

AN ABSTRACT OF THE THESIS OF

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Title PREPARATION AND LEWIS ACID PROPERTIES OF DIBORON
TETRAFLUORIDE AND RELATED COMPOUNDS

Abstract approved 
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Attempts to synthesize diboron tetrafluoride by the reduction of boron trifluoride with alkali metal solutions in 1,2-dimethoxyethane proved to be unsuccessful. No diboron tetrahalide was found when boron trifluoride, antimony trifluoride, or boron trichloride was reacted with tetra-(dimethylamino)-diboron; although there appeared to be some exchange between chloride and amine groups.

Diboron tetrafluoride was prepared by the treatment of diboron tetrachloride with antimony trifluoride. The diboron tetrachloride was produced by the acid hydrolysis of tetra-(dimethylamino)-diboron to hypoboric acid with subsequent dehydration and reaction with boron trichloride.

From the results of the formation of Lewis acid-base complexes and their acid displacement reactions the order of relative acid strength was found to be: hydrogen chloride, diboron tetrafluoride < boron trifluoride < boron trichloride.

Diboron tetrafluoride formed strong complexes with triethylamine, trimethylamine, 2,6-lutidine, N,N,N',N'-tetramethylethylenediamine, and 1,2-dimethoxyethane. A weak complex occurred with benzonitrile, whereas, no complexation was found with p-chlorobenzonitrile. Boron trifluoride displaced diboron tetrafluoride from its complexes with 1,2-dimethoxyethane, trimethylamine, and triethylamine. No displacement occurred, under the conditions investigated, with the complexes of N,N,N',N'-tetramethylethylenediamine and benzonitrile.

It was found that p-chlorobenzonitrile serves as an excellent Lewis base for the separation of boron trifluoride from hydrogen chloride and boron trichloride impurities by complex formation. p-Nitroanisole served to separate boron trichloride from hydrogen chloride and boron trifluoride by the same method.

Inasmuch as diboron tetrafluoride is a weaker Lewis acid than boron trifluoride and has a short boron-boron bond compared to diboron tetrachloride, a bond order greater than one is postulated to exist between the boron atoms. The presence of this partial π bond would tend to constrain diboron tetrafluoride in planar configuration in the gaseous state in contrast to the twisted configuration known to occur in diboron tetrachloride.

The infrared spectral range of $600-4000\text{ cm}^{-1}$ was scanned with two principal absorption peaks of 1158 and 1373 cm^{-1} indicated for gaseous diboron (11, 11) tetrafluoride. The infrared spectra of solid

diboron tetrafluoride was also obtained over the same range.

An infrared cell with a novel all-metal seal was designed and used for the spectra determination of gases. The vacuum-tight seal was obtained by placing an amalgamated lead gasket between a silvered glass cell and rock salt window. The all-metal seal was found to be less reactive toward boron halides than other common sealants.

PREPARATION AND LEWIS ACID PROPERTIES OF
DIBORON TETRAFLUORIDE AND RELATED COMPOUNDS

by

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TABLE OF CONTENTS

	Page
INTRODUCTION	1
EXPERIMENTAL	14
Purification, Separation, and Identification of Reagents and Products	14
Chemicals	16
Apparatus	18
Vacuum System	18
Infrared Cells	19
Special Reaction Vessel	22
Reactions	24
Solubility of Sodium-potassium Alloy in Tertiary Amines	24
Reduction of Boron Trifluoride by Alkali Metal in Glyme Solution	25
Characterization of the Boron Trifluoride Reduction Product	26
Synthesis of Diboron Tetrafluoride	28
Reaction of Tetra-(dimethylamino)-diboron with Boron Trifluoride, Antimony Trifluoride, Boron Trifluoride in the Presence of Antimony Tri- fluoride and Boron Trifluoride in the Presence of Boron Trichloride	30
Reaction of Boron Trichloride with Tetra-(dimethy- lamino)-diboron	31
Reaction of Boron Trifluoride with Boron Suboxide	32
Reaction of Boron Trifluoride with Glyme	33
Displacement of Boron Trifluoride from Glyme with Boron Trichloride	33
Reaction of Boron Trifluoride-Glyme Complex with Trimethylamine	35
Reaction of Boron Trifluoride-Trimethylamine Complex with Hydrogen Chloride	35
Reaction of the Boron Trifluoride-Glyme Complex with 2, 6-Lutidine	36
Attempted Displacement of Boron Trichloride from its Triethylamine Complex	37
Attempted Displacement of Boron Trichloride from its 2, 6-Lutidine Complex	37

	Page
Reaction of Boron Trifluoride-Glyme Complex with Aluminum Chloride	38
Reaction of Boron Trichloride with Trityl Chloride.	38
Reaction of Boron Trichloride with Nitrobenzene .	40
Reaction of Boron Trifluoride with Nitrobenzene .	40
Reaction of Boron Trifluoride with Benzonitrile .	40
Reaction of Boron Trifluoride with p-Chlorobenzonitrile	41
Reaction of Boron Trichloride with p-Chlorobenzonitrile	42
Reactions of Boron Trifluoride and of Boron Trichloride with p-Nitrotoluene	43
Reaction of Boron Trichloride with p-Nitroanisole .	44
Displacement of Diboron Tetrafluoride from Glyme with Boron Trifluoride	46
Reaction of Diboron Tetrafluoride with Excess N,N,N',N'-Tetramethylethylenediamine	48
Reaction of Diboron Tetrafluoride with an Equivalent Amount of TED	50
Reaction of Diboron Tetrafluoride with Triethylamine	51
Reaction of Diboron Tetrafluoride with Trimethylamine	52
Treatment of Diboron Tetrafluoride with p-Chlorobenzonitrile	53
Reaction of Diboron Tetrafluoride with Benzonitrile	53
Reaction of Diethylzinc with Diboron tetrafluoride-Glyme Complex	54
Infrared Spectrum of Diboron Tetrafluoride . . .	55
DISCUSSION	58
The Synthesis of Diboron Tetrafluoride	58
Alkali Metal Solutions	64
Lewis Acid-Base Adducts	65
Complexes of Boron Trifluoride	65
Complexes of Boron Trichloride	66
Complexes of Diboron Tetrafluoride	68
Conclusions	70
Displacement Reactions	72
Base Displacement	72
Acid Displacement	72

	Page
Displacement of Diboron Tetrafluoride	73
Conclusions	75
Infrared Spectrum of Diboron Tetrafluoride	78
BIBLIOGRAPHY	82

LIST OF FIGURES

Figure		Page
1	All metal sealed gas cell for infrared spectra . .	20
2	Special reaction vessel	23

LIST OF TABLES

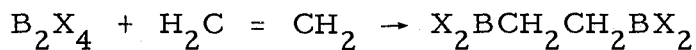
Table		Page
I	VAPOR PRESSURE EQUATIONS OF COMMON REAGENTS	15
II	COMMON COLD BATHS	16

PREPARATION AND LEWIS ACID PROPERTIES OF DIBORON TETRAFLUORIDE AND RELATED COMPOUNDS

INTRODUCTION

Knowledge of the chemistry of boron has increased rapidly in recent years as a large number of boron compounds have been synthesized and investigated. However, only a few compounds are known that contain covalent boron-boron bonds, and not much information has been reported concerning them.

Diboron tetrahalides are representatives of this group of compounds containing a covalent boron-boron bond. They are of particular interest because of generally high chemical activity and because they are precursors for a wide variety of diboron compounds and organoboranes. As examples, the tetrahalides may find utility as halogenating agents and as catalysts in acid-catalyzed reactions. Diboron tetrahalides may also have certain advantages as reducing agents. Other reactions involving addition of diboron compounds across carbon-carbon multiple bonds (12) lead to a broad class of organodiboranes.



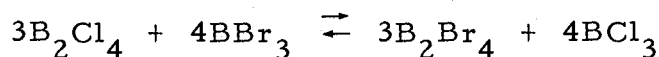
The products undergo alkylation, hydrogenolysis, ammonolysis, hydrolysis, alcoholysis, and possess the usual acceptor properties

characteristic of trisubstituted boron (24).

The first compound known to have a single boron-boron bond, was prepared by Stock, et al., in 1925 by passing boron trichloride, BCl_3 , through an arc between two zinc electrodes (44). The yields of diboron tetrachloride, B_2Cl_4 , were low, and the compound proved to be an unstable liquid. For these reasons and because of the failure of investigators to realize that diborane, B_2H_6 , a more easily obtainable material, did not contain a boron-boron bond, there was a cessation of activity in this field for more than twenty years.

Reduction of boron trihalides by alkali metals has been investigated: sodium vapor with boron trichloride yields sodium chloride and boron (20). Reduction of boron trichloride by hydrogen at 200-500° C in the presence of various metal catalysts gives diborane (27). In 1949 Schlesinger, et al. improved upon the preparation of diboron tetrachloride by passing boron trichloride through a glow discharge established between mercury electrodes (54). Variations of this method and much of the known chemistry of diboron tetrachloride have been reviewed (24).

Diboron tetrabromide has been prepared by treating diboron tetrachloride with boron tribromide at room temperature (50).



The more volatile boron trichloride is removed as formed. Diboron

tetrabromide is a thermally unstable liquid at room temperature.

The solid melts at 0.5 to 1.5° C. The only recorded vapor pressure is 5.5 mm. at 22.5° C.

Diboron tetraiodide is formed in about 15% yield by passing boron triiodide at low pressure through a radiofrequency discharge (42)

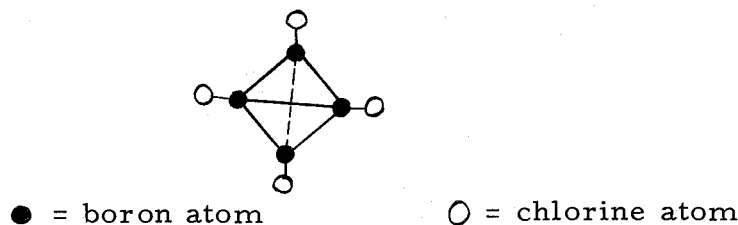
$2\text{BI}_3 \rightarrow \text{B}_2\text{I}_4 + \text{I}_2$. It is a pale yellow crystalline solid which can be sublimed in vacuum at 60-70° C. Decomposition occurs at room temperature.

During the preparation of diboron tetrachloride by the glow discharge method, other products containing boron-boron bonds are formed in very small yields (49). These include tetraboron tetrachloride, B_4Cl_4 , a pale yellow, crystalline solid, octaboron octachloride, B_8Cl_8 , a red solid, and nonvolatile boron chloride, BCl , polymers (24).

These same products result from the room temperature decomposition of diboron tetrachloride. The structures of tetraboron tetrachloride (1, 2) and octaboron octachloride (3, 28) have been determined.

Since each boron atom is bonded to one halogen atom, the structures are formally electron-deficient. In tetraboron tetrachloride four electrons (one from each boron) are assigned to the normal boron-chlorine bonds, using the 3p orbital of each chlorine atom. The remaining eight electrons of the boron atoms are assigned to the

bonding orbitals of the tetrahedron containing the four boron atoms.



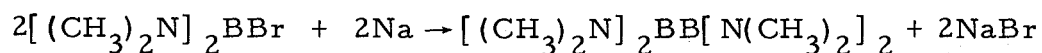
If a simple covalent bond is defined as the interaction of two unpaired electrons of opposite spin derived from one orbital overlapping with another orbital of a different atom, it is questionable whether the boron monochloride class of compounds actually contain a simple covalent boron-boron bond. This is probably true of the boron monobromide and boron monoiodide compounds as well.

All of the boron hydrides appear to be electron deficient but as in the case of boron monohalides their reactivity and structures cannot be accounted for in terms of simple covalent boron-boron bonds. An exception may be decaborane-16, $B_{10}H_{16}$, even though the molecule as a whole is electron deficient. The recent discovery and elucidation of the molecular structure of decaborane-16 disclosed a boron-boron bond between the two halves of the molecule that appeared to be a simple covalent bond (19).

A significantly new approach to the synthesis of diboron compounds was reported after this research work was undertaken. Since it led to a modification of approach in this work, it is discussed here. A series of amino, alkoxy, hydroxy and halo-substituted diborons

was prepared by this general method and appropriate interconversions.

Tetra-(dimethylamino)-diboron was prepared by the reduction of bis-(dimethylamino)-boron chloride or bromide with highly-dispersed molten sodium (10).

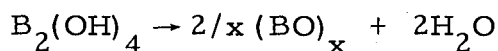
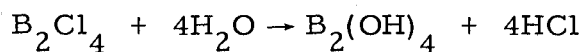


This diboron compound, which was first isolated from the reaction of diboron tetrachloride and dimethylamine (50), is a clear liquid at room temperature and is stable at 200° C in the presence of dry air.

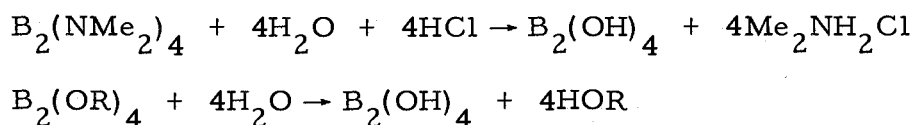
Transamination of tetra-(dimethylamino)-diboron with primary and secondary amines have led to a variety of tetra-(amino)-diborons.

Several tetraalkoxydiborons and tetraphenoxydiboron have been prepared by the reactions of tetra-(dimethylamino)-diboron with alcohols or phenol in the presence of hydrogen chloride (8).

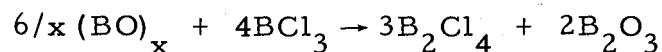
Tetrahydroxydiboron or hypoboric acid, $\text{H}_4\text{B}_2\text{O}_4$, prepared by the hydrolysis of diboron tetrachloride, is converted into boron monoxide, $(\text{BO})_x$, by dehydration at 220° C (52).



Tetrahydroxydiboron has also been prepared by hydrolysis of tetra-(dimethylamino)-diboron in aqueous hydrochloric acid solutions and by neutral hydrolysis of tetraisopropoxy or tetraethoxydiboron (36).



Boron monoxide has also been prepared from the reaction of zirconium dioxide with elemental boron at 1800°C in vacuo (59), and as a product of the reaction of boric oxide with elemental boron at 1350°C in 60-70% yields (29). Boron monoxide prepared in this manner, is reported to be more reactive than that obtained from the dehydration of tetrahydroxydiboron. Boron monoxide, obtained by dehydration, has been converted to diboron tetrachloride by reaction with boron trichloride at approximately 200°C (36).



