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ACCEPtOR STRENGTH OF CO-ORDINATED BORON HALIDES

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION OF THE UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

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By

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ABSTRACT

The Bronsted and Lewis basicity of \( R_2NBX_3^- \) (where \( R=H, CH_3 \) and \( X=Cl, F \)) has been measured using aqueous, non-aqueous, and tensimetric titrations of \( R_2NBX_3^- \) or \( R_2HNBX_3 \). Neither \( (CH_3)_2HNBF_3 \) nor \( (CH_3)_2NBF_3^- \) could be successfully titrated in aqueous solution implying a \( pK \) for both compounds of about 7. \( H_3NBF_3 \), \( CH_3H_2NBF_3 \), and \( (CH_3)_2HNBF_3 \) could be titrated in pyridine. The experimental half neutralization potentials of 172 mv, 133 mv, and 189 mv respectively demonstrate that the acidity of the amine-\( BF_3 \) complexes go through a minimum at \( CH_3H_2NBF_3 \). This behavior has been rationalized by analogy to the methylammonium ions whose acidity goes through a minimum at \( (CH_3)_2NH_2^+ \). The methylamine-\( BH_3 \) complexes could not be titrated in pyridine demonstrating that they are much weaker acids than the corresponding \( BF_3 \) complexes. Low temperature tensimetric titrations of \( (CH_3)_2NBF_3^- \) and \( (CH_3)_2NBCl_3^- \) using as reference acid \( BF_3 \) indicate that a weak complex, \( (CH_3)_2N(BF_3)_2^- \), forms while \( (CH_3)_2N(Cl)(BF_3)^- \) cannot be observed. Thus, \( (CH_3)_2NBF_3^- \) is a stronger Lewis base than is \( (CH_3)_2NBCl_3^- \). These data have been interpreted to imply that the relative acceptor strengths of the \( BX_3 \) groups \( BH_3<BF_3<BCl_3 \). Preparative routes to the new anions \( (CH_3)_2NBX_3^- \) have been developed. Both alkali metal reduction of \( (CH_3)_2HNBX_3 \) and direct reaction of \( O_3CN(CH_3)_2 \) with \( BX_3 \) have been employed in their synthesis.
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I. INTRODUCTION

The earliest reported work on a B-N compound was done at the beginning of the nineteenth century by Gay-Lussac\(^1\) who examined an adduct of ammonia with trifluoroborane. In the mid-nineteenth century boron nitride was reported by Balmain\(^1\) and later characterized by Wohler and Rose.\(^1\)

The inherent instability of many boron compounds toward water and air limited other advances in the field until high vacuum experimental techniques were developed by A. Stock\(^2\) in the early twentieth century. After Stock's early work on the boron hydrides, he and Pohland\(^3\) studied the reaction of diborane with ammonia. In the course of investigation they discovered borazine, which has become known as "inorganic benzene" because it is both isoelectronic and isosteric with benzene. Because of this isoelectronic and isosteric analogy, and since the combined covalent bond radii of the B-N bond (1.58\(\text{Å}\)) is of the same magnitude as a C-C bond (1.54\(\text{Å}\)),\(^1\) B-N compounds have frequently been compared with C-C compounds. In fact, even a nomenclature system was proposed by an analogy with a C-C system. Egon Wiberg,\(^4\) student and successor to A. Stock, observed the similarities of carbon's nearest neighbors and classified B-N containing compounds into three general classes according to the nature of the bonds. These classes are Borazane (\(\text{R}_3\text{NBH}_3\)), Borazene (\(\text{R}_2\text{NBH}_2\)), and Borazole (\(\text{(RNBH)}_N\)) which are
comparable to the German nomenclature for the organic analogs with single, double, and triple bonds. However, this system has not been adopted and the nomenclature recommended by the Committee of the American Chemical Society on the Nomenclature of Organic Boron Compounds\textsuperscript{5,6,7} for these classes of compounds are amine-boranes, amino-boranes, and borazines.

In comparing the B-N bond to the C-C bond it must be realized that, unlike the C-C bond, the B-N bond is expected to be polar since nitrogen is more electronegative than boron. Furthermore, in many instances chemical differences do occur between the B-N and C-C compounds because of this bond polarity. For example, borazine adds hydrogen halides to yield a product which has the empirical formula $B_3N_3H_6(HX)_3$ whereas the organic analog benzene undergoes no such addition.\textsuperscript{1}

In addition to the C-C analogy, other analogies have been used in the literature to explain the behavior of boranes. For example, Parry et al.\textsuperscript{8} have compared the chemistry of $H_3BPF_3$ with the $OPF_3$ in terms of the isoelectronic similarity between $O$ and $BH_3$. Another potentially useful chemical analogy rests on the fact that $BH_3$ (or $BF_3$) is isoelectronic with $CH_3^+$ (or $CF_3^+$). Thus, for example, amine-boranes ($R_3NBH_3$) can be considered to be analogs of alkyl ammonium ions ($R_3NCH_3^+$). The utility of this analogy will be demonstrated in this dissertation.
Modern studies of the amine-boranes began with Alfred Stock's investigation of the reaction of ammonia and diborane. Reaction stoichiometry indicated the formation of a product with empirical formula $\text{B}_2\text{H}_6(\text{NH}_3)_2$. A controversy which lasted more than twenty years arose over the structure of this product which was finally identified as $\text{H}_2\text{B}_(\text{NH}_3)_2^+\text{BH}_4^-$ by R. Parry and co-workers.\textsuperscript{9} As a portion of these studies on diammoniate of diborane, R. Parry and S. Shore also reported the synthesis of the simplest of the amine-borane, $\text{H}_3\text{NBH}_3$, and postulated that the following reaction took place in ammonia solutions of sodium.

$$\text{H}_3\text{NBH}_3 + \text{Na} \longrightarrow \text{Na}(\text{H}_2\text{NBH}_3) + \frac{1}{2}\text{H}_2$$ \hspace{1cm} (1)

This reaction had been suggested earlier by A. Burg and H. Schlesinger.\textsuperscript{10} Neither group, however, isolated or characterized the postulated $\text{NaH}_2\text{NBH}_3$. In work previously\textsuperscript{11} done in this laboratory, the reduction of $(\text{CH}_3)_2\text{HNBH}_3$ with sodium was investigated. Dimethylamineborane was chosen because it is more stable than ammoniaborane and is, therefore, easier to handle. Sodium dimethylamidotrihydroborate(III), $\text{Na}(\text{CH}_3)_2\text{NBH}_3$, was prepared from $(\text{CH}_3)_2\text{HNBH}_3$ according to the following equation:

$$(\text{CH}_3)_2\text{HNBH}_3 + \text{Na} \longrightarrow \frac{1}{2}\text{H}_2 + \text{Na}(\text{CH}_3)_2\text{NBH}_3$$ \hspace{1cm} (2)

This compound is still the only well-characterized $\text{BH}_3$ derivative of an amide.
The chemistry of the compound can be interpreted by analogy with the isoelectronic trimethylamine. \( \text{Na(CH}_3\text{)}_2\text{NBH}_3 \) behaves as the salt of a monoprotic weak acid, \( \text{(CH}_3\text{)}_2\text{HNBH}_3' \). The acid dissociation constant \((K_a)\) of \( \text{(CH}_3\text{)}_2\text{HNBH}_3 \) is \( 4.6 \times 10^{-11} \), or somewhat less than the corresponding \( K_a \) of \( 1.7 \times 10^{-10} \) for trimethylammonium ion. The preparation is similar to the well-known reduction of ammonium ions by sodium,\(^\text{12}\) and the borane hydrolysis closely parallels amine hydrolysis. The most important differences in the chemistry between \( \text{(CH}_3\text{)}_2\text{HNBH}_3 \) and \( \text{(CH}_3\text{)}_3\text{NH}^+ \) are probably due to the hydrolytic instability of the \( \text{BH}_3 \) group and the lower electronegativity of \( \text{BH}_3 \) compared with \( \text{CH}_3^+ \).

In all of the work which has been done with amine-boranes, the most fundamental property needed to understand any kind of interaction is the Lewis acidity of the borane. The analogies presented above are attempts to rationalize the physical and chemical properties of a variety of boron compounds. However, since every complex containing a \( \text{BX}_3 \) (\( X=\text{H}\) or halogen) is formally a Lewis acid-base complex, the factors which determine the acidity of the \( \text{BX}_3 \) group may well be central to the behavior of such compounds. Intuitively one would expect that the acidity of a \( \text{BX}_3 \) group should increase with increasing electronegativity of the \( X \) group. However, even very early thermodynamic studies\(^\text{13}\) of these compounds indicate that the order of acidity toward first period reference bases is \( \text{BCl}_3 > \text{BF}_3 > \text{BH}_3 \). This apparent anomaly has been explained in terms of a
thermochemical cycle.\textsuperscript{14}

\[
\text{BX}_3(g) + \text{BASE}(g) \xrightarrow{\Delta H_3} X_3B:BASE(g)
\]

\[
\text{BX}_3(g) + \text{BASE}(1) \xrightarrow{\Delta H_5} X_3B:BASE(1 \text{ or } s)
\]

For example, in the cases of BF\textsubscript{3} and BCl\textsubscript{3} if the reference base is held constant, it is found\textsuperscript{13} that Lewis acid-base neutralization of BF\textsubscript{3} is less exothermic (\(\Delta H_5\)) than the corresponding reaction of BCl\textsubscript{3}. The neutralization reaction is not a simple process, however, and from the above cycle it can be seen that:

\[
\Delta H_5 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4
\]

Probably \(\Delta H_2\) and \(\Delta H_4\) are fairly independent of the reference acid. The energy required to reorganize the normally planar BX\textsubscript{3} into the pyramidal form is represented by \(\Delta H_1\), and \(\Delta H_3\) is the heat of reaction of the reorganized BX\textsubscript{3} with the base. Assuming that \(\Delta H_3\) is proportional to the electronegativity of X, then the reversal in \(\Delta H_5\) between BCl\textsubscript{3} and BF\textsubscript{3} must be a result of a more positive \(\Delta H_1\) for BF\textsubscript{3} than BCl\textsubscript{3}. That is, BF\textsubscript{3} is a weaker acid than BCl\textsubscript{3} because more energy is required to reorganize BF\textsubscript{3} from planar to pyramidal form than is required for BCl\textsubscript{3}. If the above assumptions and published\textsuperscript{15} estimates of \(\Delta H_1\) are
employed, the order of acidity of the reorganized boron halide is $\text{BF}_3 > \text{BCl}_3$ as is expected from inductive effect arguments.

