N_{10.5}H_{21.0}$, and $N_2H_4 \cdot HCl$

| $N_2H_4 \cdot HCl$ | | $AlCl_3N_8H_{16}$ | | $AlCl_3N_{10.5}H_{21.0}$ | |
|---|---|---|---|---|---|
| Frequency $cm^{-1}$ | Intensity | Frequency $cm^{-1}$ | Intensity | Frequency $cm^{-1}$ | Intensity |
| 3261 | sn | 3290 | s | 3290 | s |
| 3150 | sn | * ? | | * - | |
| 3034 | sn | 3050 | m | 3050 | s |
| 2950 | s? | 2940? | | - | |
| 2903 | s? | - | | - | |
| 2716 | sb | ? | | - | |
| 2602 | sn | ? | | - | |
| 2350 | w | - | | - | |
| 1970 | mb | - | | - | |
| 1745 | wb | - | | - | |
| 1638 | mb | 1650-1550 | sb | 1615 | svb |
| 1584 | mb | - | | - | |
| 1500 | sn | 1495 | sn | 1500 | w |
| 1417 | mn | 1412 | mw | 1400 | w |
| 1246 | sn | 1238 | mw | ~ 1210 | wvb |
| 1124 | sb | 1100 | vsvb | 1115 | s |
| 1101 | sb | - | | 1091 | s |
| 973 | sn | 962 | sn | 958 | s |

*Poor resolution in the region 3200-2500 $cm^{-1}$.

s = strong m = medium w = weak v = very n = narrow b = broad hydrochloride (0.109 gm.; white crystals containing hydrazine and chlorine but no aluminum; m.p. 91°. Required for $N_2H_5Cl$: m.p. 89° (92).) and hydrazine (0.220 gm.; analyzed by the iodate method) were recovered, leaving a residue (0.613 gm.) containing aluminum and chlorine in an approximate ratio of 2:5 (Found: Al, 15.4%; Cl, 50.2%). Infrared spectral analysis indicated the presence of NH bonds in the residue.

By an independent test, hydrazine hydrochloride was found to be soluble in anhydrous hydrazine. A "Soxhlet" extraction apparatus was constructed with a thimble of porous glass "paper" in the extractor. The substance $AlCl_3N_8H_{16}$ (3.048 gm.) was placed in the thimble, the boiling flask loaded with anhydrous hydrazine (70 ml.), and the solid material extracted with <u>hot</u> hydrazine approximately thirty times under anhydrous conditions. The extraction liquid contained all the chlorine from the original sample (Found: Cl, 1.220 gm. Weight of Cl in original sample: 1.230 gm.), leaving in the thimble a small amount (the residue was slightly soluble in hydrazine) of a white solid that contained 41.8% aluminum and no chlorine. In a duplicate experiment, the residue in the thimble contained 41.4% aluminum. An attempted analysis for nitrogen by the Kjeldahl method was unsuccessful. The analytical data suggested that the residue contained two and one-half gram-atoms of nitrogen per gram-atom of aluminum, i.e., 54.0% nitrogen. The remainder (~4-5%) was presumed to be hydrogen. From the reaction scheme to be outlined in the Discussion, the most reasonable empirical formula was considered to be $Al_2N_5H_5$ (Required: Al, 41.8%).

This substance did not melt when heated to 475°. It was hydrolyzed slightly by water, dissolved partially in moderately acid solution, and dissolved completely in hot, strongly acid solution. The infrared spectrum (potassium bromide pellet technique) of the material is shown in Figure 8, and the vibration frequencies are summarized in Table XIX.

The attempted separation of $AlCl_3N_8H_{16}$ into its components by the use of absolute ethanol as the Soxhlet extraction liquid resulted in the accumulation in the boiling flask of long needle-shaped crystals containing hydrazine and chlorine but no aluminum, i.e., hydrazine hydrochloride. However, the separation process was impracticably lengthy and, since more than two-thirds of the chlorine was removed by the ethanol, there was indication that ethanolysis of the aluminum compound had occurred.

Other extraction experiments with acetone, diethyl ether, dimethylsulphoxide, $(CH_3)_2SO$, and pyridine also failed to give a separation of the reaction products.

Finally, the substance $AlCl_3N_8H_{16}$ was extracted repeatedly at room temperature with anhydrous hydrazine in a nitrogen-filled "dry box". The extract was separated each time from the solid material by centrifugation. After eleven operations, the residue was dried in vacuo at room temperature, leaving a white solid containing aluminum (30.4, 30.7%) and no chlorine. The substance was accordingly thought to contain four gram-atoms of nitrogen per gram-atom of aluminum, i.e., 63.5% nitrogen. On the basis of these analyses and the reaction scheme considered in the Discussion, the empirical formula was thought to be $AlN_4H_5$ (Required: Al, 30.7%).

This substance did not melt when heated to 350° in a sealed tube.

## TABLE XIX

## Infrared Vibration Frequencies of $(Al_2N_5H_5)_X$

| Frequency $cm^{-1}$ | Intensity | Assignment |
|---|---|---|
| ~ 3500 | vsvb | N-H stretching and Al-N vibrations |
| 1640 | sb | NH deformation (asym.) |
| 1470 | mwb | NH deformation (sym.) |
| 1385 | m | NH rocking (asym.) |
| 1195 | m | NH wagging? |
| ~ 1115 | wsh? | - |
| 1050-650 | meb | Al-N stretching? |

s = strong m = medium

w = weak v = very

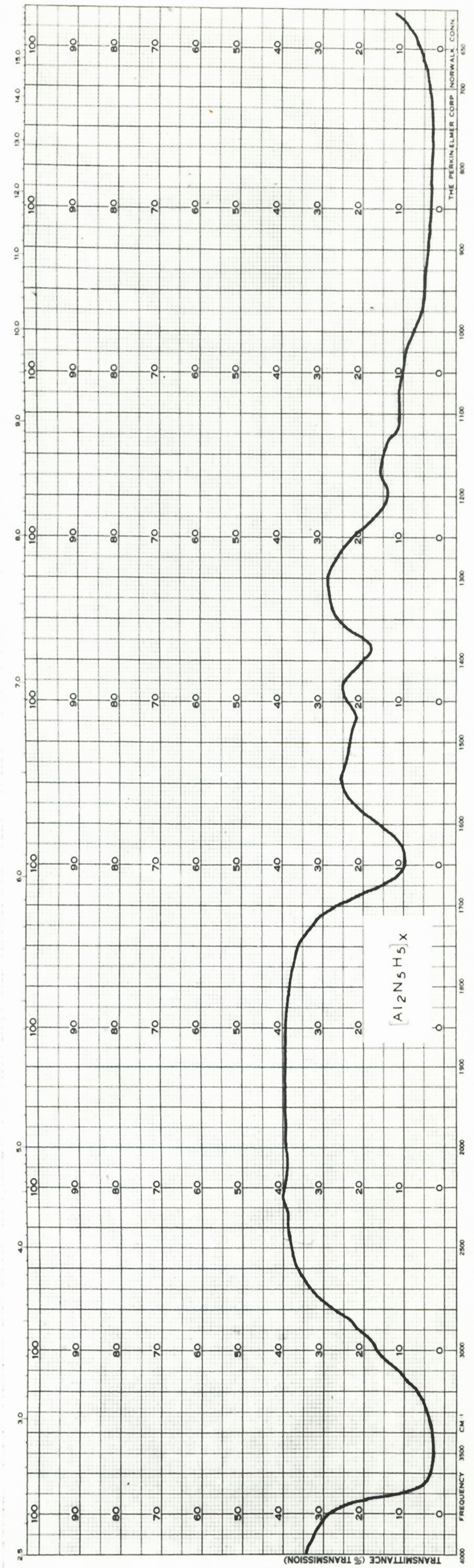
b = broad sh = shoulder

e = extremely asym = asymmetric

sym = symmetric

FIGURE 8

Infrared Spectrum of $(Al_2N_5H_5)_X$ (Potassium Bromide Pellet Technique)


$[Al_2N_5H_5]_x$
TRANSMITTANCE (% TRANSMISSION)
FREQUENCY 3500 CM⁻¹
4000
3000
2500
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
650
2.5
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
100
90
80
70
60
50
40
30
20
10
0
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It dissolved readily in nitric acid and in hydrochloric acid, and was slightly soluble in anhydrous hydrazine (which caused considerable difficulty in its separation from $N_2H_5Cl$). Water partially hydrolyzed the substance, yielding an alkaline solution. The infrared spectrum of the material, obtained by the potassium bromide pellet method, is shown in Figure 9, and the vibration frequencies are summarized in Table XX.

The reaction of aluminum bromide with hydrazine. Anhydrous hydrazine (250 mmoles) was added dropwise in an atmosphere of dry nitrogen to a suspension of aluminum bromide (44 mmoles) in carbon tetrachloride (300 ml.). An immediate reaction yielded a white precipitate which, upon decantation of the carbon tetrachloride, was dried at room temperature in the vacuum system. The crude reaction product, containing aluminum, bromine, and hydrazine, was extracted ten times with anhydrous hydrazine in a nitrogen-filled "dry box"; the extracts were separated from the solid material each time by centrifugation.

The residual material, on evaporation to dryness in vacuo at room temperature, was found to contain aluminum (31.5%) but no bromine. This substance was thought to be identical to that isolated by the same method from the aluminum chloride reaction, i.e., $AlN_4H_5$ (Required: Al, 30.7%). This substance was partially hydrolyzed by water, dissolved readily in aqueous acids, and did not melt when heated to 300°. Its infrared spectrum was identical to that shown in Figure 9 and summarized in Table XX.