The preparation of diboron tetrafluoride was first reported by Arthur Finch and H. I. Schlesinger (17) in 1958. They accomplished the synthesis of diboron tetrafluoride by treating diboron tetrachloride, previously prepared by passing boron trichloride through an electric discharge between mercury electrodes (50), with freshly sublimed antimony trifluoride.

Diboron tetrafluoride is reported to be a stable gas at room temperature in contrast to diboron tetrachloride, which is a colorless liquid and undergoes partial decomposition at temperatures of 0°C and above. Finch and Schlesinger reported that the tetrafluoride liberated only a trace of boron trifluoride when heated at 100°C for

20 minutes, and even at 200°C only about 40% of the compound was lost by decomposition in several hours. The decomposition products were boron trifluoride and a yellow, nonvolatile solid.

Holliday and Taylor (25) state the amount of decomposition of diboron tetrafluoride at room temperature to be 8.2% after 27 hours and 21% after 96 hours and complete decomposition at 140°C after 96 hours. They further report that the decomposition products are mainly boron trifluoride and a solid polymer $(\text{BF})_n$, and that glass is attacked slightly to give small amounts of silicon tetrafluoride and oxygen difluoride.

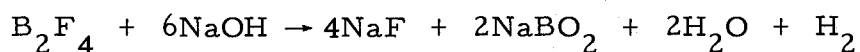
The melting point of diboron tetrafluoride is given as -56.0°C , its boiling point at -34.0°C , a heat of evaporation of about 6700 cal./mole and about 28 for the Trouton constant. Contrasting this to diboron tetrachloride, which has a melting point of -92.6°C , a boiling point of 65.5°C , a heat of evaporation of 8029 cal/mole and a Trouton constant of 23.7, we observe a higher melting point and Trouton constant and a smaller liquid range for the tetrafluoride. This difference would tend to indicate a greater intermolecular attraction for diboron tetrafluoride than for the tetrachloride in the solid and liquid state.

The chemical behavior of the tetrafluoride closely resembles that of the tetrachloride in many aspects. The Lewis acid properties of the tetrafluoride are exemplified by the stability of its dietherate

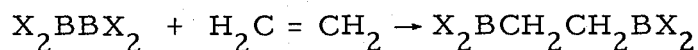
complex at temperatures below -23°C and of its mono-etherate at 0°C , which upon standing overnight at this temperature, did yield ethyl fluoride (17). This behavior toward diethyl ether is identical with that of diboron tetrachloride (50).

The tetrafluoride forms with trimethylamine a 1:2 compound, which has about 2 mm. vapor pressure at 80°C (17). From the vapor tension lowering method this complex appeared to be a tetramer $[\text{B}_2\text{F}_4 \cdot 2\text{N}(\text{CH}_3)_3]_4$. The corresponding adduct of diboron tetrachloride and trimethylamine also is a tetramer (50).

The hydrolysis of diboron tetrafluoride with 15% sodium hydroxide is like that of the tetrachloride and is represented by the equation (17)



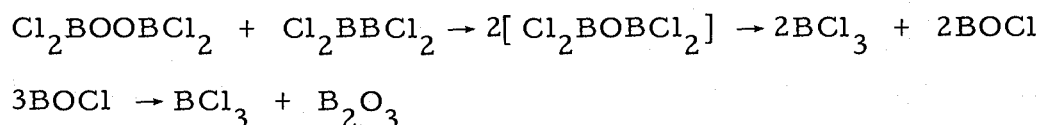
Reactions involving the boron-boron bond in diboron tetrafluoride toward unsaturated organic compounds are similar to those of the tetrachloride except that the former reacts much more slowly and the compounds it forms are much more stable.



The unsaturated compounds investigated have been ethylene, butene-2, allyl chloride, allyl fluoride, 4-chlorobutene-1, and acetylene (12). Allyl halides polymerize in the presence of diboron tetrafluoride, thus the latter may be acting as a catalyst. An interesting reaction

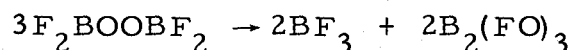
occurs between allyl fluoride and diboron tetrachloride yielding allyl chloride and diboron tetrafluoride. This indicates that allyl fluoride, in this case, acts as a fluorinating agent rather than as Lewis base. Diboron tetrahalides are inert to haloethylene compounds and add to acetylene only in a one mole to one mole ratio. Thus, either the presence of a halogen or a boron dihalide on a doubly-bonded carbon has the same effect in decreasing the reactivity of the double bond. When either the halogen or the boron dihalide are attached to α -carbons, the reactivity of the double bond is not as greatly affected.

Diboron tetrafluoride reacts explosively or with immediate inflammation with oxygen or nitric oxide (25). The reaction with oxygen produces mainly boron trifluoride and a solid residue having a composition of B_2O_3F . In contrast, the tetrachloride reacts with oxygen to produce boron trichloride and boric oxide (23). Holliday and Taylor (25) postulate that the tetrachloride can readily act as a Lewis Acid toward the $Cl_2BOOBCl_2$ oxidation intermediate and so give an overall diboron tetrachloride: oxygen reaction ratio of 2:1,

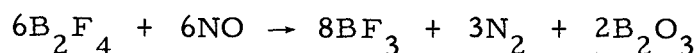
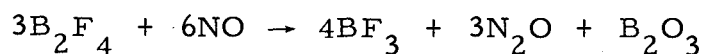


whereas the lower ratio in the case of the tetrafluoride may be due to less effective acceptance by the intermediate F_2BOBF_2 of a second diboron tetrafluoride molecule. The solid B_2O_3F may be a

mixture of boric oxide and $B_2(FO)_3$.



Diboron tetrafluoride reacts with nitric oxide to produce boron trifluoride, boric oxide, nitrous oxide and sometimes nitrogen (25).



There is no evidence of intermediate adduct formation between nitric oxide and diboron tetrafluoride whereas an adduct could be observed with nitric oxide and diboron tetrachloride at $-78^\circ C$. This suggests that diboron tetrafluoride is a weaker Lewis acid than diboron tetrachloride, a conclusion which has already been indicated by the less ready addition of olefins to the tetrafluoride than to the tetrachloride.

The structure of diboron tetrafluoride has been determined by Trefonas and Lipscomb via X-ray diffraction of a single crystal (48). The molecule has a planar, centrosymmetric structure with B-B distance of $1.67 \pm 0.04 \text{ \AA}$, B-F distance of $1.32 \pm 0.03 \text{ \AA}$, angle F-B-F equal to $120^\circ \pm 2.5^\circ$, and closest intermolecular F...F distance of $2.23 \pm 0.02 \text{ \AA}$. A comparison of the B-B bond distance of 1.67 ± 0.04 in diboron tetrafluoride with the value of 1.75 ± 0.05 in diboron tetrachloride (4) is consistent with the chemical properties of each, ie. the greater stability and less reactivity of the B-B bond in diboron

tetrafluoride. The closest F...F contact between atoms in different molecules are 3.27 $\overset{\circ}{\text{Å}}$ and 3.32 $\overset{\circ}{\text{Å}}$, which compare favorably with the 3.0 to 3.1 $\overset{\circ}{\text{Å}}$, range found in the slightly more strongly bound hydrogen-bonded or molecular-ion types of crystals. This close intermolecular distance in the solid diboron tetrafluoride indicates stronger forces than just the Van der Waal type.

The molecular structure of diboron tetrafluoride has been determined in the solid state (48) but its configuration in the liquid and gas state is unknown. Diboron tetrachloride has a unique molecular structure, for it has been shown to be planar in the solid state (4) but twisted in the liquid and gas state with one BCl₂ plane at a right angle to the other BCl₂ plane (35). Thus whether diboron tetrafluoride is twisted in the liquid or gas state comparable to diboron tetrachloride or planar like the solid state of both diboron tetrafluoride and diboron tetrachloride, would be interesting to know both from the standpoint of obtaining a better picture and understanding of the bonding within the molecule and also because of the possibility of explaining and predicting some of the chemical properties of the compound.

Since the preparation of diboron tetrafluoride is a long and tedious synthesis as well as requiring special apparatus (17), a more direct means of preparing this compound would be desirable. One interesting possibility for the synthesis of diboron tetrafluoride would be

the reduction of boron trifluoride with an alkali metal under controlled conditions to prevent the formation of other reduction products. Alkali metals dissolve in liquid ammonia and some amines to form blue solutions, and these solutions are known to be good reducing agents. Since boron halides participate in solvolysis reactions with ammonia, primary and secondary amines, the tertiary amines will be investigated as a possible reducing medium. Wilkinson, et al. (15) have reported that potassium and sodium-potassium alloy dissolve to form blue solutions in certain ethers, such as 1,2-dimethoxyethane (glyme) and tetrahydrofuran. Since ethers are aprotic solvents, blue solutions of alkali metals in 1,2-dimethoxyethane will also be investigated as a possible medium for reduction of boron trifluoride to diboron tetrafluoride.

Since the reduction of boron trifluoride takes place in glyme solvent, decomplexation and recovery of the reduced product, hopefully diboron tetrafluoride must be accomplished. One means of freeing the diboron tetrafluoride would be to use a stronger Lewis acid, which would exchange with the acid product. Since the relative acid strength of diboron tetrafluoride is not known the assumption will be made that it is intermediate between boron trifluoride and boron trichloride.

Boron trichloride has been shown to be a stronger Lewis acid than boron trifluoride (11). The reason for this appears to be that

the B-Cl bond is easily bent or distorted from 120° angles in boron trichloride to tetrahedral angles with each other when forming a complex, whereas the B-F bond, because of its greater back-coordination or partial double bonding, requires more energy to break the partial π bond in order to bend into a tetrahedral configuration as calculated by Cotton and Leto (14). If we assume that diboron tetrafluoride contains only a sigma type B-B bond and that the B-F bond has a bond order greater than one, then the former bond would require less energy to bend or distort. Comparing the $-\text{BF}_2$ group with $-\text{F}$, both appear to be strongly electronegative. If the electronegativity of the $-\text{BF}_2$ is assumed to be as great or greater than $-\text{Cl}$, one would predict that diboron tetrafluoride is a stronger Lewis acid than boron trifluoride. Assuming that the above prediction is true, then any Lewis acid considered for use in an acid exchange reaction with diboron tetrafluoride must at least displace the weaker acid boron trifluoride.

In addition to the study of the preparation of diboron tetrafluoride and its acid strength as compared to other boron compounds, some of its adducts with various Lewis bases will be prepared and their nature and properties will be investigated.

EXPERIMENTAL

Purification, Separation, and Identification of
Reagents and Products

The purification, separation, and identification of materials used in these investigations were carried out using general procedures described by R. T. Sanderson, "Vacuum Manipulation and Techniques" (41). For clarity some of these operations are described here. Determination of the purity of materials and their identification was most commonly accomplished tensiometrically. Where critical, further characterization was accomplished by means of infrared spectra and/or molecular weight determination. Vapor pressure equations for common reagents and products are listed in Table I. References to calculated vapor pressures in the discussion of experimental work apply to these equations unless otherwise annotated. Molecular weights were determined from gas densities at known temperatures by application of the ideal gas equation.

Materials were separated and purified by fractional condensation in a vacuum system unless otherwise stated. The method consists of passing a mixture through a series of traps cooled to progressively lower temperatures. Condensation of a component occurs at that temperature where its vapor pressure is negligible. Although such separations are only about as efficient as distillation separations in

TABLE I. VAPOR PRESSURE EQUATIONS OF COMMON REAGENTS.

Substance	Vapor Pressure Equation: $\log_{10} P_{\text{mm}} =$	Condensation Temperatures*	Ref.
HCl (liquid) (solid)	4.65739 - 905.53/T + 1.75logT - 0.0050077T 7.5030 - 1966.3/T + 1.1600	-196	21, 22
BF ₃ (solid) (liquid)	- 1176.6/T + 1.75log T - 0.0032084T + 6.6293 - 1174.4/T + 1.75logT - 0.013350T + 8.0536	-196	39
BCl ₃	+ 6.18811 - 756.89/(T-59)	-112	46, 32
B ₂ F ₄ (solid) (liquid)	10.82 - 1856/T 9.009 - 1466/T	-119	17
B ₂ Cl ₄	8.057 - 1753/T	-80	50, 54
CH ₃ OCH ₂ CH ₂ OCH ₃		-80	47
(CH ₃) ₃ N	-1357.8/T + 1.75logT - 3.9161 x 10 ⁻³ T + 4.6091	-112	57
(CH ₃ CH ₂) ₃ N	8.059 - $\frac{1838}{T}$	-80	37

*The maximum temperature at which a substance condenses in ordinary vacuum line operations using cold baths as listed in Table II.

a column of one theoretical plate, the method was generally satisfactory. Table I also lists the temperatures at which condensation in a high vacuum occurs for common materials used in this work. These temperatures refer to common cold baths as listed in Table II. Gases referred to as non-condensable in this work include those materials that exhibit an appreciable vapor pressure at the coldest temperature used, -196°C . Those of interest in this work include hydrogen, oxygen, nitrogen and methane gases.

TABLE II. COMMON COLD BATHS.

Bath	Temperature
Water-ice	0°C
Carbon tetrachloride slush	-23°C
Bromobenzene slush	-30.7°C
Chlorobenzene slush	-45.1°C
Chloroform slush	-63°C
Dry ice-acetone	-80°C
Toluene slush	-95°C
Carbon disulfide slush	-111.8°C
Ethyl bromide slush	-119°C
Methylcyclohexane slush	-126.7°C
Pentane slush (mixture of isomers)	-140 to -150°C
Isopentane slush	-160°C
Liquid nitrogen	-196°C

Chemicals

1. 1,2-Dimethoxyethane (glyme), obtained from the Eastman Chemical Co. , was distilled through a heated column packed

with glass helices. The glyme was placed in contact with sodium for a few hours to remove protonic impurities. It was distilled from sodium into the vacuum line as needed.