A variety of nmr,\textsuperscript{16} ir,\textsuperscript{17} and electronic\textsuperscript{17} spectroscopic investigations have also been carried out on base:BX$_3$ complexes. In these studies it was observed that BF$_3$ perturbed the spectrum of the donor base less than BCl$_3$ did. One conclusion was that bonded BF$_3$ is a weaker electron pair acceptor than bonded BCl$_3$. This conclusion, which is in direct disagreement with the hypothesis based on the thermochemical cycle presented above, was first proposed in 1966 by J. M. Miller and M. Onyschuk.\textsuperscript{16a}

In addition to the conventional spectroscopic investigations, Swanson, Schriver, and Ibers\textsuperscript{14b} have recently reported X-ray structures of acetonitrile-boron trihalides and preliminary CNDO calculations on the BF$_3$ molecule. These structural studies indicate that complexed BCl$_3$ is more nearly tetrahedral than is complexed BF$_3$. Further, their calculations indicate that the electronegativity of a BX$_3$ acid greatly increases as the molecule is distorted from its planar geometry. They then conclude that BCl$_3$ is actually a better electron acceptor than is BF$_3$. 
II. STATEMENT OF THE PROBLEM

As discussed in the introduction, there are two theories explaining the acidic trends of BX₃ compounds. One predicts that the electron withdrawing power of the co-ordinated acid is related to the electronegativity of the X atoms, and the second hypothesis predicts that the electron withdrawing ability parallels the trends in the heat of formation of the X₃B:base complexes. Unfortunately, there are no direct measurements of the electron withdrawing ability of the co-ordinated BX₃ groups. Since we had previously demonstrated that differences in Bronsted basicities of nitrogen in the compounds R₂NBH₃⁻ and R₂NCH₃ may reflect differences in electronegativity between BH₃ and CH₃⁺, we felt it was logical to attempt to extend studies on the basicity of R₂NBX₃⁻ compounds to other compounds containing other X groups. Since the electron donating ability of the nitrogen in R₂NBX₃⁻ should be directly related to the electronegativity of the co-ordinated BX₃ group, the relative Lewis or Bronsted basicities of a series of such compounds should reflect the relative electronegativities of the respective BX₃ groups. This dissertation reports the results of such studies.
III. SUMMARY OF ACID AND BASE THEORIES

As pointed out in the introduction and statement of the problem, the concept of acidity and the problem of determining the relative acidity of two acids is central to the study reported here. Hence, a short discussion of the acid-base theories used in this dissertation should be made.

Arrhenius\textsuperscript{18} first defined an acid as a substance which increases the hydrogen ion concentration and a base as a substance which increases the hydroxide concentration in aqueous solution. The obvious limitation of this theory to water solutions was corrected by the acid-base definitions suggested by Bronsted and Lowry,\textsuperscript{19} who defined a substance which donates a proton in an acid-base neutralization as an acid and a substance which accepts a proton as a base. Thus, the Bronsted theory includes all Arrhenius acids and bases, as well as some reactions in the gas phase and in non-aqueous solutions. Acidity of an acid, HA, in aqueous solution, is defined by the equilibrium constant, Ka, of the following reaction.

\[
\begin{align*}
\text{HA} + \text{H}_2\text{O} & \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+ \\
\text{acid base} & \rightleftharpoons \text{conjugate base conjugate acid}
\end{align*}
\]

\[
Ka = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \tag{4}
\]
The acidity of HA can be experimentally determined by a large variety of methods, perhaps the most common being the direct titration of the acid. The relative acidity of two acids, HA and HB, can thus be compared by comparison of their relative Ka's. The Bronsted-Lowry theory contains one serious limitation in that only substances which contain protons are considered.

G. N. Lewis⁵⁰ pointed out that the concept of acidity could be generalized even further. He defined an acid in the most general sense as an electron pair acceptor and a base as an electron pair donor. The Bronsted acid-base theory is simply a special case or subset of the Lewis theory in which the proton of the Bronsted acids acts as an electron pair acceptor and the base as an electron pair donor. The acidity of a Lewis acid, A, is defined by the equilibrium constant, K, for the following reaction.

\[
A + :B \rightarrow A:B \\
\text{acid base addition adduct}
\]

\[
K = \frac{[A:B]}{[A][:B]} \\
(6)
\]

If the acid is gaseous, a common experimental technique of determining K or a function of K is tensimetric titrations; this method was utilized in this investigation. The relative strengths of two Lewis bases, B and D, can be determined by comparing the relative stabilities of the complexes with a single reference acid A (e.g. the stability of A:B is
compared with that of A:D).

In this work both the Bronsted-Lowry acidities and Lewis basicities of appropriate compounds are determined in order to define the electronegativity of BX₃ (X = H, Cl, F) moieties.
IV. DISCUSSION AND RESULTS - PART I

BRONSTED BASICITY OF R2NBX3-

A. Preparation of Na(CH3)2NBF3

As previously mentioned, the reaction between H3NBH3 and Na was studied by several groups9,10 who never completely characterized the reaction. When attempts were made to investigate this reaction in our laboratory, no conclusive results could be obtained, probably because of the instability of ammonia-borane. The reaction of dimethylamine-borane with sodium was, however, more reproducible and the reaction was shown to be:11

\[(\text{CH}_3)_2\text{HNBH}_3 + \text{Na} \rightarrow \text{Na}(\text{CH}_3)_2\text{NBH}_3 + 1/2\text{H}_2\]  \hspace{1cm} (7)

A similar investigation was undertaken using dimethylamine-boron trifluoride instead of dimethylamine-borane. The dimethylamine derivative was chosen to facilitate comparison with the work already completed on the borane.

The only amine-BF3 alkali metal reaction which has previously been studied is that between H3NBF3 and Na and K. Keenan and McDowell21 proposed that H3NBF3 reacts quite differently with different alkali metals. Specifically, they proposed the net reaction with Na as:

\[2\text{H}_3\text{NBF}_3 + 5\text{Na} + 2\text{NH}_3 \rightarrow (\text{NH}_2)_2\text{B(NHBF(NH}_2)) + 5\text{NaF} + 2 - 1/2\text{H}_2\]  \hspace{1cm} (8)

with the reaction proceeding in two steps. In the first reaction 1 mole of Na reacts with 1 mole of H3NBF3 followed
by a 20 minute induction period after which additional Na is consumed. The borane adduct was proposed on the basis of $H_2$ and NaF production. Recently these results have been explained by Russian workers$^{22}$ who reported a simple 1:1 reaction between Na and $H_3NBF_3$ with the formation of $NaH_2NBF_3$ followed by solvolysis.

Dimethylamine boron trifluoride reacts smoothly and easily with Na in liquid Ni$_3$ at -40°C to produce $H_2$. Hydrogen evolution ceases after about 30 minutes, and typical reaction stoichiometries are reported in Table I.

### TABLE I

<table>
<thead>
<tr>
<th>STOICHIOMETRY OF $(CH_3)_2HNBF_3$ AND Na REACTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(CH_3)_2HNBF_3$</td>
</tr>
<tr>
<td>2.847 mmoles</td>
</tr>
<tr>
<td>3.002 mmoles</td>
</tr>
</tbody>
</table>

These data indicate the reaction to be:

$$(CH_3)_2HNBF_3 + Na \rightarrow Na(CH_3)_2NBF_3 + 1/2H_2 \quad (9)$$

In the first determination, 2.85 mmoles of $(CH_3)_2HNBF_3$ was reacted with 14.4 mmoles of Na. The reaction was continued for 72 hours at temperatures varying from -78°C to -40°C. The 500% excess of sodium and a long reaction time were chosen to insure that no side or solvolysis reactions were present in the case of $(CH_3)_2HNBF_3$. As can be seen
from the data, no side reaction was observed.

After the reaction had ceased, and the excess Na had been amalgamated with Hg, no suspended solid material could be seen in NH₃ solution. This solution was separated from glass particles and the mercury-sodium amalgam by filtration using standard vacuum filtration techniques. The solvent ammonia was then pumped off; a fluffy white non-crystalline or microcrystalline material remained. This very hygroscopic material, postulated to be Na(CH₃)₂NBF₃, was handled in a dry box at the dew point of P₂O₅ during all subsequent operations.

B. Characterization of Na(CH₃)₂NBF₃

1. Elemental Analyses - Methods

Boron is conventionally determined as boric acid by titration with hydroxide in the presence of mannitol. It has been observed that both nitrogen and fluorine can interfere in this analysis. In this work no interference by nitrogen has been observed in boron analysis. The interference by fluorine has been eliminated by removing the fluoride by precipitation using calcium cation. An outline of the method finally adopted for boron and fluorine analysis is given below.

1) Hydrolysis of sample ... addition of conc. HNO₃
2) Neutralization ... adjust pH to 7
3) Precipitation of Fluoride ... add excess Ca⁺² (pH = 7)
4) Separate CaF$_2$ by centrifugation  
5) Addition of few drops of Fe$^{+3}$ solution  
6) Conventional mannitol titration for boron

2. Fluorine

Fluorine was determined gravimetrically by precipitation of fluoride as CaF$_2$. This method is not new and the analysis for fluorine by precipitation as CaF$_2$ in amine-boron trifluoride complexes is reported elsewhere. The analysis is somewhat difficult because CaF$_2$ tends to form a very fine precipitate which will pass through the finest frits. To insure complete separation the precipitate was separated by centrifugation in the analysis reported here. In all analyses pH was carefully controlled to 7.0 ± .2; this was found to be essential to insure reproducibility of results. The average weight percent determined for fluorine in the known (CH$_3$)$_2$HNBF$_3$ was 55.5 as compared to the theoretical value of 50.5. High analysis for fluorine was observed in every attempt and is probably due to coprecipitation of small amounts of Ca(OH)$_2$. For Na(CH$_3$)$_2$NBF$_3$ average weight percent was found to be 44.7 compared to the theoretical value of 42.3.

3. Boron

The only modification to the standard boron procedure was the addition, before the titration, of a few drops of a Fe$^{+3}$ solution to insure complete elimination of any remaining fluoride as FeF$^{+2}$, FeF$_2$$^{+1}$, and FeF$_3$. The average
weight percent of boron determined by the mannitol titration was 7.7 compared to the theoretical of 8.0.

4. C, H, and N

Analyses of C, H, and N were done commercially by Galbraith Laboratories. The results of these analyses are summarized below.

**TABLE II**

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc.</td>
<td>17.8</td>
<td>4.49</td>
<td>10.40</td>
</tr>
<tr>
<td>Found</td>
<td>13.5</td>
<td>3.92</td>
<td>9.27</td>
</tr>
</tbody>
</table>

Only the carbon result deviates by more than normal experimental error. Its very low percentage could be due to the formation of refractories in the combustion analysis. The deviations in the N and H values are not uncommon in the analyses of B-N compounds.

5. Melting Point

The sodium salt, Na(CH$_3$)$_2$NBF$_3$, does not melt or exhibit any signs of decomposition at temperatures up to 250°.