## TABLE XX

### Infrared Vibration Frequencies of $(AlN_4H_5)_X$

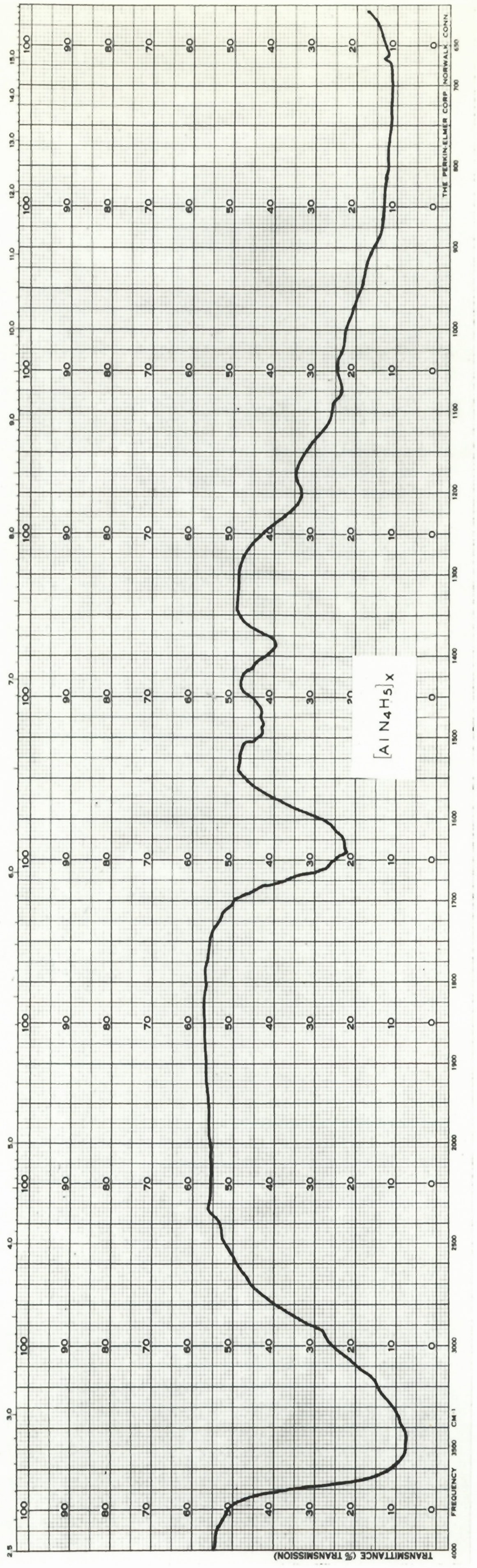
| Frequency cm$^{-1}$ | Intensity | Assignment |
|---|---|---|
| 3450 | vsvb | N-H stretching and Al-N vibrations |
| 1630 | sb | NH deformation (asym.) |
| ~1480 | mwb | NH deformation (sym.) |
| 1385 | m | NH rocking (asym.) |
| 1200 | msh | NH wagging? |
| 1075? | vwsh? | - |
| 1050-650 | meb | Al-N stretching? |

s = strong m = medium w = weak v = very b = broad sh = shoulder

e = extremely asym = asymmetric sym = symmetric

FIGURE 9

Infrared Spectrum of $(AlN_4H_5)_X$ (Potassium Bromide Pellet Technique)



[AlN$_4$H$_5$]x
TRANSMITTANCE (% TRANSMISSION)
FREQUENCY CM⁻¹
THE PERKIN-ELMER CORP. NORWALK, CONN.
2.5
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
4000
3500
3000
2500
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
650
100
90
80
70
60
50
40
30
20
10
0

The reaction of aluminum iodide with hydrazine. To a suspension of aluminum iodide (21 mmoles) in anhydrous diethyl ether (250 ml.), anhydrous hydrazine (220 mmoles) was added dropwise in an atmosphere of dry nitrogen. A white precipitate formed immediately, which, after decantation of the ether, was dried in vacuo at room temperature. This material was extracted with hydrazine in the "dry box" as previously described, and the residue, after being dried in vacuo at room temperature, was thought to be the substance $AlN_4H_5$ (Found: I, nil; Al, 31.4%. Required for $AlN_4H_5$: Al, 30.7%) by analogy with the aluminum chloride and aluminum bromide reactions.

This material was partially hydrolyzed by water, dissolved in aqueous acids, and did not melt at 300°. The infrared spectrum was the same as that in Figure 9, which is summarized in Table XX.

# DISCUSSION

## The Interaction of Boron Trifluoride and Hydrazine

The vigorous exothermic reaction in vacuo between boron trifluoride and hydrazine illustrated the strong tendency of $BF_3$ to accept an electron pair. The formation of the coordinate bond between boron trifluoride and one nitrogen atom in hydrazine evidently caused a drastic reduction in the reactivity of the lone electron pair on the other nitrogen atom, since the initial product, $BF_3 \cdot N_2H_4$, absorbed additional boron trifluoride very slowly. The substances $(BF_3)_{1.09}N_2H_4$ and $(BF_3)_{1.16}N_2H_4$ were formed after two and three hours, respectively. The decreased reactivity of the second lone electron pair in hydrazine seems to be a general rule. It is exemplified by the attraction of protons by hydrazine in aqueous solutions in that the first and second ionization constants at 25° are $8.5 \times 10^{-7}$ and $8.9 \times 10^{-16}$, respectively (54). Diacid salts of hydrazine do not exist in solution, such solutions being equivalent (54) to one containing free acid and monoacid salt in equimolar quantities:

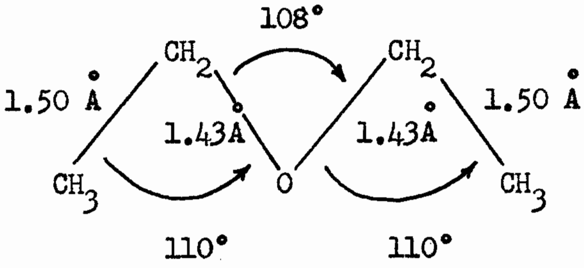
$$H_2O + N_2H_4 \cdot 2\,HX \longrightarrow N_2H_5^+ + 2\,X^- + H(H_2O)^+$$

Further, diacid salts on heating usually yield the monoacid salts as intermediate decomposition products (54). However, the ability of hydrazine to serve as an electron pair donor with two acceptor molecules in the solid state is well recognized in compounds such as $2HCl \cdot N_2H_4$ (54) and $2BH_3 \cdot N_2H_4$ (14).

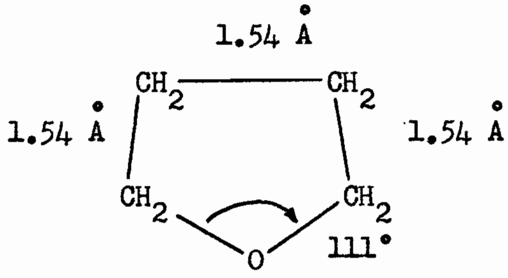
The proper experimental conditions for the preparation of 2-boron trifluoride-hydrazine, $2BF_3 \cdot N_2H_4$, were difficult to find. The reaction between $BF_3$ and $N_2H_4$ above room temperature (140°, 200°, and 300°) resulted in compounds of intermediate stoichiometry, $(BF_3)_x \ N_2H_4$ $(1 < x < 2)$. The method was limited by the decomposition of hydrazine which is appreciable above 250° (82,83,84), and its principal disadvantage appeared to be the low efficiency of mixing of the two components, resulting in the embedding of uncoordinated $NH_2$ units in the solid mass. By way of comparison, the formation of $2BF_3 \cdot P_2H_4$ (94) at -118°, at which temperature both boron trifluoride and diphosphine are liquids, was complete in less than one hour.

Seemingly anomalous results were obtained by the reaction of $BF_3$ with $N_2H_4$ in diethyl ether and in tetrahydrofuran as solvents. In several experiments using diethyl ether, products ranging in composition from $(BF_3)_{1.40}N_2H_4$ to $(BF_3)_{1.88}N_2H_4$ were obtained, but the ratio of $BF_3:N_2H_4$ was never 2. However, the reaction in tetrahydrofuran as solvent yielded 2-boron trifluoride-hydrazine, $2BF_3 \cdot N_2H_4$, without difficulty.

On the basis of <u>inductive</u> effects, diethyl ether should be about as good an electron pair donor as tetrahydrofuran, but the structures of these two ethers are such that <u>steric</u> effects play an important role in the coordination compounds of $(C_2H_5)_2O$. Diagrammatically, the two ethers are represented by the following (95,96,97,98):



diethyl ether



tetrahydrofuran*

*Puckered ring with conformation like cyclopentane.

It is immediately obvious that the alkyl groups in the β position are held back in tetrahydrofuran. Pressure measurements have shown (99) that at 99°, the extents of dissociation of the complexes $BF_3 \cdot (C_2H_5)_2O$ and $BF_3 \cdot (CH_2)_4O$ are 92.6% and 58.3%, respectively.

Since $BF_3$ is more firmly bound to tetrahydrofuran than to diethyl ether, the expectation is that addition reactions between $BF_3$ and donor molecules should proceed more readily in diethyl ether as a solvent. Precisely the opposite result was observed in the present work. Similarly (10), using $(C_2H_5)_2O$ as a solvent, boron trifluoride reacted with ethylenediamine to give initially a compound of approximately 1:1 composition which reacted very slowly with additional $BF_3$ to yield products of indefinite stoichiometry. However, with tetrahydrofuran as a solvent, excellent yields of 2-boron trifluoride-ethylenediamine were obtained.

The reduction of steric effects in the boron trifluoride-tetrahydrofuran complex, which renders this compound more stable than its diethyl ether analogue, also permits freer access of the attacking donor molecule to the boron-oxygen bond. The latter effect appears to promote increased reactivity in tetrahydrofuran. An important contributing factor in the present work was the insolubility of the reaction product in diethyl ether as compared with its complete solubility in tetrahydrofuran.

The phase diagram (Figure 2) of the system boron trifluoride-hydrazine provided convincing evidence of the existence of the two compounds $BF_3 \cdot N_2H_4$ and $2BF_3 \cdot N_2H_4$. The positions of maxima in solid-liquid equilibrium diagrams (69) are always located at the compositions of solid compounds, whether they be congruently or incongruently melting. In the $BF_3$-$N_2H_4$ diagram, one maximum was observed at 50 mole % boron trifluoride, corresponding to $BF_3 \cdot N_2H_4$, and since the curve must eventually fall to -127° at the extreme right hand side of the diagram (m.p. of pure $BF_3$ (1)), the presence of a second maximum between 50 and 100 mole % $BF_3$ was inferred. This was assumed to be at 66 2/3 mole % $BF_3$, corresponding to $2BF_3 \cdot N_2H_4$.

## Physical Properties of boron trifluoride - hydrazine compounds

Structural considerations. The lone electron pairs on the nitrogen atoms of hydrazine are located in tetrahedral $sp^3$ orbitals (11) and are therefore already in the configuration they exhibit in coordinate linkages. On the other hand, the boron trifluoride molecule has a planar structure (39) and its bonding electrons are distributed in planar $sp^2$ orbitals which are considerably strengthened by $\pi$ bonding between boron and fluorine (36). Two factors are likely to be of importance in the reorganization of the $BF_3$ molecule to the configuration necessary for coordinate bond formation. These are (a) the breaking of the $\pi$ bonds and (b) the reorganization of the BF bonds from $sp^2$ to $sp^3$ hybridization (36).

According to Pauling (100), the relative strengths of $sp^2$ and $sp^3$ bonds (involving the same atoms) are 1.99 and 2.00, i.e., almost the same. Consequently, it may be expected that the BF bond energy in boron trifluoride will differ from that in a coordination compound such as $BF_3 \cdot N_2H_4$ by an amount equal to the $\pi$ bond energy. This conclusion is justified by recent theoretical calculations (36) which indicate that the $\pi$ bond energy in $BF_3$ is 47.8 kcal./mole, and that the total reorganization energy to the configuration for coordinate bond formation is 48.3 kcal./mole. The mean energy difference in each BF bond will be $\sim$16 kcal./mole, and since the BF bond dissociation energy in $BF_3$ is 154.8 kcal./mole (28), it should be approximately 138 kcal./mole in $BF_3 \cdot N_2H_4$. It is interesting that the BF bond is not greatly weakened by the formation of a coordinate BN bond.

These considerations are of course based on the assumption that $BF_3$ and $N_2H_4$ are linked by pure $sp^3$ orbitals which necessitates a tetrahedral configuration about the BN bond. This information is not available for $BF_3 \cdot N_2H_4$, but extensive structure determinations have been made for analogous compounds. Some of these investigations are summarized in Table XXI, and the data clearly indicate a tetrahedral configuration for the boron atom. It seems reasonable to assume that this is also the case for boron trifluoride-hydrazine.