2. Boron trifluoride (Matheson Co.) was fractionated through a -145° trap into a -196° C trap with pumping. The fraction that condensed at -196° C had a vapor pressure of 5 mm at -145° C, calculated for boron trifluoride: 5.0 mm. at -145.3° C.
3. Boron trichloride (Matheson Co.) was fractionated through -80 , -112 , -196° C traps with pumping. The fraction condensing at -112° C had a vapor pressure of 4 mm at -80° C, calculated for boron trichloride: 4 mm. at -80° C.
4. Hydrogen chloride (Matheson Co.) was fractionated through -156 and -196° C traps with pumping. The fraction condensing at -196° C had a vapor pressure of 2 mm at -145° C and 28 mm at -127° C, calculated for hydrogen chloride: 2.6 mm at -145° C and 27.3 mm at -127° C.
5. N,N,N',N'-tetramethylethylenediamine was distilled into the vacuum line after standing in contact with phosphorus pentoxide for 12 hours. The N,N,N',N'-tetramethylethylenediamine had vapor pressures of 3.5 mm at 0° C and 11 mm at 22° C.
6. Trimethylamine (Matheson Co.) was passed through a

column containing phosphorus pentoxide on glass beads and fractionated through -80 , -112 , and -196° C traps. The fraction condensing at -112° C had 6 mm vapor pressure at -80° C, calculated for trimethylamine: 7 mm at -80° C.

7. Triethylamine (Eastman Chemical Co.) was distilled through a column packed with phosphorus pentoxide on glass beads into the vacuum line and collected at -80° C. It exhibited a vapor pressure of 18 mm at 0° C, calculated for triethylamine: 21 mm at 0° C.
8. Tetra-(dimethylamino)-diboron was obtained from the U. S. Borax and Chemical Corp., Anaheim, California, and was used without further purification. Tetra-(dimethylamino)-diboron is a colorless liquid with a reported 10.85 percent boron, theoretical 10.93.

Apparatus

Vacuum System

A standard all-glass vacuum system, equipped with high vacuum stopcocks, a two-stage mercury diffusion pump and a Welch Duo-Seal vacuum pump, was utilized for much of the experimental work. The stopcocks and the standard taper and ball joints were lubricated with either Kel-F#90, Kel-F#150, or Apiezon N grease. Most of the

reactions were carried out under vacuum conditions, which may therefore be assumed, unless it is stated otherwise.

Infrared Cells

The infrared cell used at liquid nitrogen temperature is similar to those of Walsh and Willis (51), and Bovey (6). It was equipped with sodium chloride windows held against the glass flange with Apiezon Q, providing a vacuum seal. In this device the gas sample is introduced through a jet directed toward an optical sodium chloride crystal mounted snugly in a copper frame. The sodium chloride crystal is held in place with a very small amount of grease. The copper frame is attached to the center glass tube by a Housekeeper seal, and maintained at low temperature by thermal contact with an exterior chamber containing liquid nitrogen.

The infrared spectra of gases were determined in a 10 cm. glass cell equipped with sodium chloride windows (See Figure 1). The use of Apiezon Q to attach the salt windows to the cell was found to be unsatisfactory for the boron halides, which interacted with Apiezon Q and other common sealants. An all-metal seal, which proved to be vacuum tight and did not appear to react with boron halides, was constructed for attaching the rock salt windows to the glass cell. This vacuum-tight metal seal was obtained by amalgamating a circular lead gasket cut from 0.005 inch thick foil. The amalgamation

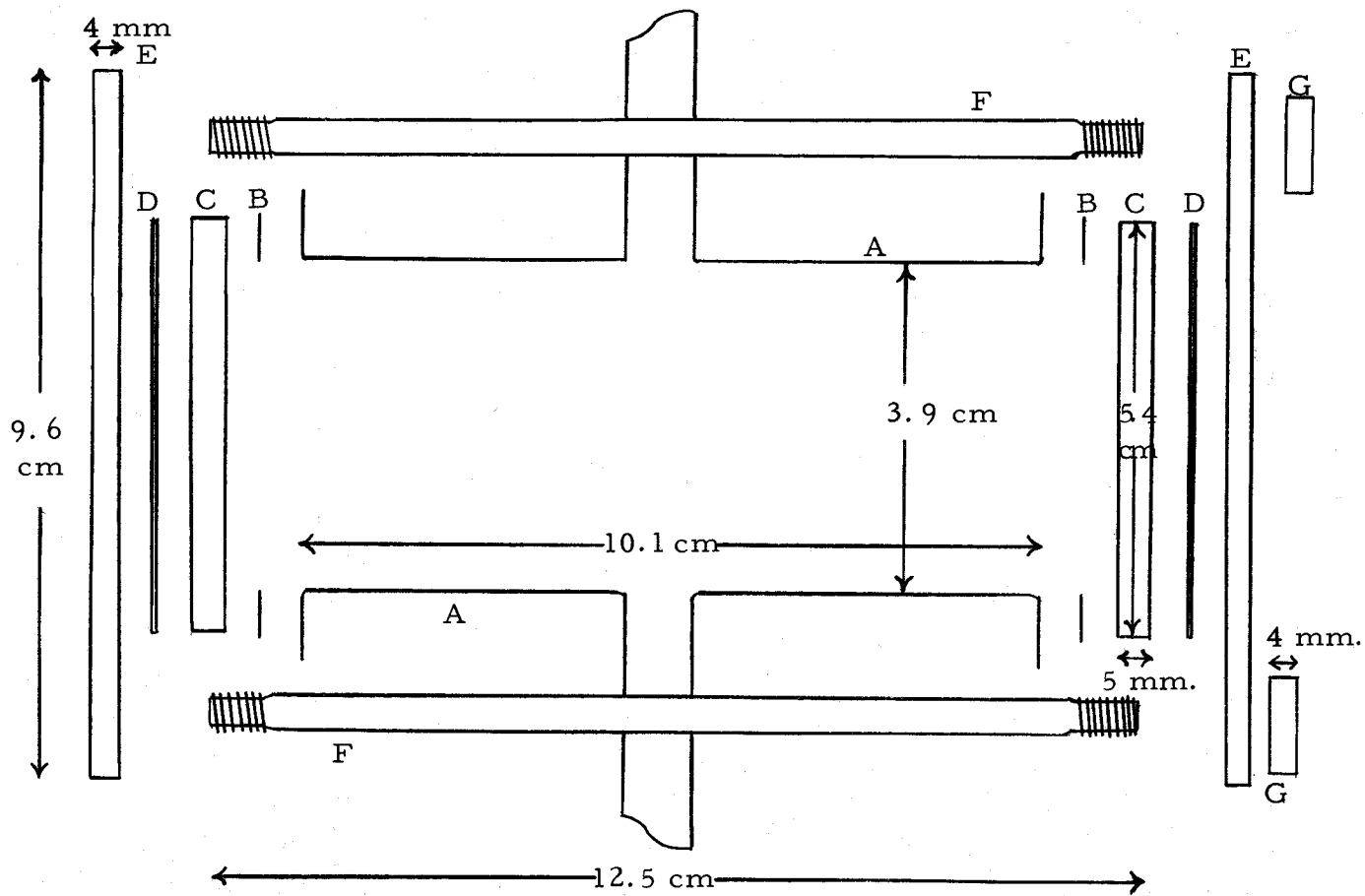


Figure 1. All metal sealed gas cell for infrared spectra. (A) Pyrex glass cylinder with flanges, (B) 0.005 inch amalgamated lead foil, (C) Salt windows, (D) Rubber gasket (E) Aluminum plate (F) Aluminum Rod (G) Nut

was accomplished by placing a few drops of mercury on the lead gasket and rubbing the surface with a rubber-gloved finger until the entire surface appeared shiny, and then repeating this operation on the reverse side. After allowing a few minutes for the gaskets to completely amalgamate, the excess mercury was wiped off with a tissue. This amalgamated gasket formed a vacuum-tight seal with the sodium chloride window. A vacuum-tight seal between the gasket and the glass cell was effected by first silvering the flange part of the cell, which can then form a silver amalgam bond with the amalgamated lead gasket. The silver plate was deposited on the clean glass surface by submerging it in an ammoniacal silver nitrate solution to which a reducing sugar had been added (13).

The windows were held to the cell mechanically by aluminum plates, which have a rectangular hole cut in them to permit a maximum amount of radiation to pass through. The plates were connected to each other with four threaded aluminum rods, with one end passing through one of the plates to a nut and the other end screwed into a threaded hole in the other plate. This was done to keep the length of the cell to a minimum so that it would easily fit into a Beckman IR-7 sample beam. The aluminum plates were separated from the windows by a rubber gasket. After the cell was assembled, it was allowed to stand overnight before evacuating. After assembly, the lead amalgam--salt and lead amalgam--glass seals had a mirror-like

appearance. When assembled in this fashion, the cell held a vacuum for periods up to several months. In disassembling the cell for cleaning it was found to be much more satisfactory to break and reassemble the glass-lead amalgam seal than the salt-lead amalgam seal. The lead gasket adheres so strongly to the salt window that fracture of small pieces of salt-window would occur when this seal was broken.

Special Reaction Vessel

A reaction vessel, illustrated in Figure 2, was constructed and used in those experiments involving reactions of solutions of sodium-potassium alloy in glyme.

Liquid sodium-potassium alloy was injected through opening B while a stream of nitrogen was passed through the nitrogen-filled apparatus from opening A. Opening B was sealed and the vessel was evacuated through opening A. Purified glyme was distilled onto the alloy and the vessel was sealed off at the constriction below A.

The vessel was then attached to the vacuum line at D and evacuated. A reactant and additional glyme were condensed in E and the vessel was sealed off at the constriction below D.

Tube C, containing glyme and alloy, was cooled in a dry ice-acetone bath to -80° C to produce the blue solution. The thin glass seal at F was broken and the alloy solution was poured through a glass wool plug into tube E containing the other reactant. When the

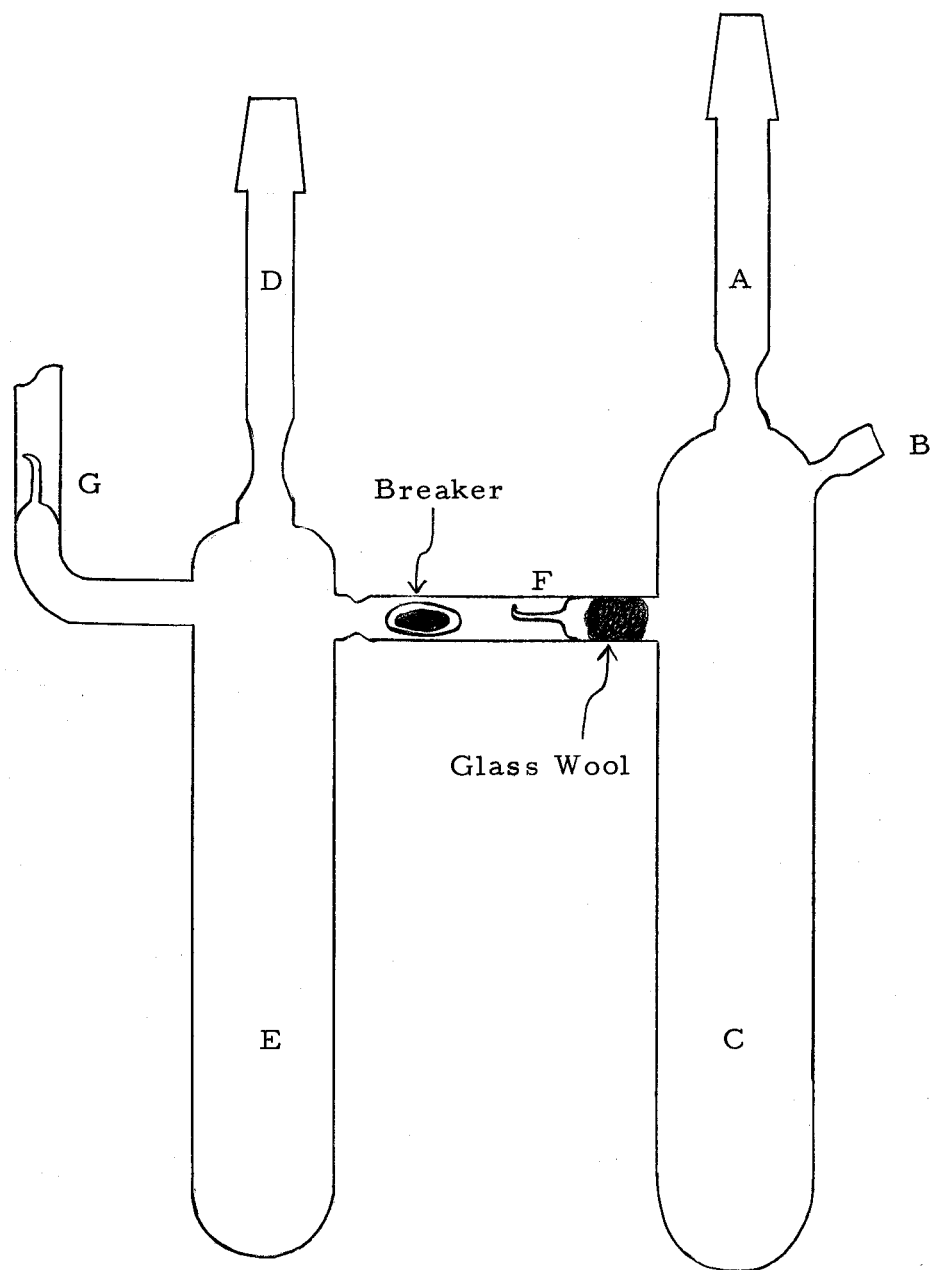


Figure 2. Special reaction vessel.

blue color of the alloy solution had disappeared, glyme was condensed back into tube C and the cycle was repeated as necessary to complete the reaction. The connection between tubes E and C was sealed off and further reactions or product removal was accomplished through closure G.

Reactions

Solubility of Sodium-potassium Alloy in Tertiary Amines

Triethylamine and N,N,N',N'-tetramethylethylenediamine dried over calcium hydride were distilled in the vacuum line into separate tubes each containing sodium-potassium alloy. Both tubes remained at room temperature for seven days, thus allowing the alloy to react completely with any impurities present. During this time only a small amount of brown material, which may have been stopcock grease, formed on the bottom of tubes. The triethylamine tube was cooled to -112° C and the N,N,N',N'-tetramethylethylenediamine tube to -63.5° C for 48 hours. Both temperatures are just above the freezing points of the respective solvents. After 48 hours neither solvent showed the blue color characteristic of alkali metal solutions. The two tubes remained at room temperature overnight and then were cooled to -112° and -63.5° C again for eight hours with the same results.