C. Aqueous Acid-Base Chemistry of Na(CH$_3$)$_2$NBF$_3$

(CH$_3$)$_2$NBF$_3^-$ and (CH$_3$)$_2$NBH$_3^-$ should be nearly isostructural. We have previously demonstrated the following
equilibrium for \((\text{CH}_3)_2\text{NBH}_3^-\):

\[
(\text{CH}_3)_2\text{NBH}_3^- + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{HNBH}_3 + \text{OH}^-
\]  

(10)

In fact, the \((\text{CH}_3)_2\text{NBH}_3^-\) anion could be titrated as a salt of a weak acid giving the Ka value for its conjugate acid, \((\text{CH}_3)_2\text{HNBH}_3\). There was every reason to believe that \((\text{CH}_3)_2\text{NBF}_3^-\) would undergo a similar hydrolysis allowing the acidity of \((\text{CH}_3)_2\text{HNBF}_3\) to be determined. The differences in the Ka's of \((\text{CH}_3)_2\text{HNBH}_3\) and \((\text{CH}_3)_2\text{HNBF}_3\) would then provide data which hopefully could be related to the electronegativities of \(\text{BH}_3\) and \(\text{BF}_3\). Further, it was hoped that data on \(\text{BCl}_3\) might become available through similar studies on the analogous borontrichloride complexes.

When \((\text{CH}_3)_2\text{NBF}_3^-\) is dissolved in water, the pH increases to 9, an observation consistent with the postulated equilibrium:

\[
(\text{CH}_3)_2\text{NBF}_3^- + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{HNBF}_3 + \text{OH}^-
\]  

(11)

Further evidence in support of this equilibrium is the formation of \((\text{CH}_3)_2\text{HNBF}_3\) from \((\text{CH}_3)_2\text{NBF}_3^-\) either in wet \(\text{CHCl}_3\) (as detected by nmr) or in moist air. \((\text{CH}_3)_2\text{HNBF}_3\) could be separated from \(\text{Na}(\text{CH}_3)_2\text{NBF}_3^-\) by sublimation after 10 minutes exposure to the atmosphere.

Titrations of \((\text{CH}_3)_2\text{NBF}_3^-\) with strong acid were undertaken and a typical titration curve is presented in Figure 1. Since the curve shows no inflection point, the conjugate base must be derived from an acid which has a pKa
Figure 1. Titration of \((CH_3)_2NBF_3^-\) with HCl in Water
of less than 7 (i.e., $K_a \approx 10^{-7}$). Since an acid with a $pK_a$ less than 7 is itself directly titratable in aqueous solution with strong base, direct titration of $(CH_3)_2HNBF_3$ was attempted. The resulting titration curves were quite similar in appearance to those obtained for the Na$(CH_3)_2NBF_3$ titrations with strong acid in that neither showed an inflection point. In this case the implication is that the $pK_a$ of the acid must exceed 7. These results indicate that $(CH_3)_2HNBF_3$ has a $pK_a \approx 7-8$ and is thus untitratable either directly as an acid or indirectly as its conjugate base in aqueous solution.

A $pK_a$ of 7 for $(CH_3)_2HNBF_3$ might seem surprising since $(CH_3)_2HNBH_3$ has a $pK_a$ of 11. However, since BF$_3$ is usually considered to be a stronger Lewis acid (or electron acceptor) than BH$_3$, we might expect $(CH_3)_2HNBF_3$ to be a stronger acid than $(CH_3)_2HNBH_3$. If we examine the effect on Bronsted acidity of the substitution of halogens for hydrogen in a series of organic acids, a rational for the large differences in acidity between $(CH_3)_2HNBH_3$ and $(CH_3)_2HNBF_3$ becomes clear. For example, consider the series of acetic acids:
TABLE III
ACIDITY OF SUBSTITUTED ACETIC ACIDS

<table>
<thead>
<tr>
<th>Acid</th>
<th>$K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_3COOH$</td>
<td>$1.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>$Cl_3COOH$</td>
<td>$1.1 \times 10^{-1}$</td>
</tr>
<tr>
<td>$F_3COOH$</td>
<td>completely dissociated</td>
</tr>
</tbody>
</table>

The successive replacement of $CH_3^+$ by the stronger Lewis acids $CCl_3^+$ and $CF_3^+$ increase the Bronsted acidity of the acid by six orders of magnitude. This increase in availability of the proton is due to a decrease in electron density at the oxygen caused by the successive replacement of more electronegative halides. Presumably this same effect is observed with the replacement of a $BF_3$ for the less electronegative $BH_3$. Unfortunately no $Ka$ data is available on the analogous $(CH_3)_2NCF_3$ adducts for direct comparison to $(CH_3)_2NBH_3^-$ but the illustration presented using substituted acetic acids adequately explains the large difference in acidity between $(CH_3)_2HNBH_3$ and $(CH_3)_2HNBF_3$.

Since the $pKa$ of $(CH_3)_2HNBF_3$ could not be precisely determined in aqueous solution, further work in this solvent was discontinued and the possibility of direct titrations of amine-boranes in non-aqueous media was investigated.
D. Non-Aqueous Titrations of Amine-BX₃ Complexes

1. Preparation of Amine-BF₃ Complexes

The literature contains an abundance of methods for the preparation²⁶,²⁷ and characterization of addition compounds between boron trifluoride and simple amines; however, the reported methods are often contradictory. Basically, all that is required to synthesize any of these compounds is to bring the two parent substances together in such a way as to minimize decomposition. The most effective method seems to be a base displacement reaction in which the amine is brought into contact with Et₂OBX₃. This was suggested by Krause and Brown²⁶ in 1929 for the preparation of H₃NBF₃, questioned by Laubengayer and Condike²⁷ in 1948, and finally suggested again by Taylor et al.²⁸ in 1969 as the best method of preparation of the pure complex.

In this study H₃NBF₃, CH₃H₂NBF₃, and (CH₃)₂HNBF₃ were all prepared by addition of the amine to ether solutions of BF₃. For example, the base displacement preparation of H₃NBF₃ is:

\[
\text{NH}_3 + \text{Et}_2\text{OBF}_3 \rightarrow \text{H}_3\text{NBF}_3 + \text{Et}_2\text{O} \quad (12)
\]

Analogous reactions can be written for both methyl- and dimethylamine.

The products were purified by crystallization of H₃NBF₃ (water or acetone) and CH₃H₂NBF₃ (isopropyl alcohol) and sublimation of (CH₃)₂HNBF₃. The sharp melting points of
163° for H₃NBF₃, 93.5° for CH₃H₂NBF₃, and 52° for (CH₃)₂HNBF₃ and the spectroscopic data presented in the next section confirm the purity of the crystalline materials.

2. Characterization of Amine-BF₃ Complexes
a. Infrared Spectra of H₃NBF₃, CH₃H₂NBF₃, and (CH₃)₂HNBF₃
1) IR - H₃NBF₃

The text book example of the compound which contains a co-ordinate covalent bond, H₃NBF₃, has received remarkably little spectroscopic investigation. In 1958 several papers²⁹,³⁰ appeared detailing its IR and Raman spectra and in 1965 Sawodhy and Goubeau³¹ in a review of similar compounds discussed and presented additional data including force constant calculations on H₃NBF₃. In this latter work several discrepancies related to assignment of fundamental modes,²⁹ as well as large differences³⁰ in reported frequencies between the results which appeared in the two 1958 papers, were not mentioned. Recently²⁸ Taylor, Gabelnick, Aida, and Amster reported a study of the isotopic frequencies and force constant calculations for H₃NBF₃ in which they discuss the discrepancies in the earlier literature. In the opinion of Taylor's group the difficulties encountered in the earlier works are probably due to the slow decomposition of H₃NBF₃ exposed to moisture. This statement is particularly significant in that H₃NBF₃ is usually purified by recrystallization²⁶,²⁷ from water. The proposed route of the decomposition is by successive
replacement of the fluorides by hydroxide. If this is the case, then the intermediate hydroxyfluoroborate complexes would be difficult to distinguish from $\text{H}_3\text{NBF}_3$ since hydroxide and fluoride are both isoelectronic and differ in mass by only two atomic units. Decomposition was observed by the appearance of a broad peak at about 800 cm$^{-1}$ and a weaker but sharper peak at 1260 cm$^{-1}$.

In Table IV the IR frequencies of $\text{H}_3\text{NBF}_3$ are listed along with the specific assignments based on the work of Taylor$^{28}$ et al.

The frequencies listed for this work are the average of three tracings of different samples all prepared as solid suspensions in KBr. Spectra were also taken in dimethylformamide, pyridine, and chloroform with no appreciable change in the observed frequencies. The data agree with the frequencies reported$^{28,29}$ in all respects. The assignments made by Taylor are based on the normal coordinate analysis and by reference to compounds of similar structure. Since no data on polarization or band contours were employed, some discrepancies may exist but they would be expected to be very minor. The assignments are further complicated by a strong non-specific electrostatic interaction$^{32}$ involving the fluorine atoms which causes a broadening of bands associated with the stretching of the in- and out-of-phase $\text{NBF}_3$ stretch in the region between 1220 cm$^{-1}$ and 1000 cm$^{-1}$. 
### TABLE IV

**INFRARED ASSIGNMENTS FOR H$_3$NBF$_3$**

<table>
<thead>
<tr>
<th>$H_3NBF_3$ (cm$^{-1}$)</th>
<th>Assignment$^{28}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>this work</td>
<td>ref 29</td>
</tr>
<tr>
<td>3250 m-br</td>
<td>3285</td>
</tr>
<tr>
<td>3152 m-br</td>
<td>3170</td>
</tr>
<tr>
<td>2900 w</td>
<td>2917</td>
</tr>
<tr>
<td>2300 w</td>
<td></td>
</tr>
<tr>
<td>1730 m-s</td>
<td>1735</td>
</tr>
<tr>
<td>1700 m-sh</td>
<td></td>
</tr>
<tr>
<td>1590 st-sh</td>
<td>1596</td>
</tr>
<tr>
<td>1440 st-s</td>
<td>1440</td>
</tr>
<tr>
<td>1430 st-br</td>
<td>1420</td>
</tr>
<tr>
<td>1220 br</td>
<td>1210</td>
</tr>
<tr>
<td>1180 bf</td>
<td></td>
</tr>
<tr>
<td>1140 br</td>
<td>1144</td>
</tr>
<tr>
<td>1110 br</td>
<td></td>
</tr>
<tr>
<td>1020 br</td>
<td>1028</td>
</tr>
<tr>
<td>980 br</td>
<td>982</td>
</tr>
<tr>
<td>860 m-sh</td>
<td>860</td>
</tr>
<tr>
<td></td>
<td>510</td>
</tr>
<tr>
<td></td>
<td>330</td>
</tr>
</tbody>
</table>

st=strong, m=medium, w=weak, s=sharp, br=broad, sh=shoulder
2) IR - CH$_3$H$_2$NBF$_3$

The observed infrared frequencies of CH$_3$H$_2$NBF$_3$ are summarized in Table V. The data is the average of three runs of different samples taken as solid suspensions in KBr. The spectra were also recorded in dimethylformamide, pyridine, and chloroform and no significant measurable differences were observed. The tentative assignments have been made, since detailed assignments have not appeared in the literature, by reference to H$_3$NBF$_3$, assigned spectrum of the parent amine and assignments for (CH$_3$)$_2$HNBH$_3$.33

The spectrum shows the expected N-H stretch at 3263 cm$^{-1}$ and C-H stretch at 3190 cm$^{-1}$. The deformation modes of the C-H, N-H are found between 1600 cm$^{-1}$ and 1200 cm$^{-1}$. The broad absorptions due to the B-F bonds from 1300 cm$^{-1}$ to 1000 cm$^{-1}$ are also distinctly in evidence and perhaps reflect the fluoride electrostatic interaction mentioned above.