## TABLE XXI

Representative Structural Data for $BF_3$ Coordination Compounds

| **Compound:** | $BF_3 \cdot NH_3$ | $BF_3 \cdot CH_3NH_2$ | $BF_3 \cdot (CH_3)_3N$ |
|---|---|---|---|
| **Reference:** | 19,20 | 101,20 | 102,20 |
| B-N | 1.60 Å | 1.57 | 1.59 |
| B-F | 1.38 | 1.38 | 1.39 |
| ∠FBF | 111° | 110.5° | 107° |
| ∠FBN | 107° | 108.5° | 112° |

Melting Points. The melting points of both $BF_3 \cdot N_2H_4$ (87°) and $2BF_3 \cdot N_2H_4$ (260°) were above room temperature, a property common to almost all boron trifluoride complexes with nitrogen donors (2). The volatilities of the two compounds were low, suggesting considerable dipole-dipole interaction.

X-ray pattern. The x-ray diffraction data for $BF_3 \cdot N_2H_4$ (Table VIII) indicated a crystallographic cell of triclinic symmetry. From the comparative x-ray data listed in Table XXII, it may be concluded that (a) molecular asymmetry is generally accompanied by crystallographic asymmetry, and (b) the unit cell of $BF_3 \cdot N_2H_4$ is comparable in size to those of the other compounds tabulated.

Infrared spectra. The symbolism used for the infrared vibrations is the following: $\nu$ = valence stretching, $\delta$ = deformation, r = rocking, w = wagging, as = asymmetric, s = symmetric. Characteristic vibrational frequencies of certain previously studied boron and nitrogen compounds are compiled

TABLE XXII

X-ray Diffraction Data for $BF_3$ Addition Compounds

| Compound | Crystallographic Cell Dimensions | | | | | Reference |
|---|---|---|---|---|---|---|
| | a | b | c | Interaxial angles | Crystal Symmetry | |
| | (Angstrom units) | | | | | |
| $N_2H_4$ | 3.56 | 5.78 | 4.53 | $\beta$ = 109.5° | monoclinic | 103 |
| $BF_3 \cdot N_2H_4$ | 6.93 | 5.50 | 6.78 | $\alpha$ = 111.5°<br>$\beta$ = 64.0°<br>$\gamma$ = 88.3° | triclinic | - |
| $BF_3 \cdot NH_3$ | 8.22 | 8.11 | 9.31 | all 90° | orthorhombic | 19,20 |
| $BF_3 \cdot CH_3NH_2$ | 5.06 | 7.28 | 5.81 | $\beta$ = 101.5° | monoclinic | 101,20 |
| $BF_3 \cdot (CH_3)_2NH$ | 7.50 | 6.06 | 12.25 | $\beta$ = 102° | monoclinic | 2 |
| $BF_3 \cdot (CH_3)_3N$ | 9.34 | - | 6.10 | - | hexagonal | 102,20 |

in Appendix I.

In the spectra of $BF_3 \cdot N_2H_4$ and $2BF_3 \cdot N_2H_4$ (Tables VI and VII), the bands in the region 3400-3240 cm$^{-1}$ have been assigned to $\nu(NH_2)$ modes and those between 1620 cm$^{-1}$ and 1440 cm$^{-1}$ to $\delta(NH_2)$ modes, by analogy with the infrared spectrum of hydrazine (12). When boron trifluoride is coordinated with electron donors such as oxygen and nitrogen, the $\nu_{as}$(B-F) vibration is shifted to lower frequencies, as indicated in the accompanying table.

$B^{11}$-F asymmetric stretching vibration

| Compound | Frequency, $cm^{-1}$ | Intensity | Reference |
|---|---|---|---|
| $BF_3$ | 1446 | vs | 68 |
| $BF_3 \cdot NH_3$ | 1144 | s | 104 |
| $BF_3 \cdot (CH_3)_2CO$ | 1175 | vs | 105 |
| $BF_3 \cdot (C_3H_7)_2CO$ | 1165 | vs | 105 |

Accordingly this frequency was expected in the range 1100-1175 $cm^{-1}$ for the compounds $BF_3 \cdot N_2H_4$ and $2BF_3 \cdot N_2H_4$. Unfortunately, this region (Figure 3) contained strong unresolved peaks which were thought to be due both to $\nu_{as}$(B-F) and $\nu$(B-N) absorptions, as the latter are also known to occur in this range. In the case of $BF_3 \cdot NH_3$ (104), for example, the latter vibration is found at 985-1030 $cm^{-1}$, while in many other boron-nitrogen coordination compounds, the $\nu$(B-N) vibration is in the range 1000-1140 $cm^{-1}$ (see Appendix I). The region 1020-1120 $cm^{-1}$ was therefore assigned to overlapping $\nu_{as}$(B-F) and $\nu$(B-N) vibrations.

In hydrazine itself, the $\nu$(N-N) absorption is rather weak as it involves an essentially nonpolar bond (12). However, in $BF_3 \cdot N_2H_4$ and to a lesser extent in $2BF_3 \cdot N_2H_4$, this bond is no longer nonpolar and the absorption should be considerable for these compounds. In $N_2H_4 \cdot HCl$ and $N_2H_4 \cdot HBr$, this vibration appears strongly at 973 $cm^{-1}$ and 965 $cm^{-1}$, respectively (91). Similarly, a strong band at 958 $cm^{-1}$ appears in the infrared spectrum of $N_2H_4 \cdot HI$ (106). The strong band at 965 $cm^{-1}$ for $BF_3 \cdot N_2H_4$

and the band of medium intensity at 970 cm$^{-1}$ for $2BF_3{\cdot}N_2H_4$ were assigned to this mode. The remaining absorption peaks below 1650 cm$^{-1}$ were assigned rather arbitrarily to different NH modes (rocking, wagging) by comparison with the spectrum of $N_2H_4$ (12).

The infrared spectra of $BF_3{\cdot}(CH_3)_3N$ and $BCl_3{\cdot}(CH_3)_3N$ were measured to provide additional comparative data (Tables X and XI). The bands in the vicinity of 1100 cm$^{-1}$ were assigned to the $\nu$(B-N) vibration, and those at 1177 and 1135 cm$^{-1}$ (for $BF_3{\cdot}(CH_3)_3N$) to the $\nu_{as}(B^{10}\text{-}F)$ and $\nu_{as}(B^{11}\text{-}F)$ vibrations. The $\nu_{as}$(C-N) frequency in trimethylamine (107), centred at 1042 cm$^{-1}$, is shifted to 980 cm$^{-1}$ in the addition compound $(CH_3)_3N{\cdot}HI$ (108). The bands at 990 cm$^{-1}$ ($BF_3{\cdot}CH_3)_3N$ ) and 1011 cm$^{-1}$ ($BCl_3{\cdot}(CH_3)_3N$) were allocated to this mode. The peaks near 835 cm$^{-1}$ were assigned to r($CH_3$) (109). The remaining absorption bands were considered to be due to $CH_3$ vibrations, with the possible exception of the strong bands at 745-780 cm$^{-1}$ in the spectrum of $BCl_3{\cdot}(CH_3)_3N$; these may be due to the $\nu_{as}$(B-Cl) mode, which occurs at 956-995 cm$^{-1}$ in pure $BCl_3$ (110). The shift of this absorption ($\sim$200 cm$^{-1}$) apparently is not as large as that of $\nu_{as}$(B-F) ($\sim$300 cm$^{-1}$) from its position for $BF_3$.

Thermochemical studies (111) indicate that the coordinate bond in molecular addition compounds is weaker than the analogous covalent bond. This deduction is illustrated by the $\nu$ (B-N) frequency, which is found at 985-1120 cm$^{-1}$ in addition compounds (see Appendix), but which occurs at higher frequencies (1330-1380 cm$^{-1}$) in compounds such as $\left[(C_2H_5)_2N\right]_3B$ (112) and $(CH_3)_2BNHC_6H_5$ (113) which contain covalent BN bonds.

## Characterization of Boron Trifluoride-Hydrazine

Pyrolysis of boron trifluoride-hydrazine. Boron trifluoride-hydrazine was stable indefinitely in vacuo at room temperature. Decomposition occurred slowly at 190° but at 300°, it was more than 90% complete after five hours, yielding nitrogen, ammonia, ammonium fluoborate, and boron nitride. From the data in Table XXIII, it was evident that the BN bond was the weakest one in $BF_3 \cdot N_2H_4$, and therefore the most likely to be broken first in the pyrolysis. The first step in the decomposition was therefore assumed to be the dissociation reaction

$$BF_3 \cdot N_2H_4 \longrightarrow BF_3 + N_2H_4$$

TABLE XXIII

Bond Dissociation Energies

| Bond | Bond Dissociation Energy, kcal./mole | Compound | Reference |
|---|---|---|---|
| NN | 60 | $N_2H_4$ | 114 |
| NN | 60 ± 4 | $N_2H_4$ | 115 |
| NH | 104 ± 2 | $NH_3$ | 116 |
| NH | 76 | $N_2H_4$ | 114 |
| BF | 154.8 | $BF_3$ | 28 |
| BN | 41.3 | $BF_3 \cdot NH_3$ | 22 |
| BN | 27.5 | $BF_3 \cdot NH_3$ | 117 |

Boron trifluoride is thermally stable (1) while hydrazine decomposes into ammonia and nitrogen (82,83,84) at 300° according to equation (2)

$$3\ N_2H_4 \longrightarrow 4\ NH_3 + N_2 \qquad (2)$$

Subsequent interaction of ammonia with boron trifluoride to form a loose complex

$$BF_3 + NH_3 \longrightarrow [BF_3NH_3] \text{ (unstable at 300°)}$$

could be followed by thermal decomposition into ammonium fluoborate and boron nitride (22):

$$4\ BF_3{\cdot}NH_3 \longrightarrow 3\ NH_4BF_4 + BN$$

The overall reaction, taken as the sum of the above reactions,

$$12\ BF_3{\cdot}N_2H_4 \longrightarrow 4\ N_2 + 4\ NH_3 + 9\ NH_4BF_4 + 3\ BN$$

accounted quantitatively for the nitrogen production (5.13 mmoles $BF_3{\cdot}N_2H_4$ yielded 1.72 mmoles $N_2$) but only qualitatively for the other observed products.

Hydrolysis of boron trifluoride-hydrazine. The apparent molecular weight (49.5, 54.5) of $BF_3{\cdot}N_2H_4$ in aqueous solution was approximately one-half the formula weight (99.9), suggesting that the initial action of water gave two ions, probably by the following reaction:

$$BF_3{\cdot}N_2H_4 + HOH \longrightarrow N_2H_5^+ + BF_3OH^-$$

Since positive tests for fluoborate ion, $BF_4^-$, were obtained, it appeared that the hydroxylfluoborate ion might have been involved in a disproportionation reaction:

$$2\ BF_3OH^- \rightleftharpoons BF_4^- + BF_2(OH)_2^-$$

Further disproportionation of $BF_2(OH)_2^-$ (118) was presumed to occur in view of the fact that the basicity of the aqueous solution increased slightly on standing:

$$\begin{array}{lll} 2\ BF_2(OH)_2^- \rightleftharpoons BF_4^- + & \left[B(OH)_4^-\right] & \text{(unstable)} \\ & \downarrow & \\ & B(OH)_3 + OH^- & \end{array}$$

Although the various ionic species were not identified (except $BF_4^-$), the results were consistent with the observation that the hydrolysis of boron trifluoride itself (1) yields a mixture of hydroxyfluoboric acids.