Reduction of Boron Trifluoride by Alkali Metal in Glyme Solution

The reduction of boron trifluoride by alkali metal in glyme was carried out in the apparatus described earlier and shown in Figure 2. Glyme, purified as described earlier, was condensed into the vacuum line at -30°C . It showed a vapor pressure of 18 mm at 0°C , slightly lower than the literature value of 20 mm at -3°C . It was stored over liquid sodium-potassium alloy until a blue solution could be formed readily by cooling to -80°C . The glyme was then distilled onto fresh alloy in the reaction vessel. Approximately two ml. of glyme was distilled into the other arm of the reaction vessel together with 1.7 mmoles of boron trifluoride.

After the first tube, containing the glyme-alloy mixture, had been cooled to -80°C for one hour, the glass seal between the two tubes was broken and the blue solution was added slowly through the glass wool plug to the boron trifluoride-glyme complex at -80°C . The blue color was discharged immediately upon contact with the complex solution.

The glyme was distilled back onto the alloy to reform an alkali metal solution which was then poured into the tube containing the complex. This procedure was repeated many times and finally terminated when the blue color persisted for about five seconds after the thirty-eight addition to the complex. From the second addition

onward a white solid, presumably alkali metal fluoride, was observed in the reaction tube after removal of glyme. Very slow formation of a non-condensable gas was also observed. There was no dark-colored material in the reaction tube to indicate the presence of elemental boron or an alkali metal boride.

Repetition of this experiment with 1.73 mmoles boron trifluoride starting material and then 2.0 mmoles boron trifluoride gave essentially the same results.

Excess boron trifluoride (2.45 mmoles) was condensed at -196°C into a vessel containing 0.91 mmole of glyme. Upon warming to room temperature a white solid was formed. Excess boron trifluoride (0.82 mmoles) was removed at -80°C leaving 1.63 mmoles boron trifluoride to 0.91 mmoles of glyme in the complex, a ratio of 1.8 to 1.0.

Treatment of this complex with alkali metal solution in glyme, gave the same results as when glyme was present in excess in the original solution of boron trifluoride.

Characterization of the Boron Trifluoride Reduction Product

The reaction vessel from the previous experiment was sealed off from the tube containing alkali metal and attached to the vacuum line. After most of the glyme had been removed, excess boron trifluoride was added in order to complex the remaining glyme and

perhaps displace the reduction product from its complex with glyme. Boron trifluoride was added until no more was readily absorbed by the remaining ether. The original pressure of about 400 mm. of boron trifluoride dropped to about 200 mm. four hours later. The gaseous products were passed through -112 to -196° C traps with only a trace of material remaining at -112° C (diboron tetrafluoride is condensable at -112° C). The -196° fraction was returned to the complex tube, where it remained 12 hours at room temperature. This gas was again passed through -112 to -196° C traps with no condensate at -112° C. Additional boron trifluoride was added to the complex and the tube was heated at 85 to 90° C for 30 hours in a water bath. The tube was cooled to room temperature, and the volatile materials fractionated through -112° C to -196° C. The -112° trap contained a small amount of material; the -196° fraction was returned to the complex tube and remained there for two weeks at room temperature. After this period, the volatile materials were again removed and fractionated through -112 to -196° C. The -112° condensates from these various separations were combined and further purified by passage through a series of traps at -80° , -112° , and -196° C. The fraction condensing at -112° consisted of 0.023 mmole of material with an experimentally determined molecular weight of 161 (calculated for diboron tetrafluoride: 97.6).

Four ml. of 17 % sodium hydroxide solution was added to the

complex tube in order to hydrolyze any boron-boron bonds present. 0.36 mmole of non-condensable gas was formed. A portion of this gas was placed in contact with 0.1 g. palladium dichloride. After 24 hours a small amount of non-condensable gas was pumped out and 0.38 mmole of gas condensable at -196° C was found. This condensable gas had vapor pressures of 120.5 mm. @ -112° C and 63.5 mm. @ -119° C (calculated for hydrogen chloride: 125.6 mm. @ -111.9° C and 60.3 mm. @ -119° C). Therefore, the original non-condensable gas was almost pure hydrogen and the total amount (0.36 mmoles) corresponded to a 42% yield of boron-boron bond based on the original amount of boron trifluoride.

Synthesis of Diboron Tetrafluoride

Tetra-(dimethylamino)-diboron was used as the starting material for the synthesis of diboron tetrachloride via McCloskey's method (36). 6N. hydrogen chloride was added slowly over a one-hour period to tetra-(dimethylamino)-diboron in a closed system forming a white precipitate of hypoboric acid. This solid was filtered off and washed with a small amount of 0.1N. hydrogen chloride. The product was dehydrated at 250° C for five hours to boron monoxide. Boron trichloride was passed slowly through the solid boron monoxide held at 250° C. The volatile materials were fractionated through -80° , and -119° to -196° C. A small amount of material

condensed at -80°C was retained (diboron tetrachloride condenses at -80°C , boron trichloride has a vapor pressure of 4 mm. at this temperature). The -119°C fraction of boron trichloride was repeatedly passed through the boron monoxide at 250°C , and each time the -80°C fraction was collected. A -196°C fraction (presumably hydrogen chloride from a hypoboric acid residue and boron trichloride) was always found after each fractionation and was discarded. The combined -80°C fraction had a vapor pressure of 42 mm. at 0°C comparing closely with the literature value of 44 mm. at 0°C for diboron tetrachloride. When a small portion of this fraction came into contact with air, it produced a blue flame, a characteristic of the diboron halides.

The diboron tetrachloride was condensed into a tube containing freshly sublimed antimony trifluoride and held overnight at -80°C (50). The volatile materials were removed and added to a fresh charge of antimony trifluoride. After a few hours at -80°C , the reaction bulb was allowed to warm to room temperature for a few minutes. The volatile material was fractionated through -95° , and -119° to -196°C . The fraction collected at -119°C had a vapor pressure of 16 mm. at -80°C and immediately inflamed in the presence of air. This is the same vapor pressure as given by Finch and Schlesinger for diboron tetrafluoride (17). This is a typical diboron tetrafluoride synthesis, which was repeated many times during

the course of this work.

Diboron tetrafluoride was found to vary in stability at room temperature from sample to sample but was never completely stable. Typically, a sample of diboron tetrafluoride, having no vapor pressure at -119° C, that remained at room temperature for a period of time, would show small residual pressure when recooled to -119° C. Upon fractionation, a small amount of boron trifluoride could be separated and a dark residue appeared on the walls of the vessel. Because of its instability, diboron tetrafluoride was always stored at -196° C.

Reaction of Tetra-(dimethylamino)-diboron with Boron Trifluoride, Antimony Trifluoride, Boron Trifluoride in the Presence of Antimony Trifluoride and Boron Trifluoride in the Presence of Boron Trichloride

Tetra-(dimethylamino)-diboron was distilled into a bulb containing freshly sublimed antimony trifluoride. The antimony trifluoride was soluble in liquid tetra-(dimethylamino)-diboron. No apparent reaction occurred in 40 hours at room temperature or in one hour at 100° C as indicated by the lack of any volatile product or change in appearance of the solution. When the container was heated briefly with a free flame, white fumes and a black solid were produced. Separation of products by fractional condensation gave silicon tetrafluoride as the only volatile substance produced in sufficient amount to allow identification. Silicon tetrafluoride can be

produced by heating antimony trifluoride in glass with no other reactants.

Boron trifluoride formed a white, slightly volatile, crystalline complex with tetra-(dimethylamino)-diboron. Treatment of this complex with excess boron trifluoride at temperatures up to 150°C gave only traces of volatile products although some reaction occurred at temperatures of 100°C and higher as indicated by darkening in color and the formation of a non-volatile, viscous liquid. Addition of boron trichloride to the boron trifluoride--tetra-(dimethylamino)-diboron complex gave 0.10 mmole of a gas, volatile at -127°C . A small amount of material, condensible at -127°C was produced which did not inflame in the presence of air.

Treatment of tetra-(dimethylamino)-diboron with boron trifluoride in the presence of antimony trifluoride gave an immediate reaction at room temperature with the formation of a black solid. Only traces of volatile material were formed.

Reaction of Boron Trichloride with Tetra-(dimethylamino)-diboron

A sample of tetra-(dimethylamino)-diboron was treated with excess boron trichloride for a 10-minute period at room temperature. The resultant liquid was cooled to 0°C , and the material volatile at this temperature was fractionated through -80°C into -196°C . The fraction condensing at -80°C had vapor pressures of 20 mm. at

room temperature and 7 mm. at 0° C. Both fractions were returned to the reaction tube for an additional period. Separation of the products by fractional condensation gave a material volatile at -80° C, and an unstable liquid with vapor pressure of 23 mm. at 22° C. Neither of these fractions were volatile enough to contain diboron tetrachloride in significant amounts so they were not further investigated.

Reaction of Boron Trifluoride with Boron Suboxide

Boron trifluoride was passed through -145° into -196° C, and then complexed with p-chlorobenzonitrile (Eastman Chemical Co.) at 0° C. The boron trifluoride recovered from the warmed complex was passed slowly through boron suboxide at $210 - 250^{\circ}$ C which had been previously in contact with boron trichloride. This was accomplished by passing boron trifluoride from a bath slightly warmer than -112° C to a -112° C bath. The volatile materials were collected from the reaction vessel and fractionated through -80° , -126° , to -196° C. In the U-tube, used to condense the volatiles before fractionation, was found a white solid material that moved slowly to the -80° C bath. This white solid apparently vaporized upon standing for 1 1/2 hours and was not recovered. The only other substance found was a compound which had a vapor pressure comparable to that of boron trifluoride at -127° C.

Reaction of Boron Trifluoride with Glyme

Boron trifluoride (1.55 mmoles) was added to glyme (0.66 mmoles) in an evacuated vessel. The white solid that formed was melted at about 100°C to insure complete complexation of the glyme. Separation of volatile materials by fractional condensation gave 0.30 mmoles of a gas volatile at -145°C , condensing at -196°C . It exhibited vapor pressures of 7 mm. at -145°C and 60 mm. at -127°C , known values for boron trifluoride are 5 mm. at -145.4° and 59.8 mm. at -127.3°C (39). Thus, 1.25 mmoles of boron trifluoride reacted with 0.66 mmoles of glyme, a 1.9 to 1.0 ratio.

Treatment of the complex with excess glyme gave a colorless solution. Subsequent removal of excess glyme at 0°C gave a white solid, slightly volatile at room temperature, condensing at 0°C .

Displacement of Boron Trifluoride from Glyme with Boron Trichloride

Boron trifluoride (7.7 mmoles) was treated with excess glyme and then the excess was removed leaving a non-volatile liquid. Addition of boron trichloride (8.1 mmoles) gave an exothermic reaction at room temperature with formation of white crystals accompanied by a slow increase in pressure. Separation by fractional condensation from -112°C gave two volatile products condensing at -145°C and -196°C respectively. The material condensing at -145°C (11.5 mmoles) had vapor pressures of 0.5 mm. at -126°C and a

molecular weight of 51.4 as determined by vapor density. Methyl chloride calculated molecular weight 50.5, has vapor pressures of 10 mm. at -92.4°C and 40 mm. at -76.0°C (13). Boron trichloride is known to react with ethers to produce alkyl chlorides (40).

The fraction condensing at -196°C had a vapor pressure of 78.5 mm. at -126°C , calculated for boron trifluoride: 80.0 mm. The amount, 4.8 mmoles, represents a 62% displacement from glyme.

The experiment was repeated at -80°C in an attempt to avoid formation of methyl chloride. The boron trifluoride-glyme complex (7.4 mmoles of boron trifluoride) treated with boron trichloride (7.9 mmoles) at -80°C gave 0.2 mmoles of methyl chloride and 1.2 mmoles of boron trifluoride over a period of 12 days.

Attempts were made to increase the recovery of boron trifluoride from glyme by displacement with boron trichloride at 50°C . In a typical experiment 1.7 mmoles of boron trifluoride as the glyme complex was treated with 5.27 mmoles of boron trichloride at 50°C for 17 hours. Fractionation of the volatile materials gave 1.25 mmoles of methyl chloride condensing at -145°C and 1.15 mmoles of boron trifluoride plus 0.46 mmoles of hydrogen chloride condensing at -196°C . Boron trifluoride and hydrogen chloride were separated by forming an anisole (Eastman Chemical Co.) complex of boron trifluoride at -30°C , from which hydrogen chloride could be separated. Hydrogen chloride was identified by its vapor pressure

at -126°C , 29 mm., calculated: 30 mm. Since hydrogen chloride forms a complex of low stability with anisole at -30°C , 0.46 mmoles is the minimum amount of hydrogen chloride produced and 1.15 mmoles of boron trifluoride the maximum amount.

Reaction of Boron Trifluoride-Glyme Complex with Trimethylamine

A 1:1 complex of boron trifluoride (10.4 mmoles) with glyme was treated with trimethylamine (4.8 mmoles) at room temperature for four days. During this time volatile material that condensed at -80°C was removed periodically yielding a total of 3.7 mmoles of gaseous product. The material exhibited a vapor pressure of 65 mm. at 21°C corresponding closely to the value of 60 mm. at 19.7°C reported for glyme.

Addition of excess trimethylamine gave a total consumption of 8.4 mmoles with the production of additional glyme in unmeasured amount.

Reaction of Boron Trifluoride-Trimethylamine Complex with Hydrogen Chloride

2.4 mmoles of trimethylamine were treated with 9.5 mmoles of boron trifluoride forming a white solid. 7.1 mmoles of boron trifluoride were recovered, thus leaving 2.4 mmoles complexed with 2.4 mmoles trimethylamine, a 1:1 ratio. 13.6 mmoles of hydrogen

chloride were added to the complex. After four hours at room temperature the gas was collected, and found to have a vapor pressure of 35 mm. at -127° C (calculated for hydrogen chloride: 27.3 mm. : calculated for boron trifluoride: 70 mm. at -127° C).

Further treatment of the complex with hydrogen chloride at $85-90^{\circ}$ C for nine hours gave the same results, a gas with vapor pressure of 34 mm. at -127° C. A mixture of 6.3 mmoles of hydrogen chloride and 3.6 mmoles of boron trifluoride was compounded and found to have a vapor pressure of 69 mm. at -127° C. Thus, hydrogen chloride does not displace boron trifluoride from its trimethylamine adduct.

A similar experiment conducted with triethylamine in place of trimethylamine gave the same general results--no displacement of boron trifluoride.

Reaction of the Boron Trifluoride-Glyme Complex with 2,6-Lutidine

Boron trifluoride-glyme complex was prepared from 5.4 mmoles of boron trifluoride and excess glyme. After removing the excess glyme the complex was treated with 2,6-lutidine for 24 hours at room temperature. Materials volatile at 0° C were removed and exhibited a vapor pressure of 32 mm. at 24° C (2,6-lutidine at room temperature has a vapor pressure of 4.5 mm.).