3) IR - (CH$_3$)$_2$HNBF$_3$

A summary of the observed infrared frequencies of (CH$_3$)$_2$HNBF$_3$ is presented in Table V. The data is an average of two KBr runs. Solution spectra in dimethylformamide, pyridine, and chloroform were taken and no significant differences were observed. The assignments were made by reference to H$_3$NBF$_3$, dimethylamine, and the earlier work on (CH$_3$)$_2$HNBH$_3$.33
### TABLE V

**INFRARED ASSIGNMENTS FOR CH$_3$H$_2$NBF$_3$ AND (CH$_3$)$_2$HNBF$_3$**

<table>
<thead>
<tr>
<th>CH$_3$H$_2$NBF$_3$ (cm$^{-1}$)</th>
<th>(CH$_3$)$_2$HNBF$_3$ (cm$^{-1}$)</th>
<th>Assignment (tentative)</th>
</tr>
</thead>
<tbody>
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<td>3370 w-sh</td>
<td>NH str</td>
</tr>
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</tr>
<tr>
<td>3263 st-s</td>
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</tr>
<tr>
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<td>2790 w</td>
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<tr>
<td></td>
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<tr>
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<td>2370 w</td>
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<td>2292 m-s</td>
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<tr>
<td></td>
<td>2258 m-s</td>
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</tr>
<tr>
<td>1608 st-s</td>
<td>1650 m-vbr</td>
<td>CH$_3$ def</td>
</tr>
<tr>
<td>1466 st-s</td>
<td>1387 w-sh</td>
<td>BF</td>
</tr>
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<td></td>
<td>1460 st-s</td>
<td>NH def</td>
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<td></td>
<td>1351 st-br</td>
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<td>1325 st-br</td>
<td>CN</td>
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<td>1179 st-br</td>
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<td></td>
<td>1161 st-br</td>
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<td>1111 m-br</td>
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<td>1058 st-br</td>
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<td>1005 st-br</td>
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<tr>
<td>720 m-s</td>
<td>800 w-br</td>
<td>NB str</td>
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<td></td>
<td>700 st-vs</td>
<td>CN str</td>
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<tr>
<td></td>
<td>570 m-sh</td>
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</tr>
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</table>

*st=strong, m=medium, w=weak, s=sharp, br=broad, sh=shoulder*
The expected sharp N-H and C-H stretching frequencies at 3260 cm\(^{-1}\) and 3170 cm\(^{-1}\) are the most pronounced features of this region of the spectra. Absolute assignment of the deformation modes are again not possible. The broad absorptions associated with the fluorine are also present in the region between 1300 cm\(^{-1}\) and 1000 cm\(^{-1}\). Here again the broadening is probably due to an electrostatic interaction.

b. NMR Spectra of H\(_3\)NBF\(_3\), CH\(_3\)H\(_2\)NBF\(_3\), and (CH\(_3\))\(_2\)HNBF\(_3\)

The donor-acceptor complexes of group III and V often exhibit complex and very interesting nmr chemical shifts and coupling constants. Specifically, in the case of amine-BF\(_3\) complexes the possibility of coupling exists between \(^1\)H (1/2), \(^{11}\)B (3/2), \(^{10}\)B (3), \(^{14}\)N (1), and \(^{19}\)F (1/2) to mention only those isotopes of natural abundance sufficiently large to cause observable spin-spin coupling.

As was mentioned in the discussion of the infrared spectra of these complexes, very little resonance spectroscopic work has been done. For example, it was not until 1965 that Heitsch\(^{34}\) reported that the methyl peaks in methylamine-boron trifluoride were split by the boron as well as the N-H proton. Confirmation of Heitsch's assignment of coupling constants for H\(_3\)NBF\(_3\), CH\(_3\)H\(_2\)NBF\(_3\), and (CH\(_3\))\(_2\)HNBF\(_3\) from spin decoupling of \(^1\)H-\(^1\)H and \(^1\)H-\(^{14}\)N as well as \(^{14}\)N spectra are presented below.
1) $^1H$ nmr of $H_3NB\text{F}_3$

The chemical shift and coupling constant data for $H_3NB\text{F}_3$ are given in Table VI and the decoupled $^1H$-$^{14}N$ double resonance spectrum is presented in Figure 2. From this seven line spectrum of relative intensity 1:4:7:8:7:4:1 the spin-spin coupling constants of $J_{HnB}$ and $J_{HnbF}$ would appear to be a 4Hz. Given this coupling, the relative intensities observed can be easily understood by allowing the 1111 quartet due to $^{11}B$ (spin 3/2) to symetrically overlap the 1331 quartet due to $^{19}F$ (spin 1/2) as can be seen by:

$$
\begin{array}{cccccccc}
& 1 & 1 & 1 & 1 \\
1 & 1 & 1 & 1 & \cdots & \cdots & \cdots & \cdots \\
& 3 & 3 & 3 & 3 \\
& 3 & 3 & 3 & 3 \\
& 1 & 1 & 1 & 1 \\
& 1 & 4 & 7 & 8 & 7 & 4 & 1
\end{array}
$$

The experimental spectrum was duplicated using a simple curve fitting technique. Each peak in the multiplet was assumed to be Lorenzian. That is, for a single peak centered at a point $x=0$, the line shape $f(x)$ is given by

$$
f(x) = \frac{1}{1 + x^2} \quad (13)
$$

For several peaks each displaced from the origin by a distance $C_i$ the shape of the multiplet can be expressed as

$$
f(x) = \frac{1}{1+(x+C_1)^2} + \frac{1}{1+(x+C_2)^2} + \cdots + \frac{1}{1+(x+C_n)^2} \quad (14)
$$
### TABLE VI

1^H CHEMICAL SHIFTS* AND SPIN-SPIN COUPLING CONSTANTS FOR AMINE-BF₃ COMPLEXES

<table>
<thead>
<tr>
<th>Compound</th>
<th>Shift (ppm)</th>
<th>$J_{HN}$</th>
<th>$J_{HcnB}$</th>
<th>$J_{HncH}$</th>
<th>$J_{HcnbF}$</th>
<th>$J_{HnB}$</th>
<th>$J_{HnbF}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3\text{NBF}_3$</td>
<td>-4.3</td>
<td>42.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.1</td>
<td>4.0</td>
</tr>
<tr>
<td>$\text{CH}_3\text{H}_2\text{NBF}_3$</td>
<td>-2.5 (CH₃)</td>
<td>**</td>
<td>2.1</td>
<td>6.2</td>
<td>**</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-4.4 (NH)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{HNBF}_3$</td>
<td>-2.5 (CH₃)</td>
<td>**</td>
<td>1.9</td>
<td>5.8</td>
<td>**</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-4.8 NH</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

*relative to tetramethyldisilane -§ downfield

**not observed
For a quartet arising from splitting by a $^{11}$B ($I = 3/2$), this expression can be rewritten as

$$f(x) = \frac{1}{1+(x-x_0+a)^2} + \frac{1}{1+(x-x_0-a)^2} + \frac{1}{1+(x-x_0+3a)^2} + \frac{1}{1+(x-x_0-3a)^2}$$

(15)

where

- $a = 1/2$ (coupling constant)
- $x_0$ = distance from origin to center of multiplet
- $x$ = position on x axis
- $f(x)$ = intensity at point $x$
- half width assumed equal to 1

If the assignment of coupling constants is as outlined above the experimental spectrum of $\text{H}_3\text{NBF}_3$ is the sum of four quartets. Choosing the origin as the center of the multiplet, then its four component quartets arising from $^{11}$B splitting will be centered at $x_0 = \pm 6$, $\pm 2$ respectively. Since the four quartets arise from splitting by three $^{19}$F ($I = 1/2$) nuclei, their relative intensities will be 1:3:3:1. Using equation 15 the effect on the observed intensities was then simulated by varying $x_0$ and $a$. In this manner with $a = 2$ and $x_0 = \pm 2$, $\pm 6$ it was possible to effectively duplicate the observed pattern.

2) $^1$H nmr of $\text{CH}_3\text{H}_2\text{NBF}_3$

The chemical shift and coupling constant data for $\text{CH}_3\text{H}_2\text{NBF}_3$ presented in Table VI agree with values appearing in the literature. The coupling assignments were con-
firmed by proton double resonance and this spectrum along with the single resonance $^1\text{H}$ spectrum is presented in Figure 3. The observed relative intensities of approximately 1:1:1:3:2:2:3:1:1:1 of the 10 line multiplet can be understood in terms of overlapping multiplets if coupling constants of $J_{\text{HcnH}} = 6$ and $J_{\text{HcnB}} = 2$ are assumed:

$$
\begin{array}{cccccccc}
1 & 2 & 1 & 2 & 1 & 2 & 1 & 1 \\
1 & 2 & 1 & 2 & 1 & 2 & 1 & 1 \\
1 & 2 & 1 & 2 & 1 & 2 & 1 & 1 \\
1 & 2 & 1 & 2 & 1 & 2 & 1 & 1 \\
\end{array}
$$

This complex methyl proton multiplet collapses into four peaks upon irradiation of the NH$_2$ protons confirming that the NH$_2$ protons couple with the methyl protons. The quartet which remains during proton decoupling arises from coupling of the H$_3$C protons with $^{11}\text{B}$ nucleus of spin 3/2. The shape of the observed quartet could be duplicated by a calculated spectrum composed of four Lorenzians of equal intensity which partially overlap one another. This quartet, then, almost certainly arises from coupling of the CH$_3$ with $^{11}\text{B}$, with overlap of the four peaks enhancing the intensities of the central absorptions. Since the spectrum does not change upon irradiation of the $^{14}\text{N}$ and no splitting could be reasonably assigned to interaction with this nucleus, any CH$_3$-$^{14}\text{N}$ coupling is probably very small. A lack of $^{14}\text{N}$ coupling is also strongly supported by direct
Figure 3. Proton NMR Spectrum of CH$_2$H$_2$NBF$_3$
$^{14}$Nmr evidence to be presented below.