<u>The reaction of boron trifluoride-hydrazine with hydrogen chloride</u>. No significant reaction occurred between anhydrous hydrogen chloride and boron trifluoride-hydrazine either at -96° or at room temperature, but at 110°, the following results were obtained:

| Experiment number | 1 | 2 |
|---|---|---|
| Initial HCl, mmoles | 8.05 | 2.73 |
| Initial $BF_3 \cdot N_2H_4$, mmoles | 3.73 | 2.71 |
| Reaction time | overnight | |
| Recovered HCl, mmoles | 4.36 | 0.604 |
| Consumed HCl, mmoles | 3.69 | 2.13 |
| Liberated $BF_3$, mmoles | 0.61 | 0.232 |
| % displacement of $BF_3$ | 16.4 | 8.56 |

Three points seem noteworthy: (a) evidently HCl is a stronger Lewis acid than $BF_3$ since the latter was displaced from the addition compound $BF_3 \cdot N_2H_4$, (b) the amount of hydrogen chloride absorbed by the complex was much greater than the amount of boron trifluoride liberated, and (c) the extent of displacement of $BF_3$ decreased when the initial concentration of HCl was lower.

The thermochemical data in the table below indicate that, with ammonia as reference base, the relative order of electron acceptor power is HCl $\geqslant BF_3$. The limited extent of the displacement reaction between HCl and $BF_3 \cdot N_2H_4$ may be ascribed to the small difference between the acceptor powers of $BF_3$ and HCl. That some sort of equilibrium was established is substantiated by the observation that the extent of displacement decreased with a lower initial concentration of HCl. Finally, since the amount of HCl absorbed by the complex far exceeded that of the liberated $BF_3$, it seems reasonable to assume that the 1:1:1 addition compound $BF_3 \cdot N_2H_4 \cdot HCl$

Thermochemical Data

| Reaction | $-\Delta H$ kcal./mole | Reference |
|---|---|---|
| $BF_3 + NH_3 \longrightarrow BF_3 \cdot NH_3$ | 41.3 | 22 |
| $BF_3 + NH_3 \longrightarrow BF_3 \cdot NH_3$ | 27.5 | 117 |
| $HCl + NH_3 \longrightarrow HCl \cdot NH_3$ | 42.3 | 119 |
| $HCl \cdot NH_3 \longrightarrow HCl + NH_3$ (sublimation) | -39.6 | 120 |
| $HCl + N_2H_4 \longrightarrow HCl \cdot N_2H_4$ | 36.9 | 119 |

was formed in substantial quantities during the reaction, but this addition product could not be isolated.

<u>The reaction of boron trifluoride-hydrazine with ammonia</u>. At -80°, boron trifluoride-hydrazine readily absorbed ammonia to form the new compound boron trifluoride-hydrazine-2-ammonia, $BF_3{\cdot}N_2H_4{\cdot}2NH_3$. On warming to room temperature, ammonia appeared to be evolved in two distinct stages, but since no stoichiometric amount could be recovered, it was not possible to isolate the monoammonia compound, $BF_3{\cdot}N_2H_4{\cdot}NH_3$. The ammonia molecules were presumed to be bound to the complex by dipole-dipole forces.

The ability of certain compounds to add on ammonia is especially characteristic of elements with small atomic volumes (121) such as boron, aluminum, nickel, silver, etc. (122). Thus the compounds $AlCl_3{\cdot}6NH_3$ (46, 47), $NiCl_2{\cdot}6NH_3$ (121), and $AgCl{\cdot}3NH_3$ (69) are well known.

Similarly, $BF_3{\cdot}N_2H_4$ absorbed indefinite amounts of $CH_3NH_2$ and $(CH_3)_3N$ at low temperatures which were released very slowly on warming to room temperature. There was some indication that trimethylamine, a stronger base than hydrazine (122,92), displaced $N_2H_4$ from $BF_3{\cdot}N_2H_4$ at room temperature to a very limited extent (~3%).

## The Relative Electron Acceptor Properties of Boron Trifluoride and Boron Trichloride

Until recently (6,26,36,123), it was thought, on the basis of electronegativity values, that the relative electron acceptor powers of the boron halides were in the order $BF_3 > BCl_3 > BBr_3$ (9). By comparing the heats of reaction of these halides with pyridine and with nitrobenzene, it was shown in a series of calorimetric experiments (26) that the order should be $BF_3 < BCl_3 < BBr_3$. The variation of dipole moment (123) due to complex formation of $BX_3$ (X = F, Cl, Br) with $(CH_3)_3N$ and with $C_5H_5N$ also suggested that the order of acceptor power was actually $BF_3 < BCl_3 < BBr_3$.

This apparently anomalous result was ascribed to $\pi$ bonding between B and X in the $BX_3$ molecules, which increases along the series $BBr_3$, $BCl_3$, $BF_3$, thereby reducing the acceptor power of boron by successive but not necessarily equal amounts. The experimental observations were supported by recent theoretical calculations (36).

Since no <u>direct</u> chemical evidence appeared to be available to substantiate these findings, it was proposed by the author that a set of experiments be undertaken to attempt the displacement of $BF_3$ from one of its addition compounds by $BCl_3$. The reference base chosen was trimethylamine; its addition compounds with boron trifluoride (23,24,77) and boron trichloride (25) have been well characterized.

A preliminary investigation (124) has shown that at 205°, the displacement reaction (all reactants in the vapour phase)

$$BCl_3 + BF_3\cdot(CH_3)_3N \longrightarrow BCl_3\cdot(CH_3)_3N + BF_3$$

occurs quantitatively, and that the reverse reaction does not occur to a detectable extent.

The results indicated that, with trimethylamine as reference base, boron trichloride is a stronger electron acceptor than boron trifluoride, in agreement with previous investigators (26,36,123). The fact that $BF_3 \cdot (CH_3)_3N$ is known to be undissociated in the vapour phase at 205° (24) suggested that a true displacement reaction had occurred.

It is interesting that the heat of the reaction

$$BF_3\ (g) + (CH_3)_3N\ (g) \xrightarrow{300^\circ K} BF_3 \cdot (CH_3)_3N\ (s)$$

has been measured as 26.6 kcal./mole (125), and calculated as 28 kcal./mole (111), while that of the reaction

$$BCl_3\ (g) + (CH_3)_3N\ (g) \xrightarrow{300^\circ K} BCl_3 \cdot (CH_3)_3N\ (s)$$

has been estimated as 30.5 kcal./mole (125).

## The Interaction of Trimethylborane and Hydrazine

Due to the electron releasing tendency of methyl groups (126), the ability of trimethylborane to accept an electron pair is considerably less than that of the boron halides. This was evident in the reaction between trimethylborane and hydrazine, which was initially very rapid, but which required a long time for completion. The new compound 2-trimethylborane-hydrazine, $2B(CH_3)_3 \cdot N_2H_4$, was the ultimate product, but it was stable only in an atmosphere of trimethylborane or at low temperatures (-80°); otherwise trimethylborane was evolved irreversibly, and at 0° it was removed rapidly, leaving the new compound trimethylborane-hydrazine, $B(CH_3)_3 \cdot N_2H_4$.

The latter material could be converted to $2B(CH_3)_3 \cdot N_2H_4$ by allowing it to react at room temperature with an excess of $B(CH_3)_3$. These results are interpreted on the basis that the attraction exerted by $B(CH_3)_3$ on the lone electron pair of one nitrogen atom in hydrazine induced a significant reduction in the coordinating ability of the lone electron pair on the other nitrogen atom. Since $B(CH_3)_3$ is a relatively weak electron acceptor compared with $BF_3$, $BCl_3$, HCl, etc., the bonding of the second molecule of $B(CH_3)_3$ to $N_2H_4$ should be weak.

Trimethylborane-hydrazine consisted of white hygroscopic crystals which were readily soluble in water or alkaline solution. However, strong acidification of the aqueous solution resulted in the displacement of $B(CH_3)_3$, and, owing to its sensitivity to oxygen (127), it ignited spontaneously and violently.

## Characterization of Trimethylborane-hydrazine

Physical properties of $B(CH_3)_3 \cdot N_2H_4$. The melting point of the new compound can be compared with those of analogous compounds:

Melting points of $B(CH_3)_3$ addition compounds

| Compound | m.p. | Reference |
|---|---|---|
| $B(CH_3)_3 \cdot N_2H_4$ | 42-43° | this work |
| $B(CH_3)_3 \cdot (CH_3)_3N$ | 120° | 128 |
| $2\,B(CH_3)_3 \cdot (CH_2NH_2)_2$ | 139° | 5 |
| $B(CH_3)_3 \cdot (CH_2)_2NH$ * | 10-12° | 129 |
| $B(CH_3)_3 \cdot (CH_2)_4NH$ ** | 43-44° | 129 |

*ethyleneimine

**pyrrolidine

The infrared spectrum of $B(CH_3)_3 \cdot N_2H_4$ is compared with that of trimethylborane-ammonia, $B(CH_3)_3 \cdot NH_3$, in Figure 5. The assignment of absorption peaks for $B(CH_3)_3 \cdot NH_3$ was the following (the regions 3100-2800 $cm^{-1}$ and 1500-1325 $cm^{-1}$ were omitted due to interference from the Nujol peaks.). The $\nu_{as}$(B-C) vibration occurs at 1150 $cm^{-1}$ for trimethylborane (130,139), while the $\nu$(B-N) frequency is at 1105 $cm^{-1}$ in the Raman spectrum (79) of $B(CH_3)_3 \cdot NH_3$. The infrared peaks of $B(CH_3)_3 \cdot NH_3$ at 1135 $cm^{-1}$ and 1103 $cm^{-1}$ were assigned to these modes. Since $r(CH_3)$ vibrations occur in the regions 985-970 $cm^{-1}$ and 860 $cm^{-1}$ for $B(CH_3)_3$ (130,139), the peaks at 985 $cm^{-1}$ and 882 $cm^{-1}$ were assigned to these vibrations. The peaks in the range 730-716 $cm^{-1}$ were allocated to NH modes (79), while the one at 682 $cm^{-1}$ was designated as $\nu_s$(B-C) by analogy (79) with the corresponding vibration in the Raman spectrum (675 $cm^{-1}$).