Treatment of the resultant complex with excess hydrogen

chloride (17.8 mmoles) gave liquefaction and some darkening of the reaction mixture. However, all of the hydrogen chloride and no other volatile product was recovered upon fractionation even when the mixture was submitted to a temperature of 95° C for two hours.

Attempted Displacement of Boron Trichloride from its Triethylamine Complex

Boron trichloride (2.64 mmoles) was complexed with excess triethylamine. After the excess amine had been removed, 12.0 mmoles of hydrogen chloride were put in contact with the complex. After three days of room temperature only hydrogen chloride could be recovered as a volatile product.

Attempted Displacement of Boron Trichloride from its 2,6-Lutidine Complex

Boron trichloride (10.6 mmoles) was complexed with 2,6-lutidine by treatment of a sample of the amine with excess boron trichloride and then removal of the excess by volatilization at room temperature.

The dark red solid complex was treated with hydrogen chloride (8.3 mmoles) at room temperature for three days and, subsequently, at 100° C for two hours. Fractionation in both cases gave no volatile material other than hydrogen chloride. Treatment of the complex with boron trifluoride (7.3 mmoles) at 100° C for two hours

gave no volatile material condensible at -127° C.

Reaction of Boron Trifluoride-Glyme Complex with Aluminum Chloride

Boron trifluoride (4.17 mmoles) was added to excess glyme. The uncomplexed glyme was removed and small pellets of anhydrous aluminum chloride were added to the remaining liquid complex. Volatile material was separated by fractional condensation at intervals up to one week later. Identifiable products included methyl chloride (0.27 mmoles), vapor pressures 0.5 mm. at -127° C and 28.5 mm. at -80° C (literature values: 10 mm. at -92.4° C and 40 mm. at -76.0° C.) (13), and hydrogen chloride (0.38 mmole), vapor pressures 28 mm. at -127° C and 123 mm. at -112° C (calculated 28 mm. at -127° C and 123 mm. at -112° C). Less volatile materials, condensing at -80° C apparently included fragments of the glyme molecule produced in the decomposition reaction with AlCl_3 but were not purified or identified. No evidence of boron trifluoride was found in the material volatile at -145° C.

Similar results were obtained using freshly sublimed aluminum chloride and reaction temperatures up to 180° C.

Reaction of Boron Trichloride with Trityl Chloride

Trityl chloride was prepared by the reaction of thionyl chloride

with triphenylmethanol in hot benzene. Petroleum ether was added and the mixture was cooled in ice water. The filtered precipitate was a yellowish white solid with a melting point of 101 - 105^o C. Resolution in benzene, followed by treatment with norite and re-separation gave a light yellow product with a melting point of 98-100^o C, much below the literature value of 111-112^o C. The impure tritylchloride was converted to tritoxyethane by treatment with absolute ethanol at 78^o C. Upon cooling in an ice bath a white, crystalline material precipitated, which was filtered and washed with petroleum ether. After recrystallization from ethanol, its melting point was 79-82^o C. The tritoxyethane was dissolved in benzene, and hydrogen chloride gas was passed through the solution for several hours. The solution was then boiled down to 15 ml., cooled in an ice bath, and diluted with petroleum ether. The precipitate was filtered, washed with petroleum ether, and dried in a vacuum dessicator. The white crystalline product had a melting point of 107-109^o C, softening at 100^o C. The trityl chloride was treated with boron trichloride (4.60 mmoles) giving a yellow product immediately. After two days at room temperature and 10 hours at 80^o C, the volatile materials were removed from the reaction bulb at 0^o C and fractionated. 3.97 mmoles of material having a vapor pressure of 4 mm. at -80^o C was separated (calculated for boron trichloride: 4 mm. at -80^o C). A mixture of more volatile material, 0.84 mmoles in total, was also produced but

was not further identified.

Reaction of Boron Trichloride with Nitrobenzene

Boron trichloride (3.64 mmoles) was allowed to come into contact with excess nitrobenzene (Mathieson Coleman and Bell) at room temperature. After condensation of all of the material at -196°C , material volatile at -23°C was removed. The boron trichloride-nitrobenzene adduct was warmed to room temperature and volatile materials were separated by fractional condensation. The products included 1.34 mmoles of boron trichloride, vapor pressure 5 mm. at -80°C , (calculated: 4 mm. at -80°C) and a more volatile fraction (0.64 mmoles), not further identified.

Reaction of Boron Trifluoride with Nitrobenzene

Excess nitrobenzene (Mathieson, Coleman and Bell) was treated with boron trifluoride (0.82 mmoles) at 0°C for three hours. The volatile materials were removed from the reaction tube at 0°C leaving a small amount of white solid residue. The volatile material was boron trifluoride (0.71 mmole) identified by its vapor pressure of 306 mm. at -112°C (calculated: 296 mm.), and nitrobenzene.

Reaction of Boron Trifluoride with Benzonitrile

Excess benzonitrile (Mathieson Coleman and Bell) was treated

with boron trifluoride (0.86 mmoles) at 0° C. The pressure due to boron trifluoride disappeared almost immediately and the liquid benzonitrile darkened slightly in color. Unreacted benzonitrile was distilled away at 80° C leaving a white, crystalline solid. The white solid sublimed at 150° C. No boron trifluoride was recovered even at this temperature.

Reaction of Boron Trifluoride with p-Chlorobenzonitrile

Excess freshly sublimed p-chlorobenzonitrile (Eastman Chemical Co.) was treated with boron trifluoride (1.02 mmoles). After 30 minutes at 45° all but a few millimeters of the boron trifluoride pressure had disappeared. However, when the reaction vessel was held at room temperature 0.92 mmoles of boron trifluoride condensed away into a cold trap in a period of 40 minutes. When the reaction vessel was held at 0° C the rate of loss of boron trifluoride was slower and at -30° C only a trace of boron trifluoride condensed into a cold trap in a period of 10 minutes. Therefore, the complex is stable at -30° C, but is unstable toward loss of boron trifluoride at temperatures of 0° C and higher.

When hydrogen chloride was placed in contact with p-chlorobenzonitrile at -80° , $+45^{\circ}$, and room temperature, no absorption of hydrogen chloride was observed.

A mixture of 0.97 mmoles of hydrogen chloride and 0.92 mmoles

of boron trifluoride was allowed to come in contact with p-chlorobenzonitrile. After one hour at 45°C , 0.98 mmoles of hydrogen chloride was condensed from reaction tube at -80°C . Measured vapor pressure 32.5 mm. at -127°C , calculated 27 mm. With the reaction vessel at 80°C , 0.80 mmoles of boron trifluoride passed a -80°C trap and condensed at -196°C . The presence of yellow solid material in the -80°C trap indicated that the remainder of the boron trifluoride was still complexed with p-chlorobenzonitrile.

Reaction of Boron Trichloride with p-Chlorobenzonitrile

Excess p-chlorobenzonitrile (Eastman Chemical Co.) was treated with boron trichloride (1.03 mmoles) at -80°C . The temperature was increased slowly to approximately 50°C . After three hours at this temperature the volatile products were separated by fractional condensation. A small fraction (0.07 mmoles) that passed a -112°C trap and condensed at -146°C consisted primarily of boron trichloride as indicated by its vapor pressures of 2.5 mm. at -112°C and 9 mm. at -80°C (calculated for boron trichloride: 4 mm. at -80°C). Splitting this fraction roughly in half by distillation left a residue with a vapor pressure of 4 mm. at -80°C .

A larger fraction (0.24 mmole) that passed the -146°C trap and condensed at -196°C consisted primarily of hydrogen chloride as indicated by vapor pressures of 123 mm. at -112°C , 30 mm. at

-126° C and 2 mm. at -148° C (calculated for hydrogen chloride: 123 mm. at -112° C, 30 mm. at -126° C, and 2 mm. at -148° C).

A portion of this fraction, dissolved in a glyme-water mixture, gave a positive chloride test when treated with silver nitrate solution followed by ammonium hydroxide.

Repetition of this experiment at temperatures up to 150° C gave essentially the same results: production of hydrogen chloride gas, other decomposition products, and only small amounts of boron trichloride recovered.

Reactions of Boron Trifluoride and of Boron Trichloride with p-Nitrotoluene

Excess p-nitrotoluene (practical grade) was degassed at room temperature by pumping for a ten minute period and then treated with boron trifluoride (0.85 mmoles) at room temperature for three hours. Only a slight decrease in pressure was observed under these conditions so the temperature was increased to 60° C, where p-nitrotoluene is a liquid, for one hour. After re-cooling the boron trifluoride pressure was the same as initially. A total of 0.75 mmoles of boron trifluoride was recovered upon separation from the p-nitrotoluene.

Boron trichloride (0.42 mmoles) was added to the p-nitrotoluene recovered from the treatment with boron trifluoride. When the

temperature was raised to room temperature gas pressure slowly increased over a 20-minute period and, upon separation, two volatile fractions were isolated. 0.19 mmoles of boron trichloride vapor pressure 5 mm. at -80°C (calculated: 4 mm.) were recovered along with a second material (0.31 mmoles) that passed a -126° trap and condensed at -196°C . This material had a vapor pressure of 43 mm. at -126°C and was assumed to be primarily hydrogen chloride, vapor pressure 30 mm. at -126°C .

In a similar experiment 0.66 mmoles of boron trichloride with excess p-nitrotoluene gave 0.24 mmoles of material more volatile than boron trichloride and 0.51 mmoles of boron trichloride was recovered. It was observed that after an initial separation of volatile materials at -80°C boron trichloride was released from the complex at 0°C and higher temperatures. Thus, in this experiment 0.33 mmoles of boron trichloride was generated at room temperature after the initial separation of volatile material (assumed to be hydrogen chloride), and upon heating to 60°C for 30 minutes additional boron trichloride was liberated from the complex.

Reaction of Boron Trichloride with p-Nitroanisole

Excess p-nitroanisole (Eastman Chemical Co.) was degassed at room temperature for ten minutes and then treated with boron trichloride (0.65 mmoles). Gas pressure decreased rapidly at room

temperature accompanied by a color change of the solid from grey to brown. After 12 hours at room temperature and five minutes at 45° C, the material volatile at 0° C was separated. It consisted of a small amount (0.10 mmoles) of a gas more volatile than boron trichloride (vapor pressure greater than 70 mm. at -80° C), but may have contained some boron trichloride.

The vessel was heated to 45° C and materials volatile at this temperature were removed and fractionated. The material that passed a -80° C trap was essentially pure boron trichloride (0.55 mmoles) (vapor pressure 9.5 mm. at -80° C in a small volume). The boron trichloride was essentially reabsorbed by the p-nitroanisole at 0° C but a small residual pressure was observed and small amounts of boron trichloride (0.05-0.14 mmoles) could be recovered by pumping at this temperature after equilibration.

Similar experiments using freshly sublimed p-nitroanisole confirmed the small decomposition pressure of the complex at 0° C and the nearly quantitative recovery of boron trichloride at 45-60° C although the resultant boron trichloride always contained small amounts of a more volatile impurity as indicated by the vapor pressure at -80° C of 6.5 mm. This result was obtained even when p-nitroanisole that had been previously treated with boron trichloride was used in a second reaction with fresh boron trichloride. Some examples of yields are: 0.58 mmoles boron trichloride recovered from 0.58

mmoles of starting material, 0.79 mmoles boron trichloride recovered from 0.91 mmoles of starting material, and 0.72 mmoles boron trichloride recovered from 0.83 mmoles of starting material.

The boron trichloride-p-nitroanisole complex had a yellow color in contrast to white p-nitroanisole.

Displacement of Diboron Tetrafluoride from Glyme with Boron Trifluoride

Glyme (0.614 mmoles) was treated with diboron tetrafluoride (0.101 mmoles) at room temperature for 90 minutes. Excess glyme was removed leaving 0.103 mmoles in the complex. The resultant white solid was treated with 1.17 mmoles of boron trifluoride at -80° C for 30 minutes and then warmed to room temperature where volatile materials were separated. 0.024 mmoles of diboron tetrafluoride was recovered by trapping at -119° C. The boron trifluoride which passed -119° C and condensed at -196° C was returned to the reaction vessel for five hours at -80° C but released no more diboron tetrafluoride.

In a second experiment glyme (2.62 mmoles) was treated with diboron tetrafluoride (0.113 mmoles) at room temperature for five minutes. A white solid, insoluble in the excess glyme, was formed. Excess glyme (2.49 mmoles) was removed and boron trifluoride (1.05 mmoles) was added to the complex. The mixture was

maintained at 0° C while exposed to an adjacent trap at -112° C for 45 minutes. The colder trap contained 0.034 mmoles of diboron tetrafluoride, separated by fractional condensation. The boron trifluoride returned to the reaction vessel for two days at room temperature and then heated to 100° C for ten minutes (where the complex liquefied), displaced additional diboron tetrafluoride yielding a total of 0.071 mmoles. The diboron tetrafluoride had a vapor pressure of 10.5 mm. at -80° C somewhat lower than the calculated value of 15 mm. at this temperature. The remaining mixture of complexes was found to be completely soluble in excess glyme.

In a similar experiment 0.13 mmoles of diboron tetrafluoride plus 1.02 mmoles of boron trifluoride were complexed with glyme in that order and the excess glyme was removed. Treatment with 1.47 mmoles of boron trifluoride gave 0.068 mmoles of diboron tetrafluoride.

In a third experiment excess glyme was treated first with boron trifluoride (1.139 mmoles) and then diboron tetrafluoride (0.147 mmoles). The mixed complex was soluble in excess glyme even at -80° C and removal of the excess glyme by distillation left a viscous liquid. Treatment with boron trifluoride (1.64 mmoles) at $70-90^{\circ}$ C for fifteen minutes displaced 0.023 mmoles of diboron tetrafluoride, separated by fractional condensation. In a similar experiment a mixed glyme complex prepared by addition first of 0.60 mmoles of

boron trifluoride and then 0.17 mmoles of diboron tetrafluoride gave a recovery of 0.10 mmoles of diboron tetrafluoride upon repeated treatment with boron trifluoride (initial amount, 2.47 mmoles) at 70-90° C. This diboron tetrafluoride had a vapor pressure of 14 mm. at -80° C (calculated: 15 mm.).