3) $^1$H nmr of (CH$_3$)$_2$HNBF$_3$

The relevant chemical shift and coupling constant data for (CH$_3$)$_2$HNBF$_3$ are presented in Table VI and agree with the literature. The relative intensities of the seven lines in the single resonance proton spectra are 1:1:2:3:2:1:1. If $J_{HcnH} = 5.8$ Hz and $J_{HcnB} = 1.8$ Hz, the splitting can be visualized as:

\[
\begin{array}{cccccccc}
1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
1 & 1 & 1 & 2 & 1 & 1 & 1 & 1 \\
\end{array}
\]

Here the inner peaks are all enhanced because of some overlap with their neighbors (actual measured heights are 50, 68, 72, 83, 70, 68, 54) causing the inner peaks to seem more intense. Making this assumption, the spectrum can be duplicated by use of the Lorenzian curve fitting technique, with $a = 1$ and $x_0 = \pm 3$. Here again double resonance experiments were also performed to confirm assignments. The proton spectrum and the decoupled spectrum are presented in Figure 4. As in the case of CH$_3$H$_2$NBF$_3$ irradiation of the $^1$N produces no change in the methyl resonance of (CH$_3$)$_2$HNBF$_3$ indicating no $^1$N coupling, an assumption which is further supported by direct $^1$N nmr evidence which will be presented below. Irradiation of NH proton collapses the multiplet into a quartet similar to that seen in CH$_3$H$_2$NBF$_3$. 
Figure 4. Proton NMR Spectrum of (CH$_3$)$_2$HNBF$_3$

(SW = 100 cps, in acetone)

$\delta = -2.5$

$1_H - (H_3)$

$\rightarrow 50$ Hz $\leftarrow$
upon irradiation of the NH protons. The splitting observed in the \((\text{CH}_3)_2\text{HNBF}_3\) experiment is also due to coupling of \(\text{H}_3\text{C}\) protons to \(^{11}\text{B}\).

4) \(^{14}\text{N}\) nmr of \(\text{H}_3\text{NBF}_3\), \(\text{CH}_3\text{H}_2\text{NBF}_3\), and \((\text{CH}_3)_2\text{HNBF}_3\)

The \(^{14}\text{N}\) nmr spectra of the amine-\(\text{BF}_3\) complexes were taken in acetone relative to \(\text{CH}_3\text{CN}\) (by sample replacement technique). The chemical shifts and line widths are reported in Table VII. In order to observe coupling of \(^{14}\text{N}\) to a proton \(J_{\text{HN}} \ll \frac{1}{T_2}\). The spin-spin relaxation time, \(T_2\), can be gotten from the observed line width in an nmr experiment.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Shift (ppm)</th>
<th>Line Widths (full 1/2 ht)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_3\text{NBF}_3)</td>
<td>+219 +1</td>
<td>350-425 Hz</td>
</tr>
<tr>
<td>(\text{CH}_3\text{H}_2\text{NBF}_3)</td>
<td>+218 +1</td>
<td>350-425 Hz</td>
</tr>
<tr>
<td>((\text{CH}_3)_2\text{HNBF}_3)</td>
<td>+214 +1</td>
<td>300-350 Hz</td>
</tr>
<tr>
<td>((\text{CH}_3)_2\text{HNBH}_3)</td>
<td>+225 +1</td>
<td>300-350 Hz</td>
</tr>
</tbody>
</table>

*+ppm are upfield from \(\text{CH}_3\text{CN}\)

The line width is determined by the relaxation of the nucleus and by coupling to other nuclei. The former represents a lower limit on \(T_2\) and the latter an upper limit. In the case of Amine-\(\text{BF}_3\) complexes fluorine\(^{16}\text{C}\) and boron\(^{16}\text{C}\) do not usually show any nitrogen coupling and proton
coupling can be no more than 50 Hz, implying an upper limit on $J_{HN}$ of $\frac{1}{1200}$ Hz. The lower limit on $J_{HN}$ calculated directly from the line widths presented in Table VII is $\frac{1}{1500}$ Hz. Both upper and lower limits of $T_2$ preclude any observable nitrogen coupling in amine-BF$_3$ complexes.

c. Mass Spectra of H$_3$NBF$_3$, CH$_3$H$_2$NBF$_3$, and (CH$_3$)$_2$HNBF$_3$

The mass spectra of H$_3$NBF$_3$, CH$_3$H$_2$NBF$_3$, and (CH$_3$)$_2$HNBF$_3$ are listed along with m/e assignments in Tables VIII, IX, and X respectively. The three adducts all show a peak at M.W.-19 (loss of a fluorine) as a major ion, a fragment which is also characteristic of most fluoro carbons. The fragmentation for CH$_3$H$_2$NBF$_3$ and (CH$_3$)$_2$HNBF$_3$ is quite similar to the patterns observed in methyl- and dimethylamine, specifically in the m/e region centered at 29 and 44 respectively. The mass spectra of H$_3$NBF$_3$, CH$_3$H$_2$NBF$_3$, and (CH$_3$)$_2$HNBF$_3$ are listed along with m/e assignments in Tables VIII, IX, and X respectively. The three adducts all show a peak at M.W.-19 (loss of a fluorine) as a major ion, a fragment which is also characteristic of most fluoro carbons. The fragmentation for CH$_3$H$_2$NBF$_3$ and (CH$_3$)$_2$HNBF$_3$ is quite similar to the patterns observed in methyl- and dimethylamine, specifically in the m/e region centered at 29 and 44 respectively. The fragmentation for CH$_3$H$_2$NBF$_3$ and (CH$_3$)$_2$HNBF$_3$ is quite similar to the patterns observed in methyl- and dimethylamine, specifically in the m/e region centered at 29 and 44 respectively.

3. Non-Aqueous Titrations - System

While (CH$_3$)$_2$HNBF$_3$ was too weak an acid to be titrated in water, the possibility existed that acidity measurements could be carried out in non-aqueous solvents. It is well known that as the basicity of a solvent is increased, the equilibrium is shifted further to the right and the apparent acidity of the acid is increased. The equilibrium constant $K_a$ defines the acidity of the acid HA.
TABLE VIII
MASS SPECTRUM COMPILATION FOR H₃NBF₃

<table>
<thead>
<tr>
<th>m/e</th>
<th>% I/I₀</th>
<th>Assignment</th>
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<td>34.5</td>
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<td>NH₃, OH</td>
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</tr>
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<td>20</td>
<td>3</td>
<td></td>
</tr>
<tr>
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<td>H₃N¹⁰BF₂, H₂N¹¹BF₂</td>
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TABLE VIII. (Continued) MASS SPECTRUM
COMPILATION FOR \( \text{H}_3\text{NBF}_3 \)

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<td>m/e</td>
<td>% I/I₀</td>
<td>Assignment</td>
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</table>
\[ K_a = \frac{[H^+][A^-]}{[HA]} \] (17)

A numerical value of \( K_a \) can often be determined from the properties of the acid's titration curve. Probably the simplest example of this is the point at which half the acid has been neutralized; that is, when \([HA] = [A^-]\), at this point (if \( \gamma_{HA} = \gamma_{A^-} \)) \( K_a = [H^+] \).

In non-aqueous solvents the conversion of the potential measured by a glass electrode to the hydrogen ion activity is difficult. Just as in water the potential measured is indeed proportional to the log of the hydrogen ion activity. However, the proportionality constant between emf and pH, which is dependent on solvent as well as the activity coefficients of A and HA, is not readily available or easily obtained in non-aqueous solution. Thus, the conversion of emf measured at half neutralization of an acid to hydrogen ion activity and then to \( K_a \) is impossible. None the less, this emf will be proportional to the pKa even though the proportionality constant is unknown. Thus, the half neutralization potential (hnp) of a series of acids in the same solvent will parallel their respective acidities, and thus allows comparison of their acid strengths. As a measure of the validity of non-aqueous acidity determinations, the ratios of hnp's determined for a series of organic acids which can be titrated in non-aqueous solution are nearly identical to the ratios of \( K_a \)'s determined in
aqueous solution by standard methods. 38

a. Solvent

Solvent selection plays a crucial role in non-aqueous $K_a$ determinations and a detailed discussion of the factors which must be considered can be found elsewhere. 18, 37, 39 Briefly, five factors must be considered. Obviously the solvent must be more basic than water—the more basic the solvent the stronger the apparent acidity of the acid. The acid must be soluble and the conjugate base must be either soluble or form a compact precipitate which will not interfere with the performance of the electrochemical cell. Further, the acid and its conjugate base must be stable for a reasonable time in the solvent. The solvent itself must be easily purified and must not decompose during the course of the experiment. Lastly, the solvent must have an electrochemical potential range suitable for the determination of the particular acid or base of interest. For example, pyridine has a potential range of +100 mv to -900 mv measured 40 with glass and calomel electrodes within which the acid must be titratable. That is, for a proton in a given solvent there is a limit to the potential $a_{H^+}$ will normally generate and this limit cannot be surpassed (typically with this electrode pair, $10^{-18} \leq a_{H^+} \leq 1$). Consideration of these points results in the choice of pyridine and $N$, $N$-dimethylformamide as solvents for an acid with a
pKa of approximately 7. Titrations of the amine-BF$_3$ complexes in pyridine demonstrated the largest potential breaks and, therefore, this solvent was chosen for this work. Pyridine is easily purified and stored by drying over Linde 3A molecular sieves followed by distillation into an apparatus which allows the solvent to be manipulated without exposure to moisture and/or CO$_2$. The solubility and stability requirements are also met for all of the amine-BF$_3$ complexes.

b. Titrant

The strongly basic quaternary ammonium hydroxides are frequently used as bases in non-aqueous acid-base titrations, with tetrabutylammonium hydroxide (TBAH) probably being the most commonly employed.$^{41}$ This compound can be easily prepared from R$_4$NCl (or R$_4$NI) by ion exchange, and was used in this study. Previous workers$^{41}$ had converted their IRA400 resin to the basic form with aqueous 1N KOH and dried the column with copious amounts of isopropyl alcohol. Because of the potential sensitivity of amine-BF$_3$ to moisture, more care was taken in this work to remove water from the resin. Details are discussed in the experimental section. Since most quaternary ammonium hydroxides are less stable in pyridine than in many alcohols, it has become common practice to use alcoholic TBAH solutions as titrants in pyridine solvent systems.$^{42}$ This method, however, results in the titration being performed in a mixed solvent
of continually differing composition. To minimize any complications which such a mixed solvent might engender, the amount of titrant is minimized and, in determinations of relative acidity, the amount of each acid is carefully chosen so that the same volume of alcoholic solution will be required for each titration. In the present study, end point volumes of base were all less than 1 ml and equal molar amounts of acid (to the nearest ±0.2 mg) were used. All titrations were carried out in 50.0 ml of pyridine, the maximum isopropynol contamination was 2%.