Most of the infrared absorptions of $B(CH_3)_3 \cdot NH_3$ also appeared in the spectrum of $B(CH_3)_3 \cdot N_2H_4$. The strong band at 1075 $cm^{-1}$ was chosen as $\nu$(B-N), and those at 1135 $cm^{-1}$ and 679 $cm^{-1}$ as $\nu_{as}$(B-C) and $\nu_s$(B-C), respectively. By analogy with the spectrum of $B(CH_3)_3$ (130,139), the absorptions at 997 $cm^{-1}$ and 851 $cm^{-1}$ were selected as $r(CH_3)$ modes. The strong absorption at 956 $cm^{-1}$ was assigned to the $\nu$(N-N) vibration since this band appears in the infrared spectra of $HCl \cdot N_2H_4$ (91), $HBr \cdot N_2H_4$ (91), $HI \cdot N_2H_4$ (106), $BF_3 \cdot N_2H_4$, and $2BF_3 \cdot N_2H_4$. The peaks at 1343 $cm^{-1}$, 1192 $cm^{-1}$, and 1103 $cm^{-1}$ were allocated to the $r_{as}(NH_2)$, $r_s(NH_2)$, and $w_{as}(NH_2)$ vibrations, respectively, by analogy with the corresponding absorptions for $N_2H_4$ (12): 1320 $cm^{-1}$, 1124 $cm^{-1}$, and 1075 $cm^{-1}$.

It was noted that the shift in the $\nu_{as}$(B-C) vibration from $B(CH_3)_3$

to either $B(CH_3)_3 \cdot NH_3$ or $B(CH_3)_3 \cdot N_2H_4$ was small ($\sim 20$ cm$^{-1}$), whereas the analogous shift for $\nu_{as}$(B-F) was large ($\sim 300$ cm$^{-1}$). This might be due to the large polarity of the B-F bond in $BF_3$, for the shift in vibration of less polar bonds appears to be small: for example, the shift for $\nu_{as}$(C-N) from $(CH_3)_3N$ (1042 cm$^{-1}$) (107) to $BH_3 \cdot (CH_3)_3N$ (1005 cm$^{-1}$) (109) is not large.

The reaction of $B(CH_3)_3 \cdot N_2H_4$ with diborane. There was no reaction between 2-trimethylborane-hydrazine and diborane at -80°. However, at room temperature, diborane reacted with trimethylborane-hydrazine to produce trimethylborane, unsym-dimethyldiborane, hydrogen, and a solid residue which evolved both methane and hydrogen on heating. Since free $B(CH_3)_3$ was obtained, it was assumed that a displacement of $B(CH_3)_3$ from the addition complex by $BH_3$ had occurred. The reaction between gaseous $B(CH_3)_3$ and excess $B_2H_6$ can result in two products (131):

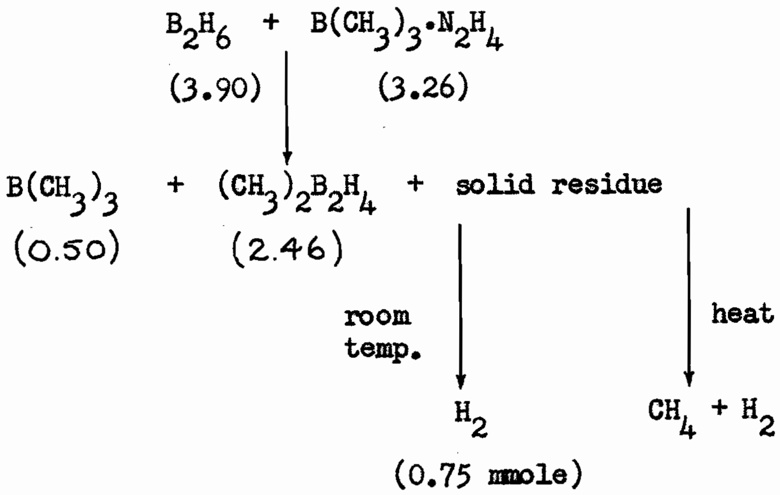
$$5\ B_2H_6 + 2\ B(CH_3)_3 \longrightarrow 6\ B_2H_5CH_3$$

$$2\ B_2H_6 + 2\ B(CH_3)_3 \longrightarrow 3\ B_2H_4(CH_3)_2 \qquad (3)$$

Monomethyldiborane is unstable and reverts either to diborane and trimethylborane, or to diborane and unsym-dimethyldiborane (131):

$$2\ B_2H_5CH_3 \longrightarrow B_2H_6 + B_2H_4(CH_3)_2$$

The evolution of methane and of hydrogen by the solid residue is characteristic of $B(CH_3)_3 \cdot N_2H_4$ (See "Pyrolysis") and $2BH_3 \cdot N_2H_4$ (13,14), respectively. The experimental data are summarized in the following scheme (numbers in brackets represent millimoles):



Since methane was evolved from the solid residue on heating, it was considered that the displacement of $B(CH_3)_3$ from the addition complex was incomplete. The production of unsym-dimethyldiborane was presumed to have occurred by reaction (3), which is rewritten as equation (4) with the experimental quantities included:

$$\underset{(1.64)}{2\ B_2H_6} + \underset{(1.64)}{2\ B(CH_3)_3} \longrightarrow \underset{(2.46)}{(CH_3)_2B_2H_4} \qquad (4)$$

The amount (0.50 mmole) of free $B(CH_3)_3$ recovered, together with that consumed (1.64 mmoles) in reaction (4) suggested that 2.14 mmoles $B(CH_3)_3$ had been displaced from the addition complex. The amount of diborane consumed in the overall reaction (3.90 mmoles), less that required (1.64 mmoles) for equation (4), indicated that a similar amount (2.26 mmoles) of diborane was used in the displacement of $B(CH_3)_3$. The extent of displacement of $B(CH_3)_3$ from the addition complex amounted to 65.6%.

Only a portion (1500-2850 $cm^{-1}$) of the infrared spectrum of unsym-dimethyldiborane has been published in the chemical literature (80). A more complete spectrum (650-4000 cm$^{-1}$) is given in Figure 6 and summarized in Table XIV. The characteristic $\nu$(B-H) vibrations appeared at 2570 cm$^{-1}$, 2495 cm$^{-1}$, and 1545 cm$^{-1}$ (80,112,132). The overlapping bands in the range 1115-1170 cm$^{-1}$ were presumed to include the $\nu_{as}$(B-C) absorption (130,139) and the characteristic $BH_2$ "scissors" mode, which normally occurs in the region 1140-1205 cm$^{-1}$ (112). The bands at 1055 cm$^{-1}$ and 920 cm$^{-1}$ were assigned to r($BH_2$) (133) and w($BH_2$) (112) vibrations, respectively.

The pyrolysis of $B(CH_3)_3 \cdot N_2H_4$. The thermal decomposition of trimethylborane-hydrazine at 150-160° was complex, yielding methane, nitrogen, ammonia, butane, butenes, and a heterogeneous residue. The presence of $C_4$ hydrocarbons among the products was remarkable, and it is difficult to account for their origin. The thermal decomposition of tri-n-butylborane (134) results in the elimination of 1-butene and 2-butene. Ethylene might be eliminated by trimethylborane-hydrazine and then catalytically dimerized to butene, an effect known to occur (135).

When trimethylborane and hydrazine were individually subjected to identical heating conditions, there was no change in the former compound while the latter was decomposed to the extent of only 5% according to

$$3\ N_2H_4 \longrightarrow 4\ NH_3 + N_2$$

## The Reaction of Trimethylaluminum with Hydrazine

Hydrazine and trimethylaluminum reacted in vacuo to yield methane, hydrogen, and a nonstoichiometric residue. In diethyl ether as a solvent, only methane was evolved by the reactants, and a substance which appeared to be sym-bisdimethylaluminohydrazine, $(CH_3)_2AlNHNHAl(CH_3)_2$, was recovered on evaporation in vacuo of the solvent and the unreacted trimethylaluminum. The most probable reaction sequence was thought to be the following:

$$\begin{tikzcd}
N_2H_4 + \left[Al(CH_3)_3\right]_2 \arrow[r] & \left[(CH_3)_3Al\cdot NH_2NH_2\cdot Al(CH_3)_3\right] \text{(unstable)} \arrow[d] \\
 & (CH_3)_2AlNHNHAl(CH_3)_2 + 2\ CH_4
\end{tikzcd}$$

The evolution of exactly two moles of methane per mole of hydrazine consumed was supporting evidence. The aluminum-containing material was very shock-sensitive and thus too unstable to be purified and characterized.

The analogous material $(CH_3)_2AlNH_2$ was stated (6,127) to have been prepared from the addition compound $Al(CH_3)_3\cdot NH_3$, but detailed characterizations have not been reported.

The Al-C bond energy in $Al(CH_3)_3$ is 13 kcal./mole less than that of the B-C bond in $B(CH_3)_3$ (116), which might account for the elimination of methane by hydrazine and trimethylaluminum whereas no methane was evolved from trimethylborane-hydrazine compounds. A second contributing factor would probably be the greater polarity of the Al-C bond as compared with the B-C bond, which is evident from a consideration of the electronegativities of carbon, boron and aluminum (122).

## A Comparison of $2BF_3\cdot N_2H_4$, $2BH_3\cdot N_2H_4$, and $2B(CH_3)_3\cdot N_2H_4$

It is of interest to compare the properties of the 2:1 addition compounds formed between $BF_3$, $BH_3$, or $B(CH_3)_3$ and $N_2H_4$ with the relative electron acceptor powers of the three parent Lewis acids. Some of the properties of the three addition compounds are listed below:

| Compound | Melting Point | Thermal Characteristics |
|---|---|---|
| $2BF_3 \cdot N_2H_4$ | 260° | Footnote A |
| $2BH_3 \cdot N_2H_4$* | >130° | Hydrogen evolved rapidly at 130°. |
| $2B(CH_3)_3 \cdot N_2H_4$ | - | $B(CH_3)_3$ evolved above −70°. |

* Reference 14.

Note A. Thermal stability probably limited by decomposition of hydrazine.

These data suggest that $2B(CH_3)_3 \cdot N_2H_4$ is the least stable of the three compounds, but of the remaining two, no choice could be made in the absence of thermochemical or other data.

Using available information in the literature (19,20,39,102,103, 136,137,138) to make scale drawings of the probable structures of the three addition compounds, it was demonstrated that steric hindrance could not be an important factor in their relative stabilities. Thus the distances of closest approach of the H atoms on hydrazine to the F, H, and $CH_3$ groups on boron were found to be approximately 2.40, 2.25, and 1.75 Å, respectively. These distances should be sufficiently large to preclude steric interaction. By way of contrast, the distance of closest approach of H atoms of adjacent methyl groups in ethane is calculated as ~ 2.30 Å from available structural data (97).

Although considerations of electronegativity indicate that the order of electron acceptor power should be $B(CH_3)_3 < BH_3 < BF_3$, studies (123) of the dipole moments of appropriate coordination compounds has indicated that the acceptor power of $BH_3$ is perhaps greater than that of $BF_3$. A similar conclusion can be drawn from the following data (125):

$$1/2\ B_2H_6 + (CH_3)_3N \longrightarrow BH_3\cdot(CH_3)_3N \qquad (5)$$
$$\Delta H = -17.3 \text{ kcal./mole}$$

$$BH_3 + BH_3 \longrightarrow B_2H_6 \qquad (6)$$
$$\Delta H = -28.5 \text{ kcal./mole}$$

$$B(CH_3)_3 + (CH_3)_3N \longrightarrow B(CH_3)_3\cdot N(CH_3)_3 \qquad (7)$$
$$\Delta H = -17.6 \text{ kcal./mole}$$

$$^{*}\ BF_3 + (CH_3)_3N \longrightarrow BF_3\cdot N(CH_3)_3 \qquad (8)$$
$$\Delta H = -26.6 \text{ kcal./mole}$$

* The heat of this reaction was estimated as 28 (111) and 30.5 (6) kcal./mole.