Reaction of Diboron Tetrafluoride with Excess N, N, N', N'-
Tetramethylethylenediamine

N, N, N', N'-Tetramethylethylenediamine (TED) (3.59 mmoles) was treated with diboron tetrafluoride (0.157 mmoles) at -80° C for seven hours and then warmed to room temperature. A white solid, insoluble in the excess TED, had formed. Excess TED was distilled away leaving 0.248 mmoles in the complex which then contained a 1.57: 1.00 TED to diboron tetrafluoride ratio. In other experiments where diboron tetrafluoride was complexed with excess TED, ratios of TED to diboron tetrafluoride varying from 1.37: 1.00 to 1.84: 1.00 were observed. The complexes were solids at temperatures up to 100° C and did not decompose at that temperature. They were insoluble in TED, trimethylamine, benzene, glyme, and acetone, but appeared to be slightly soluble in methanol without reaction.

The complexes were soluble in water with production of hydrogen gas. Thus a sample prepared from 0.130 mmoles of diboron tetrafluoride and 0.229 mmoles TED (1.76: 1.00) dissolved almost

completely in 0.52 g. of water. Approximately 0.1 mmoles of non-condensable gas, presumably hydrogen, was formed. The reaction was complete at room temperature: heating to 100° C gave no more hydrogen. Removal of excess water left a white solid which redissolved readily. A sample prepared from 0.073 mmoles of diboron tetrafluoride was treated with 7.5 ml. of 15% sodium hydroxide. In fifteen minutes at 75° C approximately 0.04 mmoles of non-condensable gas were formed.

The complexes absorbed boron trifluoride in small amounts and reacted with boron trichloride to produce boron trifluoride. Thus, a sample prepared from 0.248 mmoles of TED and 0.157 mmoles of diboron tetrafluoride (1.57: 1.00) when treated with excess boron trifluoride (1.33 mmoles) at room temperature for twelve hours and then 100° C for 30 minutes absorbed 0.15 mmoles of boron trifluoride. There was no further reaction. This same sample, after removal of excess boron trifluoride, was treated with boron trichloride (0.376 mmoles). After ten minutes at room temperature, 0.298 mmoles of boron trichloride were recovered plus a small amount of material volatile at -119° C. The products were returned to the reaction vessel where the mixture was stored for two days and then heated briefly to 98° C. The products included 0.079 mmoles of boron trichloride and 0.356 mmoles of more volatile material, vapor pressure 59 mm. at -127° C. This latter material presumably

contained impure boron trifluoride (vapor pressure 70 mm. at -127° C). The residue reacted with excess 15% sodium hydroxide (80° C for four hours) producing 0.20 mmoles of non-condensable gas.

Reaction of Diboron Tetrafluoride with an Equivalent Amount of TED

Diboron tetrafluoride (0.155 mmoles) was added to TED (0.157 mmoles) and the mixture was stored at room temperature for four hours. At the end of this period 0.008 mmoles of TED was recovered as the only volatile product. The solid white complex sublimed slowly at 90° C, rapidly and completely at $140-160^{\circ}$ C.

Diboron tetrafluoride (0.252 mmoles) was added to a deficiency of TED (0.103 mmoles) at -196° C. When the mixture was warmed to room temperature a violent reaction took place with the formation of a white solid. The mixture was warmed briefly to 70° C and then fractionated. The only volatile material recovered was diboron tetrafluoride (0.155 mmoles) (vapor pressure 16 mm. at -80° C; calculated: 15 mm.) leaving a TED to diboron tetrafluoride ratio in the complex of 1.06:100. Further treatment of the complex with diboron tetrafluoride led only to decomposition. Thus, when the complex was treated with 0.125 mmole of diboron tetrafluoride at 160° C the volatile products were 0.025 mmoles of diboron tetrafluoride, 0.066 mmoles of boron trifluoride and a small amount of silicon tetrafluoride, identified by its infrared spectrum. Treatment

of the residue with excess 15% sodium hydroxide at 70° C for thirty minutes gave 0.084 mmoles of non-condensable gas.

In later experiments it was observed that complexes containing excess TED did not completely sublime at 160° C in contrast to those complexes containing an approximate 1:1 ratio of amine and B₂F₄. However, upon treatment of a complex containing excess TED with diboron tetrafluoride or boron trifluoride it was converted to a form completely volatile at 160° C.

A sample of complex containing diboron tetrafluoride and TED in approximately equivalent amounts (0.19 mmoles) was treated with diethylzinc (0.551 mmoles) at 0° C for one day and then at room temperature for twelve hours. Separation and fractionation of volatile materials gave ethane, identified by its infrared spectrum (43), excess diethylzinc and triethylboron, identified by its infrared spectrum (33) and its vapor pressure of 12 mm. at 0° C, literature value 12.5 mm. at 0° C (45). The residual non-volatile material gave 0.084 mmoles of non-condensable gas when treated with excess 15% sodium hydroxide for one hour at 75° C.

Reaction of Diboron Tetrafluoride with Triethylamine

Diboron tetrafluoride (0.178 mmoles) condensed with triethylamine (4.71 mmoles) at -196° C. The mixture was allowed to warm to room temperature where a white solid was formed, insoluble in

the excess triethylamine. Excess amine was removed leaving 0.390 mmole complexed with 0.178 mmole of diboron tetrafluoride, a ratio of 2.2:1.0. 1.05 mmoles of boron trifluoride was added to the complex and, upon warming, the white solid disappeared leaving a clear liquid. The volatile materials were separated by fractionation from 0° C through -80, -119, and -196° C traps. Nothing condensed at -80° C. 0.092 mmole of diboron tetrafluoride condensed at -119° C (vapor pressure 16 mm. at -80° C, calculated: 15 mm.). The infrared spectrum was the same as authentic diboron tetrafluoride. 0.792 mmoles of boron trifluoride was recovered in the -196° C trap, thus, 0.26 mmole of boron trifluoride reacted. No further recovery of diboron tetrafluoride could be attained by allowing boron trifluoride to remain at room temperature in the reaction tube for four hours, or by heating the reaction tube with boron trifluoride present for one minute at 70-90° C.

Reaction of Diboron Tetrafluoride with Trimethylamine

Trimethylamine (0.723 mmole) and diboron tetrafluoride (0.145 mmole) were condensed together at -196° C, forming a white solid when warmed to room temperature. The solid could be sublimed at room temperature, indicating at least a slight vapor pressure at this temperature. 0.386 mmole of trimethylamine was recovered from the reaction vessel at 0° C, leaving 0.337 mmole complexed with

0.145 mmole of diboron tetrafluoride, a ratio of 2.32:1.00.

Treatment with boron trifluoride (1.32 mmoles) at room temperature gave no displacement of diboron tetrafluoride but 0.18 mmoles of boron trifluoride was absorbed. When the treatment with boron trifluoride was repeated at 75° C for five hours, 0.094 mmoles of diboron tetrafluoride was recovered (vapor pressure 16 mm. at -80° C, calculated: 15 mm.).

The non-volatile residue gave no hydrogen gas when treated with 3 ml. of 15% sodium hydroxide at 65° C for 30 minutes.

Treatment of Diboron Tetrafluoride with p-Chlorobenzonitrile

Diboron tetrafluoride (0.13 mmoles) was condensed into a vessel containing freshly sublimed p-chlorobenzonitrile (Eastman Chemical Co.). The vessel was warmed to room temperature and then briefly to 70-90° C. Essentially, all of the diboron tetrafluoride, 0.12 mmoles, was recovered unchanged (vapor pressure 16.5 mm. at -80° C). No other volatile materials were formed.

Reaction of Diboron Tetrafluoride with Benzonitrile

Diboron tetrafluoride (0.114 mmole) was treated with excess benzonitrile (Mathieson Coleman and Bell), at 0° C for two and one half hours. Only a trace of volatile material remained after this period. A white solid phase coexisted with the liquid benzonitrile.

Excess benzonitrile was distilled away at 70-90° C leaving a small residue of white solid material and non-volatile liquid. Treatment with excess boron trifluoride at room temperature did not displace diboron tetrafluoride from the complex. An undetermined amount of boron trifluoride was absorbed by the residue forming a white, slightly volatile, solid.

Reaction of Diethylzinc with Diboron Tetrafluoride-Glyme Complex

Diethylzinc was prepared by the method of Krug and Tang (31). A zinc-copper couple was produced by heating a mixture of zinc dust (Baker and Adamson reagent grade) (5.2 g.) and copper citrate (1.0 g.) with a free flame under a nitrogen atmosphere. A mixture of 0.02 moles of ethyl iodide (Mathieson Coleman and Bell) and 0.02 moles of ethyl bromide (Eastman Chemical Co.) was added and the mixture was heated to 60° C for one hour. Separation of the volatile material gave a 1-2 ml. fraction condensing at -45° C, with vapor pressures of 4 mm. at 0° C and 14 mm. at 20° C. Calculated values for diethylzinc are 3.6 mm. at 0° C and 12.1 mm. at 20° C (5).

1.05 mmoles of diethylzinc was added to diboron tetrafluoride-glyme complex, prepared from 0.510 mmoles of diboron tetrafluoride and 0.500 mmoles of glyme. At room temperature an immediate reaction produced a black solid. Volatile products, separated by fractional condensation, included ethane (0.138 mmoles) identified

by its infrared spectrum (43), diethyl boron fluoride (0.048 mmoles), identified by its infrared spectrum¹, and triethylboron, also identified by its infrared spectrum (33). There was no evidence for a volatile product containing a boron-boron bond.

Infrared Spectrum of Diboron Tetrafluoride

A 10 cm. all-metal sealed cell (see Figure 1) was used for the diboron tetrafluoride gas samples. A Beckman IR-7 equipped with sodium chloride optics was used to measure the following infrared spectra. A double beam was used with the speed at $40 \text{ cm}^{-1}/\text{min.}$, period at eight, gain 40/100, and the slit width twice standard. The spectral range of $600\text{-}4000 \text{ cm}^{-1}$ was scanned. The following maxima are assigned to gaseous diboron tetrafluoride:

<u>Wave numbers in Cm^{-1}</u>	<u>Intensity</u>
1151	shoulder
1158	very strong
1171	shoulder
1220	shoulder
1362	shoulder
1373	very strong
1419	medium
2520	very weak
2760	very weak

0.04 mmoles of diboron tetrafluoride gave a full-scale absorption in the 148 cc. gas sample cell. Repeated runs one hour and 15

¹F. G. A. Stone, Queen Mary College, London, England. Private Communication.

minutes apart, with the sample in the all-metal sealed gas cell mounted continuously in the infrared beam, showed an intensity decrease of approximately one to two percent. Common impurities observed in the diboron tetrafluoride spectrum are boron trifluoride and silicon tetrafluoride. The boron (11) trifluoride absorption maxima are observed at 693, 1450, and 1461 cm^{-1} , boron (10) trifluoride maxima at 721, 1503, and 1511 cm^{-1} , while a small amount of silicon tetrafluoride exhibits strong maxima at 1031 and 1036 cm^{-1} .

The infrared spectrum was obtained for solid diboron tetrafluoride at a temperature slightly greater than -196°C , the boiling point of liquid nitrogen. A double beam was used with the speed 40 $\text{cm}^{-1}/\text{min.}$, period at eight, gain 40/100, slit width set at twice standard, and a #47 screen placed in the reference beam. The spectral range of 600-4000 cm^{-1} was scanned. The following maxima are assigned to solid diboron tetrafluoride:

<u>Wave Length in cm^{-1}</u>	<u>Intensity</u>
815	weak
910	very weak
932	very weak
1051	medium
1070	medium
1082	shoulder
1104	shoulder
1137	very strong
1154	very strong
1210	weak
1327	very strong
1382	very strong

Wave Length in cm^{-1} (cont.)

Intensity (cont.)

1411	shoulder
1434	medium
1439	very weak-shoulder
1463	very weak
1643	weak
2460	weak
2540	very weak
2720	very weak
2855	very weak
2920	very weak
3250	strong, broad

DISCUSSION

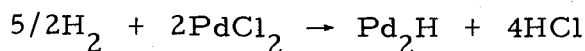
The Synthesis of Diboron Tetrafluoride

The preparation of diboron tetrafluoride by reduction of boron trifluoride with alkali metal solutions in glyme proved to be unsuccessful. The alkali metal solutions were very tedious to handle in vacuo, firstly because of the low solubility of the alkali metal, reported to be 5×10^{-3} M (58), and secondly because of the apparent slow reaction of metal with solvent to produce a non-condensable gas. Because of the low solubility of alkali metal in glyme repeated additions of alkali metal solution to boron trifluoride solution were required. Small amounts of non-condensable gas inhibited the back distillation of solvent to reform new alkali metal solutions for further addition. If the temperature of the receiver was lowered to -196° C during back distillation of solvent, some boron trifluoride-glyme complex apparently was also transferred since it then was difficult to again form the blue solution of alkali metal. It was observed that the complex had a small vapor pressure at room temperature.

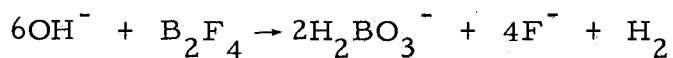
The alternative possibility of using a large volume of solution appeared even less attractive inasmuch as the low temperature operations would have been more complex and the separation of a small amount of product from a large amount of solvent would have been difficult if at all possible.

Using approximately 10 ml. of saturated solution, 0.05 mmoles of alkali metal was introduced at each addition. Thus, twenty additions of alkali metal solution, assuming saturation, were required to give one mmole of metal and potentially form 0.50 mmoles of diboron tetrafluoride. This amount of product would be readily identifiable by partial displacement from glyme by boron trifluoride. Even when about 1.8 mmoles (38 additions of 10 ml. of solution) of alkali metal were added no diboron tetrafluoride could be isolated. It was demonstrated (p. 46) that boron trifluoride displaces diboron tetrafluoride from glyme in 25-30% yields at room temperature and up to 75% yield at 100° C.