Because of the large difference in acidity between benzoic acid, the substance used to check the overall operation of the system, and any of the amine-BF₃ complexes the titer of the TBAH determined with benzoic acid gives erronious equivalent weights for the borane complexes. For this reason H₃NBF₃ was taken as the "primary" standard for the determination of the concentrations of TBAH. As Table XI clearly demonstrates, this results in accurate equivalent weights for the other amine-BF₃ complexes.

c. Electrodes and Electrometer

The electrode pair used was a standard glass electrode (Sargent S-30050-15C) and a standard calomel electrode (Sargent S-30080-15C) with the usual saturated KCl salt bridge replaced by a saturated KCl methanol solution. The use of this electrode pair for acid strength determinations
<table>
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<th>Equivalent Wt.</th>
<th>h.n.p. (mv-ave dev)</th>
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<td>$\text{H}_3\text{NB}F_3$</td>
<td>0.720</td>
<td>84.8</td>
<td>172 (3)</td>
</tr>
<tr>
<td>$\text{CH}_3\text{H}_2\text{NB}F_3$</td>
<td>0.715</td>
<td>98.8</td>
<td>99.0 133 (2)</td>
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<tr>
<td>$(\text{CH}_3)_2\text{HN}F_3$</td>
<td>0.720</td>
<td>112.8</td>
<td>113.0 189 (8)</td>
</tr>
</tbody>
</table>
in pyridine is discussed in the literature.\textsuperscript{43} No significant problems with the electrodes were observed in this work.

The electrometer, discussed in detail on p. 101 was used because a high input impedance is necessary to conduct titrations in pyridine.

d. Titration of Benzoic Acid

The precision of the complete system for the titration of weak acids in pyridine was determined by titrating benzoic acid. A representative titration curve is presented in Figure 5. These results are in complete agreement with the predicted behavior and demonstrate the feasibility of performing the titration with the apparatus described here. To optimize the precision of subsequent work, the standardization using benzoic acid and the actual half neutralization potential measurements were all performed on the same day in the shortest possible time which is approximately 45-60 seconds for each point taken (overall, approximately 5 hours).

4. Non-Aqueous Titration - HNP Determinations

a. Titration of H\textsubscript{3}NBF\textsubscript{3}, CH\textsubscript{3}H\textsubscript{2}NBF\textsubscript{3}, and (CH\textsubscript{3})\textsubscript{2}HNBF\textsubscript{3}

The titrations of methylamine-BF\textsubscript{3} complexes with TBAH in pyridine exhibit sufficiently large potential changes (of the order of 400 mv/ml) to allow the relative acidities of the series to be determined. In Figures 6, 7, and 8 the
Figure 5. Titration of Benzoic Acid with TBAH in Pyridine
Figure 6. Titration of H$_3$NEF$_3$ with TBAH in Pyridine
Figure 7. Titration of $\text{CH}_2\text{H}_2\text{NBF}_3$ with TBAH in Pyridine
Figure 8. Titration of \((\text{CH}_3)_2\text{HNBF}_3\) with TBAH in Pyridine
full titration curves for $\text{H}_3\text{N}^-$, $\text{CH}_3\text{H}_2^-$, and $(\text{CH}_3)_2\text{HNBF}_3$ are
given with the data being summarized in Table XI.

b. Titration of $(\text{CH}_3)_2\text{HNBH}_3$

Attempts to titrate $(\text{CH}_3)_2\text{HNBH}_3$ in pyridine proved
unsuccessful; the addition of 0.1 ml of TBAH to $(\text{CH}_3)_2\text{HNBH}_3$
immediately brought the solvent to its basic potential. In
retrospect this is not surprising since the pKa of
$(\text{CH}_3)_2\text{HNBH}_3$ in water is known to be 10.3,\textsuperscript{11} which is close
to the lower limit of pKa's ($\sim$11) which can be determined
in pyridine.\textsuperscript{39} A number of other solvents were examined,
including chlorobenzene, formamide, N, N-dimethylformamide,
and isobutanol; unfortunately none was found in which both
the BH$_3$ and BF$_3$ adduct could be titrated.

Non-aqueous titrations of analogous BC$_3$ adducts were
not attempted since most simple amine-BC$_3$ complexes
intramolecularly eliminate HCl\textsuperscript{1} preventing comparisons of
acidity between simple amine-BC$_3$ adducts and amine-BF$_3$
or BH$_3$ analogs.

5. Non-Aqueous Titrations - Acidity of Amine-BF$_3$ Complexes

Even though the primary objective of this study, the
comparison of the acidity of analogous BH$_3$, BF$_3$, and BC$_3$
amine adducts, was not realized in these non-aqueous titra-
tions, an interesting trend in the acidity of the amine-BF$_3$
complexes was observed. The effect of successive replace-
ment of hydrogen by methyl groups on the acidity of amine-BF$_3$
complexes is diagramatically represented in Figure 9. Obviously the acidity is not a monotonic function of the extent of methyl substitution but rather exhibits a minimum acidity at $\text{CH}_3\text{H}_2\text{NBF}_3$. While at first glance this trend may appear unique, it finds a close parallel in the acidity of the analogous ammonium ions (e.g. $\text{H}_3\text{NCH}_3^+$, $\text{H}_2\text{N(CH}_3)_2^+$ and $\text{HN(CH}_3)_2^+$) in which the acidity is a minimum for $(\text{CH}_3)_2\text{NH}_2^+$.

It is of interest also to compare the trends observed in the acidity of these complexes with the $^{14}\text{N}$ chemical shifts listed in Table VII and shown diagramatically in Figure 10. Although the chemical shift of any nucleus is not a simple function of its electron density, a number of investigators$^{16,34}$ have had marginal success with correlations of acidity and chemical shift in complexes of the type considered in this work. In this research it would appear that the $^{14}\text{N}$ chemical shifts of amine-$\text{BF}_3$ complexes do not accurately reflect the acidity of these adducts.

The existence of a minimum in acidity of ammonium ions and amine-$\text{BF}_3$ complexes might imply a competition between two or more effects. In such a balance one factor tends to increase acidity with successive replacement of hydrogen while the other tends to decrease the acidity. Competition of two effects has been used to explain the observed acidity of methylammonium ions and we believe similar arguments can be applied to amine-$\text{BF}_3$ complexes. The nature of the two factors have been postulated to be largely solvent effects.$^{44}$
Figure 9. Acidity of Amine-BF$_3$ Complexes in Pyridine
Figure 10. Trends in $^{14}$N Chemical Shifts with Methyl Substitution
or, alternatively, as intrinsic electronic interactions within the molecules.\textsuperscript{45}

Solvent arguments are concerned with general non-specific interactions as well as specific solvent-solute interactions. The former will certainly be of little use here since this work was done in pyridine which has little, if any, structure and, therefore, only very slight solvent structure reorganization during the acid-base reactions studied here. Specific solvent effects might produce the type of opposing trends observed in this work and in the methylammonium ions. The pair of trends which are invoked in specific solvent approaches are: the basicity of a series of alkyl substituted amines is increased by the inductive effect $R_3N > R_2HN > RH_2N$ while concurrent specific hydrogen bonds formed between NH protons and solvent molecules would cause the basicity to be increased for amines having more hydrogens (i.e. $RNH_2 > R_2NH > R_3N$). The net result is the observed maximum in basicity at $R_2NH$. However, it is unlikely that even specific solvent effects can explain the trends in the ammonium ions (or amine-BF\textsubscript{3}) since the order of basicities of the ammonium ions is invariant (e.g. $NH_3 < RNH_2 \cong R_2NH > R_3N$) in benzene,\textsuperscript{46} chlorobenzene,\textsuperscript{47} acetonitrile,\textsuperscript{48} nitrobenzene,\textsuperscript{49} chloroform,\textsuperscript{50} carbon tetrachloride,\textsuperscript{50} and water. Probably the strength of the base is primarily a function of its molecular and electronic structure and, to a first approximation,
independent of solvent interactions, although there may be occasional examples which necessitate predominant solvent effects.\textsuperscript{18}

These acidity trends in amines (and the amine-\textit{BF}_3 complexes) can also be rationalized considering only the intrinsic electrical nature of the complexes using either a polarization\textsuperscript{45} or a hybridization model.\textsuperscript{51} Since the differences between these approaches are more semantic than substantive, only the polarization model will be discussed.

In the polarization model the factors which are postulated to affect amine basicity with successive methyl substitution are a loosening of nitrogen's charge cloud which increases the basicity of the amine and a shift of the lone pair toward the nitrogen which decreases the basicity. Methyl groups (and alkyl groups in general) are thought to be more effective electron donating groups than hydrogen. Thus, when a methyl group is substituted for a hydrogen on an amine, this group promotes electron release\textsuperscript{45} (inductive effect) increasing the nitrogen electron cloud density and, therefore, tends to increase its basicity. From ammonia to dimethylamine this effect exerts a dominant influence on the nitrogen basicity. In addition to the increase in electron density about the nitrogen upon methyl substitution is a concomitant shift in the lone pair toward the nitrogen. This latter effect is indicated experimentally by amine and phosphine dipole moments which can only be explained if the
center of the lone pair is shifted toward the nitrogen nucleus (i.e. electron pair more nearly centered on nitrogen) with each successive replacement of a \( \text{CH}_3^+ \) for a \( \text{H}^+ \). The shift of the lone pair toward nitrogen would have the effect of reducing the ease by which a reference acid could polarize it and, therefore, would reduce the basicity at the nitrogen. The reduction of basicity from a lone pair shift occurs with each methyl addition with the calculated lone pair moment decreasing the most with replacement of the last proton. The dominant role of this change in lone pair moment has been offered as the probable cause for the decrease in base strength in going from dimethyl- to trimethylamine.\(^{45}\)
V. DISCUSSION AND RESULTS - PART II

LEWIS BASICITY OF R₂NBX₃⁻

A. Introduction

As mentioned earlier, the Bronsted acid-base theory can be viewed as a subset of the more general Lewis acid-base theory. Since experimental difficulties precluded the comparison of Bronsted acidity between different amine-BX₃ complexes, an alternative method of determining the basicity of R₂NBX₃⁻ toward a reference acid was attempted. Specifically, the interaction of R₂NBX₃⁻ with BF₃ was studied. The advantage of this method is that since BF₃ is a gas, the dissociation pressure of its complexes give the dissociation constant, K_d, directly. The synthesis of (CH₃)₂NBH₃⁻ and (CH₃)₂NBF₃⁻ by alkali metal reduction of the appropriate dimethylamine borane has already been discussed (p. 11). However, since this preparation is rather arduous and not well suited to the preparation of large quantities of (CH₃)₂NBX₃⁻ an alternative preparative route was sought.

In 1967 Shriver and Biallas reported that the bifunctional Lewis acid F₂BCH₂CH₂BF₂ reacts with triphenylmethyl ethers,⁵² and triphenylmethyl amines⁵³ to form Ø₃C⁺RO(F₂BCH₃)₂⁻ and Ø₃C⁺R₃N(F₂BCH₃)₂⁻. In both cases F₂BCH₃CH₃BF₂ behaves as a bidentate Lewis acid; i.e. both boron atoms bonded to the base. He further observed⁵⁴ that BF₃ reacts with Ø₃CN(CH₃)₂, apparently cleaving to the
Ø₃C-N bond, and forming what might be a 1:1 complex, which was not characterized. In hopes of obtaining a general synthetic route to R₂NBX₃⁻ compounds, we further investigated the reaction between Ø₃CNR₂ and boranes. Indeed with BF₃ and BCl₃ the desired anion could be formed by the direct reaction

$$\text{Ø}_3\text{CN}(\text{CH}_3)_2 + \text{BX}_3 \rightarrow \text{Ø}_3\text{C}^+(\text{CH}_3)_2\text{NBX}_3^-$$

(18)

The description of the preparation and characterization of these compounds plus determinations of the Lewis basicities of R₂NBX₃⁻ follow.