Adding equations (5) and (6),

$$BH_3 + (CH_3)_3N \longrightarrow BH_3\cdot(CH_3)_3N \qquad (9)$$
$$\Delta H = -31.6 \text{ kcal./mole}$$

and comparing the values of $\Delta H$ for equations (7), (8), and (9), an order of electron acceptor power $B(CH_3)_3 < BF_3 \leqslant BH_3$ is indicated.

Similarly, the heat of the reaction

$$1/2\ B_2H_6\ (g) + C_5H_5N\ (\text{in } C_6H_5NO_2) \longrightarrow BH_3\cdot C_5H_5N\ (\text{in } C_6H_5NO_2)$$

has been measured calorimetrically as 17.9 kcal./mole (34). Using the value of equation (6) for the diborane-borane dissociation, the enthalpy change accompanying the reaction

$$BH_3\ (g)\ +\ C_5H_5N\ (\text{in } C_6H_5NO_2) \longrightarrow BH_3{\cdot}C_5H_5N\ (\text{in } C_6H_5NO_2)$$

is calculated as 32.2 kcal./mole. The heat of reaction of boron trifluoride gas with pyridine in nitrobenzene is 32.9 kcal./mole (35). Thus the heats of formation in nitrobenzene of the addition compounds $BH_3{\cdot}C_5H_5N$ and $BF_3{\cdot}C_5H_5N$ are very similar, indicating that $BH_3$ and $BF_3$ are of comparable strength as electron pair acceptors. This result (6) is an illustration of the danger of making stability predictions based entirely on steric and electronegativity concepts.

Two comments on the apparent similarity of $BH_3$ and $BF_3$ as electron acceptors seem appropriate. (a) It should be realized that the energy required to break the $\pi$ bonds in $BF_3$ will probably cause the enthalpy of $BF_3$ addition reactions to be relatively low. Comparable $\pi$ bonds are absent in $BH_3$. (b) When the ligand atom is from the second or later rows of the periodic system, borane addition products appear to be stabilized by delocalization of the orbitals. For example, the complex $BH_3{\cdot}(CH_3)_2S$ is more stable than $BF_3{\cdot}(CH_3)_2S$ (51); this apparent anomaly was explained by a release of electron density by $BH_3$ to available sulphur 3d orbitals. Such supplementary bonding was presumed not to occur in the boron trifluoride compound.

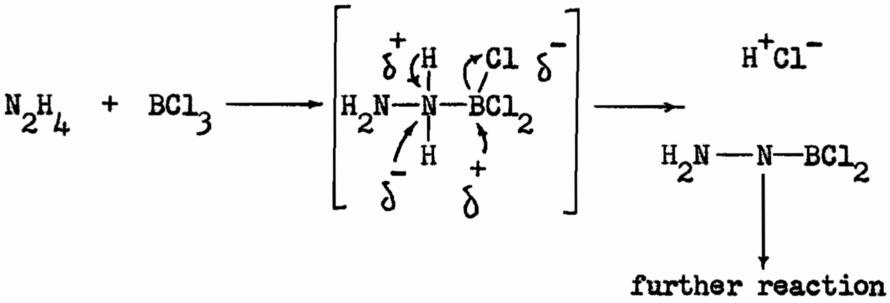
The results of the present research support the view that $BF_3$ is a stronger electron acceptor than $B(CH_3)_3$, but no distinction could be made between $BF_3$ and $BH_3$. The evolution of hydrogen by $2BH_3 \cdot N_2H_4$ (13,14) reflects only the difference in the dissociation energies of the B-H bond in $BH_3$ (93.3 kcal./mole) and of the B-F bond in $BF_3$ (154.8 kcal./mole) (28).

Some knowledge of the influence of steric hindrance on the electron acceptor properties of $BF_3$, $BH_3$, and $B(CH_3)_3$ with a reference base from the hydrazine system of compounds might be obtained from the study of the addition products of unsymmetrically disubstituted hydrazines such as 1,1-diethylhydrazine. With this donor molecule, the 2:1 addition compound with trimethylborane should not form, and steric interplay should be significant in the reaction with boron trifluoride.

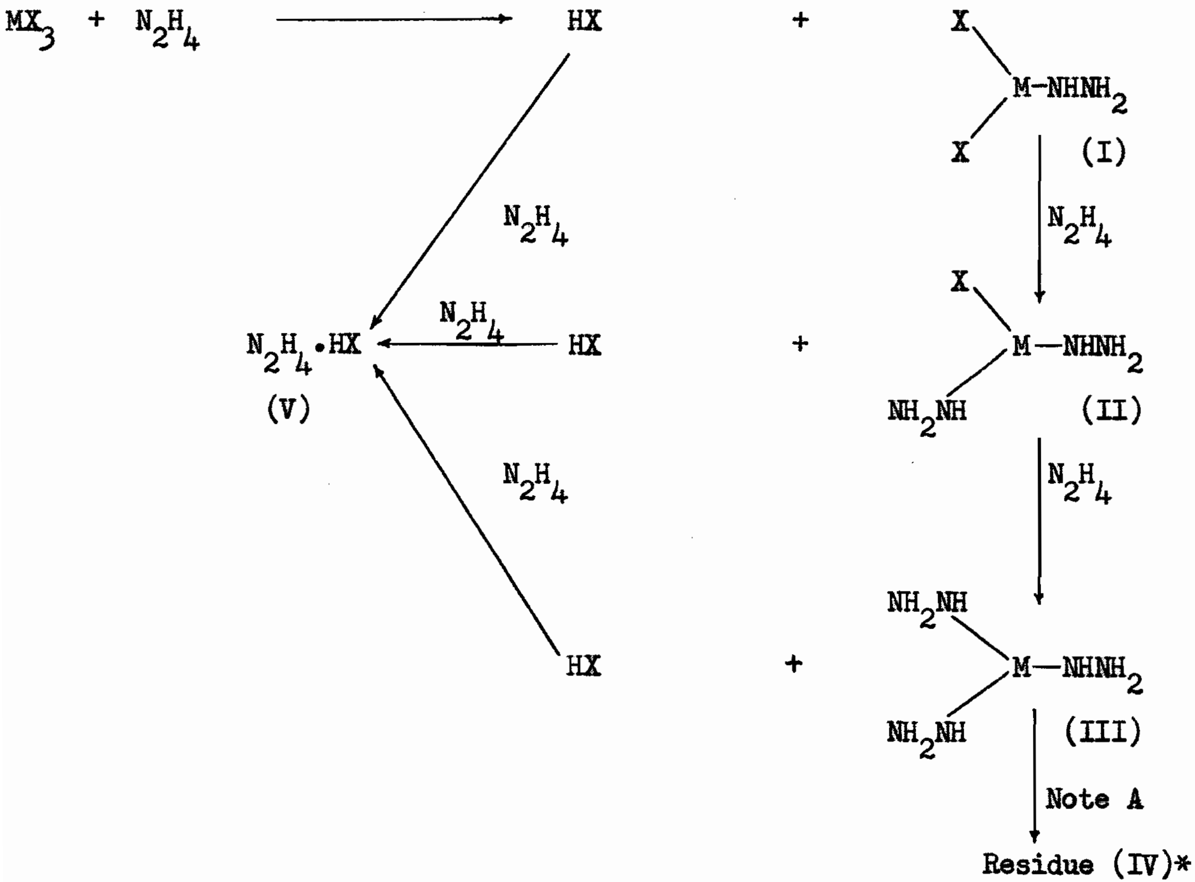
## The Reactions of Hydrazine with $BCl_3$, $BBr_3$, $AlCl_3$, $AlBr_3$, $AlI_3$

Experimental work reported in this thesis indicated that the reaction of hydrazine with $BX_3$ (X = Cl, Br) or $AlX_3$ (X = Cl, Br, I) was characterized by the elimination of hydrogen halide, which appeared among the reaction products as hydrazine hydrohalide, $N_2H_5X$. Analogous reactions are known to occur between the boron halides $BX_3$ (X = Cl, Br, I) and ammonia (29,30,31,93), in which the hydrogen halide appears as ammonium halide, $NH_4X$. It has been reported (140) that aluminum chloride is slightly soluble in anhydrous hydrazine ($\sim$0.01 gm./ml.), but no evidence of a reaction was given.

Since hydrazine is a powerful nucleophilic reagent, the elimination of hydrogen halide probably occurred through the formation of an intermediate addition compound which lost HCl by a rapid unimolecular elimination reaction:



The preparation of product mixtures of empirical formula $MX_3N_8H_{16}$ (M = B, Al; X = halogen) and $MX_3N_{12}H_{24}$, and the eventual isolation of substances which appeared to contain four gram-atoms of nitrogen per gram-atom of aluminum (or boron), suggested that the path of the overall reaction might be the following:



* Residue contained four gram-atoms N per gram-atom M.

Note A. This operation involved the separation of $N_2H_4$ • HX by repeated washing with anhydrous hydrazine and the drying of the residue in vacuo.

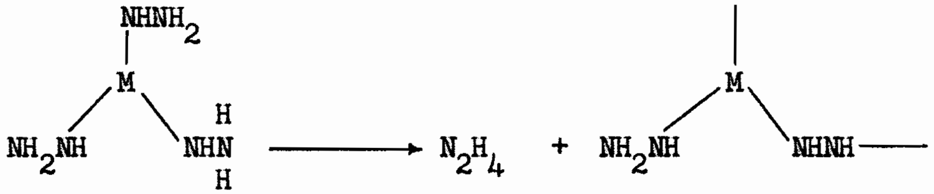
It appears that different solvents gave rise to some variations in reaction mechanism within the scheme just outlined. Reactions done in vacuo or in carbon tetrachloride resulted in substances of empirical formula $MCl_3N_8H_{16}$ (M = B, Al), which were thought to consist of II (1 mole) and V (2 moles) (see reaction scheme). However, when tetrahydrofuran was used as a solvent, the materials of empirical formula $BX_3N_{12}H_{24}$ (X = Cl, Br), which were considered to contain III (1 mole) and V (3 moles), were obtained.

Thus the reaction of $MX_3$ (M = B, Al; X = halogen) with $N_2H_4$ in vacuo or in carbon tetrachloride as a suspension medium seemed to be characterized by the cleavage of two MX bonds, whereas in an ethereal solvent (e.g., tetrahydrofuran), which forms a coordinate bond with $MX_3$, the rupture of all three MX bonds was probable.

Two reasons may be advanced for this difference. (a) The MX bonds of isolated $MX_3$ molecules are strengthened by $\pi$ bonding which vanishes in the formation of the coordinate bond to oxygen. Thus greater reactivity of the MX bond may be anticipated in ethereal solvents. (b) The inductive effects of the ethereal oxygen might give the halogen atoms a greater relative negative charge, leading to increased reactivity.