The exact nature of the reduction product remains in doubt. That reduction occurred is demonstrated by the formation of a white solid material and the discharge of the blue color characteristic of alkali metal solutions upon an addition to the boron trifluoride in glyme. The product solution also gave a non-condensable gas upon hydrolysis with sodium hydroxide solutions. The non-condensable gas was shown to be hydrogen by its reaction with palladium chloride (38)

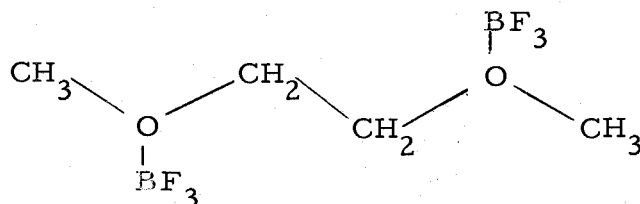


and identification of hydrogen chloride from this reaction. Hydrogen is formed by alkaline hydrolysis of compounds containing boron-boron bonds:



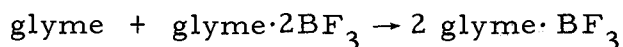
The absence of dark-colored materials precludes the possibility of elemental boron or a boride appearing as a product. There may be a higher boron-fluorine polymer present, such as $(\text{BF})_x$, that is of low volatility or diboron tetrafluoride may be complexed with the newly formed potassium fluoride, KB_2F_5 . Such a complex may not enter into an acid exchange reaction with boron trifluoride as easily as does the diboron tetrafluoride-glyme complex.

In one instance a boron trifluoride-glyme complex was utilized as a starting material wherein the boron trifluoride-glyme ratio was 1.8:1.0. Such a complex contains primarily material in which both oxygens of a glyme molecule are attached to boron trifluoride units,



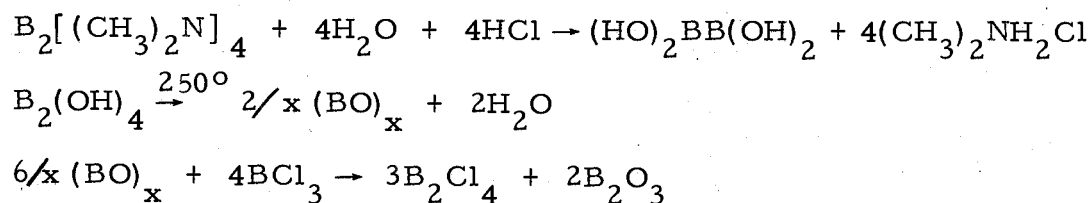
The close proximity of the two boron atoms in a single molecule can allow ring closure upon reduction and impart greater stabilization of complexed diboron tetrafluoride toward further reduction.

The addition of alkali metal in glyme solution may, however, allow migration of boron trifluoride leaving only singly complexed glyme molecules.

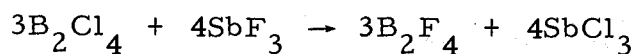


In any case no better results were obtained than with solutions in which the original boron trifluoride-glyme complex was prepared in excess glyme.

McCloskey's method (36) was ultimately used to prepare diboron tetrachloride.



The diboron tetrachloride was then treated with antimony trifluoride to form diboron tetrafluoride (50).



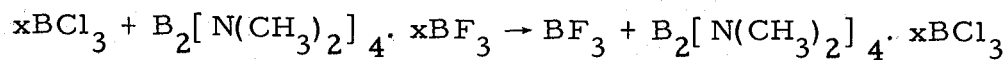
The diboron tetrafluoride was never found to be completely stable in vacuo as reported by Finch and Schlesinger (17). The observed instability does agree with corresponding observations of Holliday and Taylor (25). In most cases of diboron tetrafluoride decomposition to boron trifluoride and non-volatile materials the pressure remained constant indicating one boron trifluoride molecule was formed as a diboron tetrafluoride molecule decomposed. The black solid material that formed simultaneously may be a boron subhalide



or even elemental boron.

Since the synthesis of diboron tetrafluoride by the above method and by the electrical discharge method of Schlesinger (17) is tedious, both giving low yields and involving an unstable intermediate, diboron tetrachloride, reactions of tetra-(dimethylamino)-diboron with antimony trifluoride and boron trifluoride were investigated with the hope that diboron tetrafluoride could be formed by a fluoride displacement of the amine group on the boron. Antimony trifluoride didn't appear to react with the tetra-(dimethylamino)-diboron since silicon tetrafluoride formed from antimony trifluoride and glass was the only reaction product that was isolated.

Boron trifluoride reacted with tetra-(dimethylamino)-diboron to form a white solid, which appeared to have some vapor pressure at 100° C. This complex decomposed slightly at high temperatures to produce small amounts of volatile products but not in identifiable amounts. When boron trichloride was added to the boron trifluoride complex, boron trifluoride was recovered. Apparently the stronger Lewis acid, boron trichloride, replaced the weaker acid, boron trifluoride, from the basic amine.

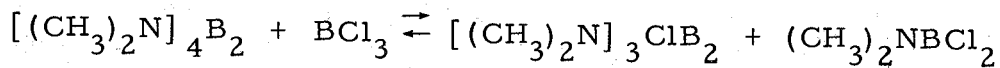


No evidence for formation of diboron tetrachloride was found.

The dative bond formed between boron trifluoride and the

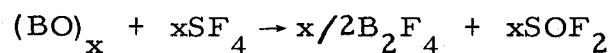
nitrogens in tetra-(dimethylamino)-diboron may weaken the covalent boron-nitrogen bond enough to allow fluorination to take place at that site in the presence of antimony trifluoride. A reaction occurred both at room temperature and at higher temperatures with the formation of black material, but there was no evidence for diboron tetrafluoride. Whether the reaction that takes place is incomplete fluorination or complete fluorination with the product, diboron tetrafluoride, quickly decomposing to boron trifluoride and $(BF)_x$, is not known. Boron trifluoride and antimony trifluoride together gave no immediate reaction.

No diboron tetrachloride was observed when boron trichloride reacted with tetra-(dimethylamino)-diboron, but a liquid was formed that had vapor pressures comparable to dimethylaminoboron dichloride, $(CH_3)_2NBCl_2$ (55). The white solid material observed after twenty-four hours probably was the dimer, $[(CH_3)_2NBCl_2]_2$, which is known to be formed slowly at room temperature. Since dimethylaminoboron dichloride is a product in this reaction, there is probably some exchange between chloride and amine groups, but not sufficient to produce the desired product.



Boron trifluoride did not react with boron suboxide at temperatures up to $250^\circ C$ to produce diboron tetrafluoride. Subsequent to

the completion of the experimental work of this thesis Brotherton et al. reported (9) the preparation of diboron tetrafluoride by reaction of boron suboxide with sulfur tetrafluoride.



Alkali Metal Solutions

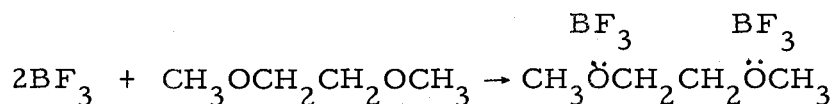
Attempts to develop a solvent system for alkali metals where reactions could be studied under non-solvolytic conditions were not fruitful. Investigation of the solubility of alkali metals in tertiary amines and tertiary diamines at low temperature showed that the inverse solubility curve observed for alkali metals in aprotic diethers did not apply to similar nitrogen derivatives.

The mechanism of solvation of alkali metals in diethers is not known. Presumably, the solutions contain solvated electrons since a similar absorption spectrum is observed in these solutions as in liquid ammonia. Solubilities, however, are low, severely limiting the utility of these solutions in synthetic work. When the factors controlling solubilization of alkali metal are known it may be possible to develop a solvent system combining the relatively high solubilities observed in liquid ammonia with the aprotic conditions of diether solutions.

Lewis Acid-Base Adducts

Complexes of Boron Trifluoride

Boron trifluoride was observed to form both 2:1 and 1:1 complexes with glyme dependent upon the initial ratio of reactants. The 2:1 complex, in which all oxygen



sites are occupied was a white, slightly volatile solid at room temperature, soluble in excess glyme. When a complex was formed by addition of boron trifluoride to excess glyme the product had a 1:1 ratio of boron trifluoride to glyme and was a liquid at room temperature in contrast to the 2:1 complex. The 2:1 complex did not react with excess glyme after it was once formed. The white solid dissolved in excess glyme but was recovered unchanged upon evaporation of the solution.

Boron trifluoride formed strong complexes with trimethylamine, triethylamine, 2,6-lutidine, and benzonitrile, but did not react with nitrobenzene nor with p-nitrotoluene. Boron trifluoride and p-chlorobenzonitrile form a weak complex which is stable at -30°C , but at 0°C some dissociation is observed.

Brown and Holmes (11) reported that boron trifluoride can be purified by forming a weak complex with anisole and then

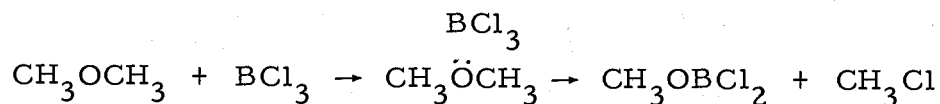
regenerated by heating. Since hydrogen chloride and boron trifluoride are common products of many reactions, because commercial tank boron trifluoride contains a hydrogen chloride impurity, and because these gases are difficult to separate by fractional condensation a separation using anisole to complex boron trifluoride was considered. However, hydrogen chloride was found to partially complex with anisole at -30°C , whereas boron trifluoride complexes completely at this temperature. *p*-Chlorobenzonitrile was found to be a much more satisfactory base for this separation. It is unreactive toward hydrogen chloride and forms a stable complex with boron trifluoride at -30°C from which the boron trifluoride can be recovered almost quantitatively at room temperature.

The Lewis base *p*-chlorobenzonitrile is also effective in the separation of boron trifluoride and boron trichloride since its complex with boron trichloride is stable at temperatures up to 150°C .

Complexes of Boron Trichloride

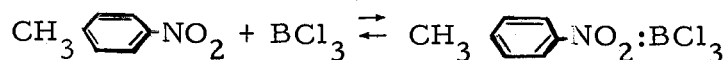
Boron trichloride formed complexes with triethylamine, 2,6-lutidine, *p*-chlorobenzonitrile, *p*-nitroanisole, and glyme but interacted only weakly with trityl chloride, nitrobenzene, and *p*-nitrotoluene. In many reactions complex formation was accompanied by a further elimination reaction to produce hydrogen chloride or methyl chloride. Such reactions were previously known to occur (40) with

boron trichloride complexes with ethers:



These secondary reactions considerably complicated interpretation of experimental data particularly for displacement reactions of other Lewis acids from bases with boron trichloride. These reactions will be discussed later.

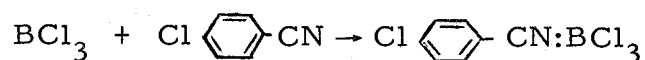
The complex between boron trichloride and glyme was not studied directly, but it was observed that boron trichloride displaced boron trifluoride from glyme so that a stable complex is known to exist. The displacement reaction will be discussed later. Wiberg and Heibaum (56) reported a weak complex between boron trichloride and trityl chloride. The complex, if it exists at all, was much too weak to be of use in this work. Similarly, the weak complex formed by boron trichloride and nitrobenzene, as reported by Brown and Holmes (11), dissociated at room temperature with some decomposition of the materials. p-Nitrotoluene also gave a weak complex with boron trichloride



with the complexation reaction accompanied by an elimination reaction. After the separation of the volatile product (assumed to be hydrogen chloride) 76% of the initial amount of boron trichloride was

recovered when the complex was heated to 60° C.

Boron trichloride associated very strongly with p-chlorobenzonitrile. No boron trichloride could be recovered at 150° C.

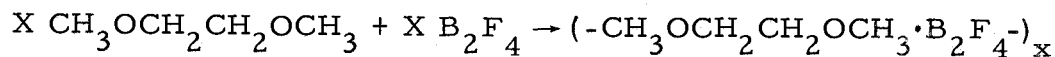


Some hydrogen chloride was eliminated in agreement with Gerrard et al. (18), who observed hydrogen chloride as a pyrolysis product of 1:1 complexes of boron trichloride with nitriles.

p-Nitroanisole and boron trichloride form a complex at 0° C which has a slight dissociation pressure at that temperature. At room temperature and above the dissociation increased so that boron trichloride could be recovered almost quantitatively by sublimation of the complex. Of the Lewis bases investigated p-nitroanisole appears to be the best suited for the separation and purification of boron trichloride.

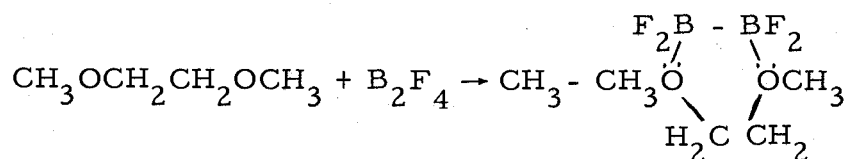
Complexes of Diboron Tetrafluoride

Diboron tetrafluoride was observed to form a solid 1:1 complex with glyme insoluble in excess glyme. The complex may be polymeric, accounting for the insolubility of the complex in excess glyme.



The monomer might involve a six-member ring which may also be

insoluble in glyme.



The initial presence of boron trifluoride interferes with the formation of the insoluble diboron tetrafluoride-glyme complex but permits the formation of a soluble one. Boron trifluoride would interfere with both polymerization and ring structure formation.

When diboron tetrafluoride was complexed with excess N,N,N',N'-tetramethylethylenediamine, ratios varying from 1.37:1.00 to 1.84:1.00 were observed. The solid complexes were insoluble in N,N,N',N'-tetramethylethylenediamine, triethylamine, benzene, glyme, and acetone. The complexes appear to be slightly soluble in methanol and produce hydrogen gas when dissolved in water.

When an excess or equivalent amount of diboron tetrafluoride was complexed with N,N,N',N'-tetramethylethylenediamine a 1:1 complex was formed. This white solid complex sublimed slowly at 90° C, rapidly and completely at 140-160° C. The complexes having a ratio greater than 1:1, amine to diboron tetrafluoride, did not completely sublime at 160° C but could be converted to a volatile form by treatment with diboron tetrafluoride or boron trifluoride. Since the diboron tetrafluoride-N,N,N',N'-tetramethylethylenediamine complex is insoluble in excess amine and has a low vapor

pressure at elevated temperatures, it probably has either a polymeric or ring structure comparable to the glyme complex.

Diboron tetrafluoride forms white solid complexes with both trimethylamine and triethylamine in approximately 1:2 ratios. This is an agreement with Finch and Schlesinger (17), who reported a 1.0:2.0 ratio of diboron tetrafluoride to trimethylamine. They also observed that this complex had a vapor pressure of about two mm. at 80° C and that molecular weight measurements in hexane and benzene indicated a tetramer $[B_2F_4 \cdot 2N(CH_3)_3]_4$.