B. Preparation and Characterization of Ø₃CN(CH₃)₂

1. Preparation

The preparation of N, N-dimethyltriphenylmethylamine in (CH₃)₂CO has been reported. Biallas has found that the direct reaction of Ø₃CCl with dimethylamine more

$$\text{Ø}_3\text{CCl} + (\text{CH}_3)_2\text{NH} \rightarrow \text{Ø}_3\text{CN}(\text{CH}_3)_2 + (\text{CH}_3)_2\text{NH}_2^+\text{Cl}^-$$

(19)

conveniently produces the desired product, in good yield. This latter route was used in these studies.

2. Characterization

Ø₃CN(CH₃)₂ was characterized by mass, nmr, and ir spectroscopy, and melting point. The spectroscopic measurements have not been previously reported for this compound and thus will be discussed in detail.
a. Mass Spectrum

The mass spectrum and tentative m/e assignments of $\varnothing_3\text{CN(CH}_3)_2$ are given in Table XII. No fragmentation mechanism has been proposed, but the cracking pattern appears to be similar to that of other multiphenyl substituted amines.\textsuperscript{36} The presence of $\varnothing_3\text{CH}^+$, which arises from $\varnothing_3\text{C-N}$ bond cleavage and proton migration, as the most abundant ion may imply that the $\varnothing_3\text{C-N}$ bond is easily broken. A second characteristic of the fragmentation is the stepwise elimination of hydrogen from the fragments containing one or more phenyls at m/e = 245, 229, and 163. Such eliminations are commonly observed in the mass spectra of compounds of this type.\textsuperscript{36} Little if any trace can be found of $\varnothing_3\text{CCl}$, a most likely contaminant in the preparation.

b. IR Spectrum

The infrared absorptions (observed under conditions favoring high resolution on the IR-9) and postulated peak assignments for $\varnothing_3\text{CN(CH}_3)_2$ are presented in Table XIII. The phenyl envelope (normally observed at 3100 cm\textsuperscript{-1})\textsuperscript{56} was centered at 3035 cm\textsuperscript{-1} and was composed of five sharp absorptions at 3085, 3060, 3035, 3030, and 3000 cm\textsuperscript{-1}. The four absorptions of 2945, 2850, 2885, and 2795 cm\textsuperscript{-1} are assigned to the CH stretch which normally occurs\textsuperscript{56} in this region. The remainder of the absorptions were assigned by reference to published data on phenylamines.\textsuperscript{56} As in the mass spectra
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TABLE XII. (Continued) MASS SPECTRUM COMPILATION
FOR $\text{C}_2\text{H}_5\text{C}_2\text{H}_5$

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<td>243</td>
<td>5.0</td>
<td>$\text{C}_3$</td>
</tr>
<tr>
<td>244</td>
<td>100</td>
<td>$\text{C}_3(+\text{H})$</td>
</tr>
<tr>
<td>245</td>
<td>25.9</td>
<td>$\text{C}_3(+2\text{H})$, $\text{C}<em>3\text{CH}(</em>{13}\text{C},\text{D})$</td>
</tr>
<tr>
<td>260</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>287</td>
<td>1.7</td>
<td>$\text{C}_3\text{CN(CH}_3)_2$</td>
</tr>
<tr>
<td>288</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE XIII

**INFRARED ASSIGNMENT FOR Ø₃CN(CH₃)₂**

<table>
<thead>
<tr>
<th>Ø₃CN(CH₃)₂ (cm⁻¹)</th>
<th>Assignment (tentative)</th>
<th>Ø₃CN(CH₃)₂ (cm⁻¹)</th>
<th>Assignment (tentative)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3085 ms</td>
<td>ØH str</td>
<td>985 w-sh</td>
<td>CH₂ Wag</td>
</tr>
<tr>
<td>3060 ms</td>
<td>935 w-sh</td>
<td>903 vst-s</td>
<td></td>
</tr>
<tr>
<td>3035 ms</td>
<td>3030 ms</td>
<td>3000 ms</td>
<td>855 vm</td>
</tr>
<tr>
<td>2945 st-s</td>
<td>772 st-s</td>
<td>643 m-s</td>
<td></td>
</tr>
<tr>
<td>2850 st-s</td>
<td>760 st-br</td>
<td>1915 w-br</td>
<td>639 w-sh</td>
</tr>
<tr>
<td>2885 st-s</td>
<td>745 st-br</td>
<td>1822 w-br</td>
<td>629 m-s</td>
</tr>
<tr>
<td>2795 st-s</td>
<td>705 vst-vbr</td>
<td>1780 vw-br</td>
<td>572 m-s</td>
</tr>
<tr>
<td>1965 w-br</td>
<td>overtones &amp; combinations</td>
<td>540 m-s</td>
<td></td>
</tr>
<tr>
<td>1592 st-s</td>
<td>1490 st-br</td>
<td>1475 w-sh</td>
<td>Ø</td>
</tr>
<tr>
<td>1475 w-sh</td>
<td>1460 st-s</td>
<td>1445 st-br</td>
<td>Ø</td>
</tr>
<tr>
<td>1490 st-br</td>
<td>ØH-def</td>
<td>1319 m-s</td>
<td>Ø</td>
</tr>
<tr>
<td>1319 m-s</td>
<td>1250 w-s</td>
<td>1208 st-s</td>
<td>CH₃ rock</td>
</tr>
<tr>
<td>1250 w-s</td>
<td>1180 w-sh</td>
<td>1175 st-s</td>
<td>Ø</td>
</tr>
<tr>
<td>1180 w-sh</td>
<td>1157 st-s</td>
<td>1147 m-sh</td>
<td>Ø</td>
</tr>
<tr>
<td>1175 st-s</td>
<td>1092 w-s</td>
<td>1082 m-s</td>
<td>Ø</td>
</tr>
<tr>
<td>1147 m-sh</td>
<td>1082 m-s</td>
<td>1070 vw-sh</td>
<td>C-C str</td>
</tr>
<tr>
<td>1092 w-s</td>
<td>1070 vw-sh</td>
<td>1042 m-s</td>
<td>C-H wag</td>
</tr>
<tr>
<td>1082 m-s</td>
<td>1070 vw-sh</td>
<td>1030 st-s</td>
<td>Ø₃</td>
</tr>
<tr>
<td>1042 m-s</td>
<td>1005 st-br</td>
<td>1005 st-br</td>
<td>C-C str</td>
</tr>
</tbody>
</table>

st=strong, m=medium, w=weak, s=sharp, br=broad, sh=shoulder, v=very
no evidence to indicate the presence of any $\text{CCL}_3$ was observed.

c. $^1\text{H} \text{nmr Spectrum}$

The proton nmr spectrum in CH$_2$Cl$_2$ taken at 100 MHz is presented in Figure 11. The nmr consists of a singlet at -1.88$\delta$ due to the methyl protons and a complex multiplet at -6.98$\delta$ resulting from the phenyl protons. The methyl to phenyl proton peak area ratio of 1:2.6 is in excellent agreement with the proposed compound's peak area ratio of 1:2.5. The complex splitting of the phenyl protons was not analyzed in detail, but qualitatively similar spectra have been reported for the phenyl resonances in similar compounds.$^{35}$

d. Physical Properties

The compound $\text{C}_{6}\text{H}_5\text{CN}($CH$_3$)$_2$ is a white crystalline material which melts very sharply at 94°, a value which is in good agreement with the literature value of 94-95°.$^{55}$ The compound is very soluble in most common organic solvents from which it can be recovered without any sign of decomposition as determined by ir spectroscopy.

C. Preparation and Characterization of $\text{C}_{6}\text{H}_5\text{CN}($CH$_3$)$_2$NBF$_3^-$

1. Reaction of $\text{C}_{6}\text{H}_5\text{CN}($CH$_3$)$_2$ and BF$_3$

The overall reaction of $\text{C}_{6}\text{H}_5\text{CN}($CH$_3$)$_2$ and BF$_3$ at room temperature is:
Figure 11. Proton NMR Spectrum of $\Phi_3\text{ON}(\text{CH}_3)_2$

($SW = 500$ cps, in acetone)

$\delta = -6.9$

$\delta = -1.8$
Gas solid and solution reactions in CH\textsubscript{2}Cl\textsubscript{2}, benzene and toluene were investigated. At ambient temperatures the \(\tilde{\text{C}}\text{-}N\) bond was instantly cleaved by BF\textsubscript{3}, as witnessed by a yellow coloration which appeared in the reaction mixture simultaneously with the introduction of the borane. However, below room temperature, this instantaneous color change did not occur and the BF\textsubscript{3}-\(\tilde{\text{C}}\text{N(CH}_{3}\text{)}_{2}\) mixture remained white for several days at \(-78^\circ\). This apparent induction period may be quite significant to the overall descriptive chemistry of the \(\widetilde{\text{C}}\text{NR}_{2}-\text{BF}_{3}\) system and will be discussed in more detail on p. 85.