Although attempts to separate mixtures of II and V by the techniques of fractional sublimation and solvent extraction were unsuccessful, partial separations of hydrazine hydrohalide were achieved in several instances, thereby aiding in the confirmation of the overall reaction scheme.

The residue IV (p. 107), which seemed to contain aluminum (or boron) and nitrogen in a ratio of 1:4 (from analytical data), probably was formed by the elimination of $N_2H_4$ from the material $M(NHNH_2)_3$ when the latter was dried in vacuo:



residue (IV)

There appeared to be three possibilities for the constitution of the residue IV: (a) the monomeric molecule hydrazinohydrazonoaluminum (or boron):

$$NH_2NH{-}Al{=}NNH_2$$

The absence of any sign of melting up to 350° and the lack of resolution of the infrared absorption bands indicated that such a structure was unlikely. Monomeric, covalently bonded materials are usually characterized by low melting points and boiling points (122). Further, the structure depicted requires a double bonding of nitrogen to aluminum. There do not seem to be any known examples of compounds containing a double bond to aluminum (141).

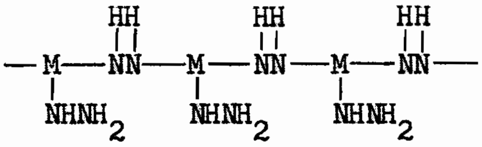
(b) A zwitterion structure:

$$^{+}NH_3NH{-}Al{=}NNH^{-}$$

A substance of this nature might have a high melting point, but its infrared spectrum should be well defined by analogy with other compounds containing $NH_3^+$ groups, e.g., $N_2H_5X$ (X = Cl, Br, I) (91,106) and $N_2H_6X_2$ (X = F, Cl) (142).

This formulation requires an improbable double bond between nitrogen and aluminum (141). Finally, whereas an ionic material should be very soluble in a highly polar solvent such as hydrazine, the substance $AlN_4H_5$ was only slightly soluble.

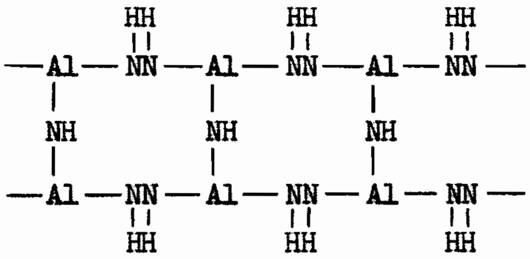
(c) A polymeric substance:



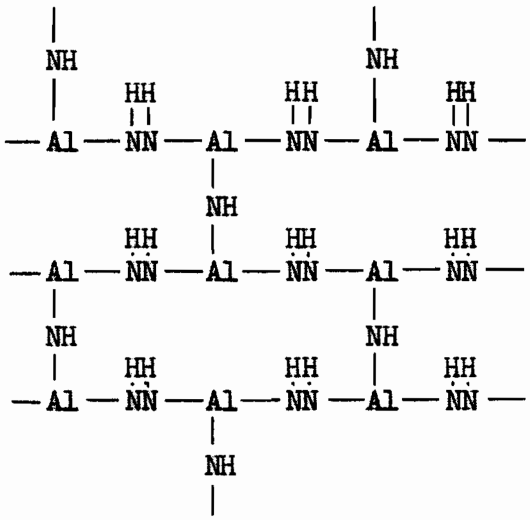
$$-\underset{\underset{NHNH_2}{|}}{M}-\overset{\overset{HH}{||}}{NN}-\underset{\underset{NHNH_2}{|}}{M}-\overset{\overset{HH}{||}}{NN}-\underset{\underset{NHNH_2}{|}}{M}-\overset{\overset{HH}{||}}{NN}-$$

The absence of a melting point up to 350°, the unresolved character of the infrared spectra (Figures 7 and 9), the striking similarity of certain regions of the latter to the spectra (88) of boron and aluminum nitrides (polymeric materials), and the low solubility in anhydrous hydrazine, were considered to be reasonably strong evidence for a polymeric structure. The monomer unit of the polymer shown has an empirical formula $AlN_4H_5$ (Required: Al, 30.7%. Found: Al, 30.4, 30.7, 31.4, 31.5%). Similarly, the boron-containing polymer has the empirical formula $BN_4H_5$ (Required: B, 15.05%. Found: B, 15.31, 15.61%).

The residue obtained from the "Soxhlet" extraction of the reaction product $AlCl_3N_8H_{16}$ with hot hydrazine appeared to contain two and one-half gram-atoms of nitrogen per gram-atom of aluminum (by analysis). This substance was thought to be formed by a cross-linking of the polymer just described: e.g.,



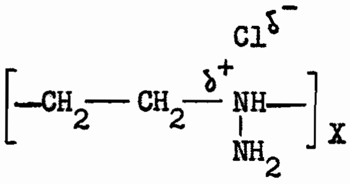
or



The monomer unit of these substances has the empirical formula $Al_2N_5H_5$ (Required: Al, 41.8%. Found: Al, 41.4, 41.8%). The formation of an NH cross-link rather than NHNH casts considerable doubt on the above structure, but since the N-H (76 kcal./mole) (114) and the N-N (60 kcal./mole) (114,115) bond energies are of the same order of magnitude (values are for hydrazine), it is possible that $N_2H_4$, $NH_3$, $N_2$ or $H_2$ could be eliminated in a cross-linking process.

The substance $(Al_2N_5H_5)_X$ did not melt up to 475°, and its infrared spectrum consisted of broad, poorly resolved bands (Figure 8). Although the polymeric substances $(AlN_4H_5)_X$ and $(BN_4H_5)_X$ dissolved readily in mild aqueous acid and water, respectively, the material $(Al_2N_5H_5)_X$ required hot, concentrated acid for complete dissolution. This observation is in accord with the more extensive bonding structure of $(Al_2N_5H_5)_X$.

By way of comparison, the reaction of $ClCH_2CH_2Cl$ with hydrazine was thought (143) to yield the polymeric substance



$$\left[-CH_2-CH_2\overset{\delta^+}{-}\underset{NH_2}{\overset{Cl^{\delta^-}}{NH}}-\right]_X$$

as one of the products.

The reaction product $MX_3N_{12}H_{24}$ was probably a mixture of $N_2H_5X$ (3 moles) and $M(NHNH_2)_3$(1 mole). When this mixture was washed repeatedly with anhydrous hydrazine, the residue, on evaporation to dryness, was probably the polymer $(MN_4H_5)_X$. It was presumed that the substance $M(NHNH_2)_3$ was unstable in the absence of $N_2H_5X$ or $N_2H_4$ (since $N_2H_4$ was evolved on drying), and that there was accordingly a stabilizing coordinate bond between $N_2H_5X$ and substances II and III (see reaction scheme). In some respects this is similar to the compound $AlCl_3 \cdot 3N_2H_5Cl$ (144) formed between $AlCl_3$ and $N_2H_5Cl$ in concentrated aqueous solution.

There was a remarkable similarity among parts of the infrared spectra of the three polymeric substances and those of boron and aluminum nitrides (88). The five spectra are summarized in Table XXIV.

For the aluminum compounds, the peaks between 1650 and 1050 $cm^{-1}$ were assigned to NH modes, leaving unassigned the peaks at 3500 and 1050-650 $cm^{-1}$. Since the latter absorptions also appear in the spectrum of aluminum nitride, they are probably associated with aluminum-nitrogen

TABLE XXIV

| Compound | AlN[a] | $(Al_2N_5H_5)_X$ | $(AlN_4H_5)_X$ | $(BN_4H_5)_X$ | BN[a] |
|---|---|---|---|---|---|
| | ~3450 vsvb | ~3500 vsvb | 3450 vsvb | 3350 svb | 3340 mw |
| | 1600 w | 1640 sb | 1630 sb | 1620 sb | -- |
| | -- | 1470 mwb | ~1480 mwb | -- | -- |
| Infrared | -- | 1385 m | 1385 m | -- | -- |
| absorptions: | -- | -- | -- | ~1330 svb | 1375 s |
| (cm$^{-1}$) | -- | 1195 m | 1200 msh | -- | -- |
| | -- | ~1115 wb | ~1075 wb | ~1050 svb | -- |
| | 1000 to 625 meb | 1050 to 650 meb | 1050 to 650 meb | ~700 mvb | 812 m |

[a] Peaks unassigned in the literature.

See Tables XVI, XIX, XX for infrared symbolism.

vibrations. The absorption at 3500 cm$^{-1}$ is also associated with the $\nu$(N-H) modes.

For covalent single BN bonds, $\nu$(B-N) is found in the range 1330-1380 cm$^{-1}$ (112), and accordingly, this assignment was made for the peak at 1330 cm$^{-1}$ in the spectrum of $BN_4H_5$. The peak at 3350 cm$^{-1}$ was presumed to arise from boron-nitrogen vibrations as well as $\nu$(N-H) vibrations.

There is a great dissimilarity in the reactions of boron trichloride and boron tribromide with hydrazine as compared with the reaction of the latter with boron trifluoride. This result is readily explained on the basis of BX bond dissociation energies, the value of which is very high (154.8 kcal./mole) for $BF_3$ but much less for $BCl_3$ (108.5 kcal./mole) and $BBr_3$ (90.2 kcal./mole) (28). The BF bond is sufficiently stable that $BF_3$ will not undergo a condensation reaction with compounds containing "active" hydrogen ($NH_3$, $C_2H_5OH$, etc.). The behaviour of the boron halides towards ammonia is essentially the same as that towards hydrazine. Boron trifluoride forms an addition product with ammonia (22), but boron trichloride (29) and boron tribromide (30,31) condense with ammonia to form boron amide and boron imide, respectively.

The reactions of the aluminum halides with ammonia are in sharp contrast with those of the boron halides. The condensation reaction with ammonia which characterizes $BCl_3$ and $BBr_3$ does not occur with the aluminum halides; instead, addition compounds are formed, as described in the Introduction. With hydrazine, on the other hand, the aluminum halides, like the boron halides, readily eliminate hydrogen halide to form compounds with aluminum-nitrogen covalent bonds. The relatively weak NH bond (76 kcal./mole) in hydrazine (114), compared with that of ammonia (104 kcal./mole) (116), seems to permit condensation reactions to occur between hydrazine and aluminum halides.

It was noted that the reaction of <u>boron trichloride</u> (B-Cl bond energy: 108.5 kcal./mole (28)) with hydrazine resulted in a rapid elimination of HCl by the two reactants, but the reaction of <u>trimethylborane</u> (B-C bond energy: 89.0 kcal./mole (28)) with hydrazine was not characterized by the elimination of methane. This was ascribed both to the difference in bond energies and to the much greater polarity of the B-Cl bond ($\sim$22% ionic character (100)) as compared with the B-C bond ($\sim$6% ionic character).

There appears to be considerable scope for the further study of the reactions of hydrazine with inorganic halides. Of particular interest should be the reactions of the halides of Groups IV-VI of the Periodic System, of which only those of carbon have been studied thus far (see Introduction). Three aspects of the problem should prove interesting.