A white solid complex was formed between diboron tetrafluoride and benzonitrile, whereas, essentially no complexation occurred with p-chlorobenzonitrile.

The reaction of diethylzinc with the diboron tetrafluoride-N,N,N',N'-tetramethylethylenediamine complex produced triethylboron and its decomposition product ethane. When diethylzinc was added to diboron tetrafluoride-glyme complex, the volatile products were ethane, diethyl boron fluoride, and triethylboron. There was no evidence for a volatile product containing a boron-boron bond.

Conclusions

Hydrogen chloride, boron trifluoride, boron trichloride, and diboron tetrafluoride are relatively strong Lewis acids and, therefore, form strong complexes with amines. Strong complexes are

also formed with simple aliphatic ethers, with which boron trichloride further reacts forming alkyl chlorides. Boron trichloride forms a stronger complex with p-chlorobenzonitrile than boron trifluoride. Boron trichloride also forms weak complexes with nitrobenzene and p-nitrotoluene, whereas, no complexation occurs with boron trifluoride. Thus, boron trichloride is a stronger acid than boron trifluoride in agreement with the observations of Brown and Holmes (11).

Boron trifluoride forms a weak complex with both p-chlorobenzonitrile and anisole, whereas, hydrogen chloride does not complex with the former and only very weakly with the latter. Diboron tetrafluoride also failed to form a complex with p-chlorobenzonitrile but does complex weakly with benzonitrile, which forms a relatively strong addition compound with boron trifluoride. Since the basic nitrogen site in benzonitrile is located at some distance from the phenyl group, steric hindrance cannot account for the difference in acidity between boron trifluoride and diboron tetrafluoride. Thus, boron trifluoride is a stronger acid than either hydrogen chloride or diboron tetrafluoride.

Based on their ability to form complexes, the relative acid strength increases in the order: hydrogen chloride, diboron tetrafluoride < boron trifluoride < boron trichloride.

Displacement Reactions

Base Displacement

Kraus and Brown (30) reported that dimethylether was replaced from its boron trifluoride-etherate complex by a trialkylamine. In this work both trimethylamine and 2,6-lutidine replaced glyme from its boron trifluoride complex.



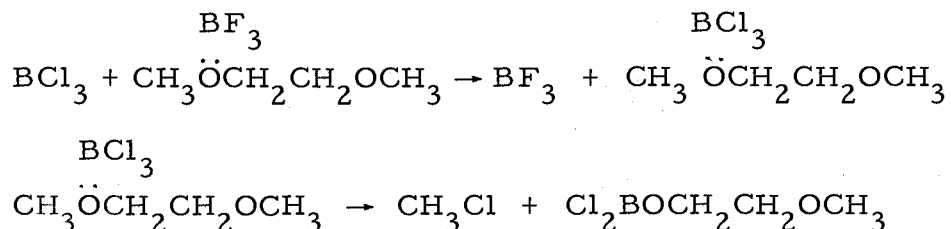
Acid Displacement

Wartik and Apple (53) obtained boron trifluoride from its etherate complex by displacement with aluminum chloride. In this work attempts to replace boron trifluoride from its glyme complex with aluminum chloride were unsuccessful. Instead hydrogen chloride, methyl chloride, and other less volatile materials thought to be derived from decomposition of glyme were formed.

No acid exchange occurred between hydrogen chloride and boron trifluoride complexes of trimethylamine, triethylamine, or 2,6-lutidine. Similar results were observed when complexes of boron trichloride with triethylamine and 2,6-lutidine were treated with hydrogen chloride.

Boron trichloride replaced 62% boron trifluoride from its glyme

complex at room temperature. The other reaction product was methyl chloride, produced by the reaction of boron trichloride with ether (40).

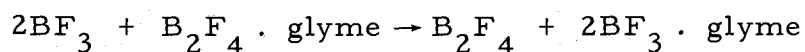


When the reaction mixture was heated, hydrogen chloride was also formed as a product. Boron trifluoride did not replace boron trichloride from its 2,6-lutidine complex.

Displacement of Diboron Tetrafluoride

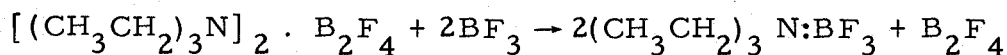
Boron trifluoride was found to displace diboron tetrafluoride from its glyme, triethylamine, and trimethylamine complexes, whereas, no displacement occurred, under the conditions investigated, with the complexes of diboron tetrafluoride with N, N, N', N'-tetramethylethylenediamine and benzonitrile.

Boron trifluoride was found to displace up to 60% diboron tetrafluoride from its glyme complex.



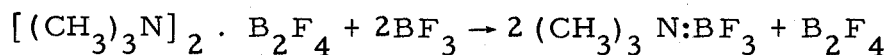
Heating the reaction appears to favor acid exchange, for larger amounts of diboron tetrafluoride were recovered.

The addition of boron trifluoride to a solid diboron tetrafluoride-triethylamine complex produced a liquid from which 52% diboron tetrafluoride was recovered.



The formation of liquid is probably due to the boron trifluoride-triethylamine complex, which melts at about 30° C.

Treatment with boron trifluoride at room temperature gave no displacement of diboron tetrafluoride from its trimethylamine complex, but acid exchange did take place at



higher temperatures with a recovery of 65% of diboron tetrafluoride. Since noncondensable gases were not produced by alkaline hydrolysis of the residue, no material containing boron-boron bonds remained apparently.

When the addition compound of N,N,N',N'-tetramethylethylenediamine-diboron tetrafluoride (containing excess amine) was treated with either boron trifluoride or boron trichloride, no acid exchange took place. Boron trichloride reacted with the complex to form some boron trifluoride. Apparently halogen exchange took place between boron trichloride and diboron tetrafluoride, since the preservation of the boron-boron bond is indicated by the

formation of hydrogen from the alkaline hydrolysis of the residue.

A mass spectrometric study showed that halogen exchange occurs between boron trifluoride and organoboron halides (7), and also halogen exchange occurs between boron tribromide and diboron tetrachloride (50). These examples indicate that halogen exchange is possible in the present instance.

Acid displacement was not attempted with the 1:1 complex of N, N, N', N'-tetramethylethylenediamine-diboron tetrafluoride.

Boron trifluoride did not displace diboron tetrafluoride from its benzonitrile complex at room temperature. The absorption of boron trifluoride to form a complex with excess benzonitrile may have interfered with the acid exchange reaction.

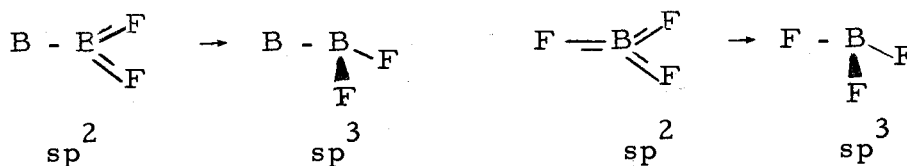
Conclusions

The results of the acid displacement reactions corroborate the order of relative acid strength indicated in the Lewis acid-base adduct section (hydrogen chloride, diboron tetrafluoride < boron trifluoride < boron trichloride).

Boron trichloride replaced boron trifluoride from its glyme complex, whereas, the latter did not displace the former from 2,6-lutidine. Boron trifluoride displaced diboron tetrafluoride from glyme, triethylamine and trimethylamine. Displacement of boron trifluoride and boron trichloride from their amine complexes by

hydrogen chloride did not occur.

These results lead to the question, why is diboron tetrafluoride a weaker Lewis acid than boron trifluoride? Comparing the $-BF_2$ group with $-F$, both appear to be strongly electronegative. As mentioned in the introduction, if we assume that the boron-fluorine bond has partial multiple or π bonding and a bond order greater than one and that the boron-boron bond is a sigma bond with a bond order of one, then the reorganization energy needed for the boron to change its hybridization from sp^2 to sp^3 in diboron tetrafluoride should be less than in boron trifluoride.



Thus in changing from the planar to the pyramidal form only two π bonds must be broken in diboron tetrafluoride, whereas, three π bonds must be broken in boron trifluoride. The energy change in the sigma bonds when the boron changes its hybridization from sp^2 to sp^3 is assumed to be small (14). The energy change caused by the formation of a sigma bond with the donor is assumed to be the same with either Lewis acid.

If this were the case, diboron tetrafluoride would be predicted to be the stronger acid. Since the reverse appears to be true, the

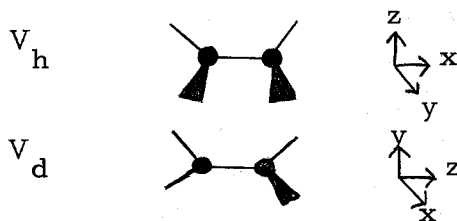
assigned bonding in the diboron tetrafluoride molecule must be reconsidered. The fact that the boron-boron bond in diboron tetrafluoride is shorter than in diboron tetrachloride (48, 4), indicates that the boron-boron bonding is not identical in these two molecules. The recent discovery and elucidation of the molecular structure of decaborane-16, $B_{10}H_{16}$, disclosed a previously unknown boron hydride structural feature: two adjacent boron atoms without hydrogen atoms attached to either boron (19). These two boron atoms appear to have a single covalent bond between them and have an interatomic distance of 1.74A, similar to the boron-boron bond distance in diboron tetrachloride.

Since multiple bonding is a possible explanation for decreasing bond distance, as in the case of the carbon-carbon distance in ethane versus ethylene, this also may be the reason for the decrease in boron-boron bond length in diboron tetrafluoride. Since boron trichloride is a stronger acid than boron trifluoride (11, 14) partially because of the multiple bonding of the latter, the relatively weak acidity of diboron tetrafluoride may be interpreted as being due to the π electrons donated by the fluorines to the vacant p-orbitals of boron and consequently to the whole molecule, so that π bonding also exists between the two boron atoms. Essentially π delocalization occurs throughout the entire diboron tetrafluoride molecule. This interpretation would explain both the short boron-boron bond

and the relatively weak acid properties of diboron tetrafluoride. A corollary of this hypothesis is that a multiple boron-boron bond would increase the internal rotational barrier energy and, therefore, the structure of gaseous diboron tetrafluoride might well be planar rather than twisted as is gaseous diboron tetrachloride. Complete structural determination of gaseous diboron tetrafluoride as a function of temperature via electron-diffraction or infrared-Raman structure analysis can clarify this point.

Infrared Spectrum of Diboron Tetrafluoride

The infrared spectrum of gaseous diboron tetrafluoride showed two principal or fundamental absorption peaks, 1158 and 1373 cm^{-1} . The 1158 cm^{-1} peak is tentatively assigned either to the b_{3u} or b_2 species, change of electric moment parallel to the boron-boron bond, with the former species of V_h or D_{2h} symmetry, which is the planar molecule, and the latter species of V_d or D_{2d} symmetry, which is the twisted molecule.



The 1373 cm^{-1} peak is tentatively assigned, depending upon the geometric configuration, to either the b_{2u} or e species, change of

electric moment perpendicular to the boron-boron bond. Both of these fundamentals are ν characteristic, that is pertaining to the stretching motion. It is felt that the above are fundamental frequencies because of their very strong absorption and because the correlation between diboron tetrachloride and tetrachloroethylene (35) would be very similar to that of diboron tetrafluoride and tetrafluoroethylene (34).

Whereas the above fundamentals are associated with diboron (11) tetrafluoride, the 1171 or 1220 cm^{-1} and 1419 cm^{-1} peaks may be due to the diboron (10, 11) tetrafluoride molecule. Statistically there should be twice as many diboron (11, 11) tetrafluoride molecules as there are diboron (10, 11) tetrafluoride molecules, thus the latter peaks would be expected to be weaker. Since the ratio of diboron (10) tetrafluoride to the total diboron tetrafluoride is 1:25, its absorption peaks would be very weak and difficult to observe.

The 2520 cm^{-1} peak may be a combination of the two fundamental modes at 1158 and 1373 cm^{-1} . The 2760 cm^{-1} peak could be a combination of an antisymmetric and a symmetric stretch frequency.

The assigned spectrum of solid diboron tetrafluoride was determined from at least two spectra exhibiting each peak. The 1051 and 1070 cm^{-1} absorption peaks are similar to peaks appearing in the blanks after volatile products were removed at an elevated temperature. The peaks obtained from the blanks are 5 to 25 cm^{-1} .

lower, therefore, the 1051 and 1070 cm^{-1} are included in the spectrum. The spectrum between 1400 and 2000 cm^{-1} is difficult to detect and assign, since the water vapor absorption is high.

The 1137 and 1154 cm^{-1} are tentatively assigned fundamentals of the b_{3u} species and ν characteristic of the V_h or D_{2h} symmetry. The 1137 cm^{-1} frequency may be due to the diboron (11, 11) tetrafluoride molecule and the weaker 1154 cm^{-1} peak to the diboron (10, 11) tetrafluoride molecule. The 1327 and 1382 cm^{-1} peaks are tentatively assigned to the b_{2u} species and ν characteristic of V_h geometry. The former peak is probably due to diboron (11, 11) tetrafluoride and the weaker latter peak to diboron (10, 11) tetrafluoride. The V_h geometry, planar molecule, is assumed to be correct, based on x-ray structure analysis (48). Thus the V_d geometry, twisted molecule, was not considered for the solid diboron tetrafluoride. These fundamental assignments are based on the reasons discussed in respect to the gaseous diboron tetrafluoride.

Considering the diboron (11, 11) tetrafluoride molecule, the assigned gaseous fundamental frequencies are higher than the solid's fundamental frequencies. [Boron trifluoride also exhibits a shift to lower frequencies when comparing the gas to the solid (26, 16)]. These differences may be explained by the greater intermolecular association in the solid state as indicated by the high Trouton constants of 28 for diboron tetrafluoride and 27 for boron trifluoride.

Only two fundamental frequencies are expected for diboron tetrafluoride in the spectrum range investigated. Four more fundamental vibrations should appear at lower wave numbers in the infrared spectrum, and six fundamental peaks should appear in the Raman spectrum if V_h geometry persists. However, the torsional mode in a_u would be located at a very low wave number in the infrared spectrum, therefore, difficult to observe. If the molecule has V_d symmetry, again only two fundamental absorption frequencies are expected in the infrared range investigated. Three fundamentals peaks should also appear at the lower infrared frequencies, and at least four fundamentals should be found in the Raman spectrum. In order to determine the structure of the diboron tetrafluoride molecule via a spectral analysis the rest of the infrared as well as the Raman fundamental frequencies must be obtained and analyzed.

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