(a) Considerable information might be obtained through a comparison of the reactivities toward hydrazine of the halides of one particular group. For example, it has been shown (145) that the extent of ammonolysis of the chlorides of Group IVB (including thorium for the sake of comparison) decreases with increasing atomic number of the metal. The reaction of ammonia with $TiCl_4$ and $ZrCl_4$ gave the compounds $Ti(NH_2)_3Cl$ and $Zr(NH_2)Cl_3$ while $ThCl_4$ formed only an addition compound $ThCl_4 \cdot 6NH_3$. Since the radius of the central atom increases with increasing atomic number, from Ti to Th, the "specific surface intensity charge" (145), which determines the energy available for the polarization of the MCl and NH bonds, decreases with increasing atomic number, and therefore hydrogen chloride elimination should take place most easily with $TiCl_4$. It should be useful to undertake similar studies involving hydrazine.

(b) The choice of different solvents may lead to unusual results. For instance, in the present research, the reaction of aluminum chloride with hydrazine in absolute ethanol as a solvent resulted in a precipitate of hydrazine hydrochloride, with the aluminum remaining in solution. Since aluminum ethoxide, $Al(OEt)_3$, is almost insoluble in ethanol, the aluminum compound remaining in solution probably contained Al-Cl bonds.

(c) New and interesting inorganic polymers may be formed.

# SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

1. Boron trifluoride and hydrazine reacted vigorously at room temperature in vacuo to yield boron trifluoride-hydrazine, $BF_3 \cdot N_2H_4$, (m.p. 87°) which absorbed additional boron trifluoride very slowly.

2. The reaction of $BF_3$ with $N_2H_4$ either in vacuo above room temperature (140°, 200°) or at room temperature in diethyl ether as solvent gave the complex mixtures $(BF_3)_X N_2H_4$ $(1 < X < 2)$. However, with tetrahydrofuran as solvent, the compound 2-boron trifluoride-hydrazine, $2BF_3 \cdot N_2H_4$ (m.p. 260°), was obtained. The portion of the phase diagram $BF_3$-$N_2H_4$ from 46.5 to 66.7 mole % $BF_3$ was investigated.

3. The crystallographic unit cell of $BF_3 \cdot N_2H_4$ was found to have the following dimensions (triclinic symmetry):

$$a = 6.93\ \mathring{A} \qquad \alpha = 111.5°$$
$$b = 5.50\ \mathring{A} \qquad \beta = 64.0°$$
$$c = 6.78\ \mathring{A} \qquad \gamma = 88.3°$$

4. The pyrolysis of $BF_3 \cdot N_2H_4$ in vacuo at 275-300° yielded mainly nitrogen, ammonia, ammonium fluoborate, and boron nitride. The aqueous solution of $BF_3 \cdot N_2H_4$, which was acidic, appeared to contain the following species: $N_2H_5^+$, $BF_3OH^-$, $BF_4^-$, $BF_2(OH)_2^-$, $H_3BO_3$, $OH^-$.

5. At 110°, $BF_3$ was displaced to an extent of only 16% from $BF_3 \cdot N_2H_4$ by hydrogen chloride. The solid residue seemed to be largely the mixed addition compound $BF_3 \cdot N_2H_4 \cdot HCl$.

6. $BF_3 \cdot N_2H_4$ readily absorbed ammonia at -80° to form boron trifluoride-hydrazine-2-ammonia, $BF_3 \cdot N_2H_4 \cdot 2NH_3$. Under similar conditions, $BF_3 \cdot N_2H_4$ absorbed indefinite amounts of $CH_3NH_2$ or $(CH_3)_3N$ which were released very slowly on warming.

7. The reaction of trimethylborane and hydrazine in vacuo at room temperature yielded 2-trimethylborane-hydrazine, $2B(CH_3)_3 \cdot N_2H_4$, but this compound was stable only in an atmosphere of trimethylborane or at low temperatures; otherwise trimethylborane was evolved irreversibly, leaving trimethylborane-hydrazine, $B(CH_3)_3 \cdot N_2H_4$ (m.p. 42-43°). The two compounds were interconvertible.

8. Hydrazine was not displaced to any significant extent from $B(CH_3)_3 \cdot N_2H_4$ by ammonia at room temperature. The displacement of $B(CH_3)_3$ from $B(CH_3)_3 \cdot N_2H_4$ by diborane at room temperature was followed by its reaction with $B_2H_6$ to yield unsym-dimethyldiborane, $(CH_3)_2B_2H_4$.

9. The thermal decomposition of $B(CH_3)_3 \cdot N_2H_4$ at 150-160° was complex, yielding nitrogen, ammonia, methane, butane, the isomeric butenes, and a heterogeneous residue. Under identical heating conditions, $B(CH_3)_3$ itself was unchanged while $N_2H_4$ was only slightly decomposed.

10. Hydrazine and trimethylaluminum reacted in diethyl ether to yield a substance which was thought to be sym-bisdimethylaluminohydrazine, $(CH_3)_2AlNHNHAl(CH_3)_2$. This material was shock-sensitive and decomposed violently when subjected to mechanical stress.

11. The reaction of boron trichloride or aluminum chloride with

hydrazine in vacuo or of $AlCl_3$ with $N_2H_4$ in carbon tetrachloride yielded reaction products of empirical composition $MCl_3N_8H_{16}$ (M = B, Al). (I).

12. The reaction of boron tribromide or boron trichloride with hydrazine in tetrahydrofuran gave products of empirical composition $BX_3N_{12}H_{24}$ (X = Cl, Br) (II).

13. The reaction of aluminum bromide with hydrazine in $CCl_4$, and of $AlCl_3$ or $AlI_3$ with $N_2H_4$ in diethyl ether gave nonstoichiometric reaction products (III).

14. The attempted separation of I into its components by the techniques of fractional sublimation or solvent extraction were unsuccessful. The "Soxhlet" extraction of $AlCl_3N_8H_{16}$ with hot hydrazine led to the isolation of a polymeric material tentatively formulated as $(Al_2N_5H_5)_X$ (IV).

15. The repeated extraction of I, II, or III with $N_2H_4$ at room temperature and the subsequent evaporation of excess $N_2H_4$ yielded the polymeric materials $(MN_4H_5)_X$ (M = B, Al). (V). The material IV was thought to be a cross-linked version of the polymer V.

16. The infrared spectra of ten compounds of boron or aluminum were measured and vibration assignments were made for absorptions in the range 625-4000 $cm^{-1}$.

17. An experiment was proposed to determine by direct chemical evidence the relative electron acceptor power of $BF_3$ and $BCl_3$. Results were quoted to show that the order is $BCl_3 > BF_3$.

18. Mechanisms were proposed for (a) the pyrolysis of $BF_3 \cdot N_2H_4$, (b) the hydrolysis of $BF_3 \cdot N_2H_4$, and (c) the reactions of $MX_3$ ($M = B, Al$; $X$ = halogen) with $N_2H_4$ and the formation of the polymers $(MN_4H_5)_X$ ($M = B, Al$) and $(Al_2N_5H_5)_X$.

# APPENDIX I

## Representative Infrared Vibration Frequencies of Boron-Nitrogen Compounds (600-3600 $cm^{-1}$)

| Vibration | Frequency | Compound | Reference |
|---|---|---|---|
| ($NH_2$) | 3270-3360 | $BF_3 \cdot NH_3$ | 104 |
| | | $B(CH_3)_3 \cdot NH_3$* | 79 |
| | | $N_2H_4$ | 12 |
| ($CH_3$) | 2780-3040 | $(CH_3)_3N$ | 107 |
| | | $BH_3 \cdot (CH_3)_3N$ | 109 |
| | | $B(CH_3)_3$ | 130,139 |
| | | $B(C_2H_5)_3$ | 146 |
| ($B\text{-}H_{terminal}$) | 2270-2600 | $B_2H_6$ | 147 |
| | | $H_2BHN(CH_3)_2BH_2$ | 133 |
| | | $BH_3 \cdot (CH_3)_3N$ | 109 |
| | | $R_nB_2H_{6-n}$ $(n < 4)$ | 80 |
| | | $H_2BN(CH_3)_2$ | 148 |
| ($NH_2$) | 1565-1640 | $NH_3$ | 71 |
| | and | $N_2H_4$ | 12 |
| | 1440-1500 | $N_2H_6Cl_2$, $N_2H_6F_2$ | 142 |
| | | $N_2H_5Cl$, $N_2H_5Br$ | 91 |
| | | $BF_3 \cdot NH_3$ | 104 |
| ($B\text{-}H_{bridge}$) | 1500-1610 | $B_2H_6$ | 147 |
| | | $R_nB_2H_{6-n}$ $(n < 4)$ | 80 |

* Raman spectrum

## APPENDIX I (cont'd.)

| Vibration | Frequency | Compound | Reference |
|---|---|---|---|
| $(CH_3)$ | 1405-1460<br>and | $B(CH_3)_3$ | 130,139 |
| (bound to boron) | 1280-1320 | many others | 112 |
| $NH_X$** | 730-1420 | $NH_3$ | 71 |
| | | $N_2H_4$ | 12 |
| | | $BF_3 \cdot NH_3$ | 104 |
| | | $N_2H_5Cl$, $N_2H_5Br$ | 91 |
| $CH_3$** | 860-1200 | $B(CH_3)_3$ | 130,139 |
| | | $BH_3 \cdot (CH_3)_3N$ | 109 |
| | | $(CH_3)_3N$ | 107 |
| | | $(CH_3)_2BNHC_6H_5$ | 113 |
| $BH_2$ "scissors" | 1140-1200 | $B_2H_6$ | 147 |
| | | $H_2BHN(CH_3)_2BH_2$ | 133 |
| | | others | 112 |
| $_{as}$ (B-C) | 1120-1150 | $B(CH_3)_3$ | 130,139 |
| | | $B(C_2H_5)_3$ | 146 |
| | | $(CH_3)_2BCl$ | 149 |
| | | $(CH_3)_2BBr$ | 150 |
| (B-N) | 982-1138 | $BF_3 \cdot C_5H_5N$ | 151 |
| | | $BF_3 \cdot NH_3$ | 104 |
| | | $B(CH_3)_3 \cdot NH_3$* | 79 |

*Raman spectrum

**rocking, wagging.

## APPENDIX I (cont'd.)

| Vibration | Frequency | Compound | Reference |
|---|---|---|---|
| ($BH_2$) | 1075 | $H_2BHN(CH_3)_2BH_2$ | 133 |
| w ($BH_2$) | 945-975 | $B_2H_6$ | 147 |
| | | $H_2BHN(CH_3)_2BH_2$ | 133 |
| | | others | 112 |
| (N-N) | 958-973 | $N_2H_5Cl$, $N_2H_5Br$ | 91 |
| | | $N_2H_5I$ | 106 |
| $_s$ (B-C) | 620-720 | $B(CH_3)_3^*$ | 79,130 |
| | | $B(C_2H_5)_3^*$ | 146 |
| | | $B(CH_3)_3 \cdot NH_3^*$ | 79 |
| | | $(CH_3)_2BNC_4H_4$, $(CH_3)_2BNHC_6H_5$ | 113 |

*Raman spectrum

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