Stoichiometry was obtained from a gas-solid tensimetric titration (see p. 82). While reactions run in solvents usually came to equilibrium quite rapidly, the solvent reactions were not ultimately utilized to characterize the reaction because the stoichiometries obtained from reactions run in CH\textsubscript{2}Cl\textsubscript{2}, benzene, and toluene were not reproducible. Some of the problems encountered with the solution reactions were proton extraction from CH\textsubscript{2}Cl\textsubscript{2} by \((\text{CH}_{3}\text{)}_{2}\text{NBF}_{3}\) to form \((\text{CH}_{3}\text{)}_{2}\text{HNBF}_{3}\) and an uncharacterized interaction of BF\textsubscript{3} with benzene which prohibited the separation of these two compounds. The product obtained from reactions in benzene, however, is identical (X-ray powder patterns) to that from the gas-solid reactions (described on p. 82). Unquestionably the preferred synthetic method is the reaction of

\[
\tilde{\text{C}}\text{N(CH}_{3}\text{)}_{2} + \text{BF}_{3} \rightarrow \tilde{\text{C}}\text{N(CH}_{3}\text{)}_{2}^{+}\text{NBF}_{3}^{-}
\]
2. Characterization of $\varnothing_3C^+(CH_3)_2NBF_3^-$

a. IR Spectrum

The infrared spectrum of $\varnothing_3C^+(CH_3)_2NBF_3^-$ is presented in Figure 12 and tentative assignments are listed in Table XIV. The ir spectrum of this BF$_3$ complex and that of the corresponding BCl$_3$ complex proved most difficult to assign with certainty. In $\varnothing_3C^+(CH_3)_2NBF_3^-$ strong peaks at about 1000 cm$^{-1}$ are evident. Absorptions in this region have previously been assigned to BF stretching frequencies in other complexes containing tetrahedrally co-ordinated boron,$^{52}$ but as phenyl deformation modes are also usually seen in this region,$^{56a}$ the assignment of these peaks is difficult. The C-H and $\varnothing$-H stretching regions were observed as envelopes of bands, probably made up of several different stretching modes, and appeared at 3050 cm$^{-1}$ and 3260 cm$^{-1}$ respectively. Assignment of these peaks is made by analogy to a large number of compounds in which similar frequencies are observed.$^{56}$

b. Electronic Spectrum

The electronic spectrum of $\varnothing_3C^+(CH_3)_2NBF_3^-$ in benzene exhibits twin absorption maxima at 410 and 430 nm which is characteristic of the triphenylmethyl cation.$^{52}$

c. $^1$H nmr Spectrum

The methyl resonance of $\varnothing_3C^+(CH_3)_2NBF_3^-$ in benzene is a
Figure 12. Infrared Spectrum of $\phi_3O^+(CH_3)_2NBF_3^-$
TABLE XIV

INFRARED ASSIGNMENT FOR $\Phi_3^+(CH_3)_2NBF_3^-$

<table>
<thead>
<tr>
<th>$\Phi_3^+(CH_3)_2NBF_3^-$ (cm$^{-1}$)</th>
<th>Assignment (tentative)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3260 env</td>
<td>$\Phi$H str</td>
</tr>
<tr>
<td>3050 env</td>
<td>CH str</td>
</tr>
<tr>
<td>1960 m-br</td>
<td></td>
</tr>
<tr>
<td>1890 m-br</td>
<td>comb</td>
</tr>
<tr>
<td>1820 m-br</td>
<td></td>
</tr>
<tr>
<td>1590 st-s</td>
<td></td>
</tr>
<tr>
<td>1490 st-s</td>
<td>$\Phi$H def</td>
</tr>
<tr>
<td>1450 st-s</td>
<td>CH$_3$-def</td>
</tr>
<tr>
<td>1380 st-s</td>
<td>CH$_3$ rock</td>
</tr>
<tr>
<td>1210 m-s</td>
<td></td>
</tr>
<tr>
<td>1100 vbr</td>
<td>C-C str, $\Phi$-def, BF str</td>
</tr>
<tr>
<td>860</td>
<td>C-N str</td>
</tr>
<tr>
<td>820</td>
<td></td>
</tr>
<tr>
<td>765</td>
<td></td>
</tr>
<tr>
<td>745</td>
<td></td>
</tr>
<tr>
<td>710</td>
<td></td>
</tr>
</tbody>
</table>

env=envelope, m=medium, br=broad, st=strong, s=sharp, v=very
broad singlet approximately 7Hz at half peak height occurring at -1.38. In terms of the analogy developed in the introduction between the $X_3B$ amine complexes and the methyl ammonium ions, the methyl resonance of $(\text{CH}_3)_2\text{NBF}_3^-$ should be shifted relative to $(\text{CH}_3)_2\text{HNBF}_3$ in the same direction and by approximately the same magnitude as the corresponding resonance in $(\text{CH}_3)_2\text{NCH}_3$ is shifted relative to that of $(\text{CH}_3)_2\text{HNCH}_3^+$. In these systems the methyl resonance associated with the quaternary nitrogen is downfield from the methyl resonance associated with the tertiary nitrogen by about 0.7 ppm. Clearly, a similar trend is seen between $(\text{CH}_3)_2\text{HNBF}_3$ and $(\text{CH}_3)_2\text{NBF}_3^-$ where (Table XV) the methyl protons in the former resonate 1.3 ppm downfield from those in the latter.

**TABLE XV**

**METHYL PROTON RESONANCE OF QUATERNARY AND TERTIARY NITROGEN COMPOUNDS**

<table>
<thead>
<tr>
<th>Quaternary (ppm)</th>
<th>Tertiary (ppm)</th>
<th>Difference</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{CH}_3)_2\text{HNCH}_3^+$</td>
<td>$(\text{CH}_3)_2\text{NCH}_3$</td>
<td>.7</td>
<td>54</td>
</tr>
<tr>
<td>-2.9</td>
<td>-2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{HNBH}_3$</td>
<td>$(\text{CH}_3)_2\text{NBH}_3^-$</td>
<td>1.3</td>
<td>11</td>
</tr>
<tr>
<td>-2.5</td>
<td>-1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{HNBF}_3$</td>
<td>$(\text{CH}_3)_2\text{NBF}_3^-$</td>
<td>1.3</td>
<td>--</td>
</tr>
<tr>
<td>-2.6</td>
<td>-1.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The methyl resonances of the borane systems occur at a higher field than those in the \((\text{CH}_3)_3\text{N}^-(\text{CH}_3)_3\text{NH}^+\) system. This agrees with the premise that \(\text{CH}_3^+\) is a more efficient electron withdrawing group than \(\text{BH}_3\) or \(\text{BF}_3\). The methyl protons of the borane adduct are thus more shielded and their resonances occur at a higher field than they do in the trimethylamine and trimethylammonium ion pair.

Since the only suitable solvents for \(\text{CH}_3^+(\text{CH}_3)_2\text{NBF}_3^-\) seemed to be either benzene or toluene, the phenyl region of \(\text{CH}_3^+(\text{CH}_3)_2\text{NBF}_3^-\) could not be examined in any detail. Only a tentative chemical shift assignment of \(-75\) for the complex multiplet could be attempted. Good nmr spectra were difficult to obtain for this compound because of its low solubility.

d. X-ray Diffraction

X-ray powder patterns were taken of \(\text{CH}_3^+(\text{CH}_3)_2\text{NBF}_3^-\) prepared in benzene and indirect gas-solid reactions. As was mentioned above, these patterns were identical in intensity and d spacing. The d spacing for \(\text{CH}_3^+(\text{CH}_3)_2\text{NBF}_3^-\) taken as a powder using a 57.3 cm powder camera are listed in order of decreasing intensity in Table XVI.

e. Physical Properties

1) Melting Point

\(\text{CH}_3^+(\text{CH}_3)_2\text{NBF}_3^-\) is a very hygroscopic material which darkens and begins to decompose at approximately 100° in a
sealed tube.

TABLE XVI

d SPACINGS FOR $\phi_3C^+(CH_3)_2NBF_3^-$ AND $\phi_3C^+(CH_3)_2NBCl_3^-$

<table>
<thead>
<tr>
<th></th>
<th>$\phi_3C^+(CH_3)_2NBF_3^-$</th>
<th>$\phi_3C^+(CH_3)_2NBCl_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.05 Å</td>
<td>1.01 Å</td>
<td></td>
</tr>
<tr>
<td>1.28</td>
<td>1.51</td>
<td></td>
</tr>
<tr>
<td>1.20</td>
<td>1.28</td>
<td></td>
</tr>
<tr>
<td>1.13</td>
<td>1.16</td>
<td></td>
</tr>
<tr>
<td>2.25</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td>0.933</td>
<td>0.822</td>
<td></td>
</tr>
<tr>
<td>0.863</td>
<td>2.16</td>
<td></td>
</tr>
<tr>
<td>0.826</td>
<td>0.916</td>
<td></td>
</tr>
<tr>
<td>1.61</td>
<td>0.868</td>
<td></td>
</tr>
<tr>
<td>0.796</td>
<td>0.798</td>
<td></td>
</tr>
</tbody>
</table>

2) C, H, and N Analyses

Analyses done by Galbraith Laboratories are presented below. The carbon and hydrogen values are well within the

TABLE XVII

C, H, AND N ANALYSES OF $\phi_3C^+(CH_3)_2NBF_3^-$

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc.</td>
<td>70.90</td>
<td>5.91</td>
<td>3.94</td>
</tr>
<tr>
<td>Found</td>
<td>72.36</td>
<td>6.32</td>
<td>1.78</td>
</tr>
</tbody>
</table>

range expected in compounds of this type; nitrogen, however, is quite low. Repeated nitrogen analyses of this compound (and the analogous BCl$_3$ adduct, see p. 79) gave irreproducible low results. This anomaly may be due to the formation of refractories in the combustion analysis. This,
however, does not usually result in such very low nitrogen percentages. No firm explanation of these results can be offered at present.

3) Solubility

No solvent was found in which \( \text{O}_3\text{C}^+(\text{CH}_3)_2\text{NBF}_3^- \) was markedly soluble. Its solubility in benzene and toluene, estimated from \( ^1\text{H} \) nmr, appears to be only a few percent. Attempts to use other solvents, even after scrupulous drying, usually resulted in the rapid fading of the yellow color associated with \( \text{O}_3\text{C}^+ \). The solvents investigated include 1,2-dimethoxyethane, 2-methoxydiethyl ether, formamide, and \( \text{N, N-dimethylformamide} \) in which the compound was at most only slightly soluble.

D. Preparation and Characterization of \( \text{O}_3\text{C}^+(\text{CH}_3)_2\text{NBCl}_3^- \)

1. Reaction of \( \text{O}_3\text{CN(CH}_3)_2 \) and \( \text{BCl}_3 \)

The interaction of \( \text{BCl}_3 \) with \( \text{O}_3\text{CN(CH}_3)_2 \) is represented by the equation:

\[
\text{O}_3\text{CN(CH}_3)_2 + \text{BCl}_3 \rightarrow \text{O}_3\text{C}^+(\text{CH}_3)_2\text{NBCl}_3^- \quad (21)
\]

Reactions run in benzene and toluene solution, as well as gas-solid reactions, were investigated. In all determinations, instantaneous rupture of the \( \text{O}_3\text{C-N} \) bond was noted by the formation of the yellow triphenylmethyl cation immediately upon contact of the \( \text{BCl}_3 \) with \( \text{O}_3\text{CN(CH}_3)_2 \). Unlike the \( \text{BF}_3 \) reaction, no temperature induced induction
period was observed. The descriptive chemistry of this system will also be further discussed on p. 85.

The stoichiometry of the reaction between BCl₃ and \( \text{C}_3\text{CN(CH}_3\text{)}_2 \) was determined by tensimetric titration discussed on p. 85. The product obtained from reactions in benzene was confirmed to be the same as the material obtained in gas-solid reaction by X-ray diffraction. Quantities of \( \text{C}_3\text{C}^+(\text{CH}_3)_2\text{NBCl}_3^- \) were prepared in benzene for characterization of the adduct.

2. Characterization of \( \text{C}_3\text{C}^+(\text{CH}_3)_2\text{NBCl}_3^- \)
   a. IR Spectrum

The ir spectrum presented in Figure 13 is a compilation of several spectra of suspensions of \( \text{C}_3\text{C}^+(\text{CH}_3)_2\text{NBCl}_3^- \) taken in KBr, nujol and solid \( \text{C}_3\text{C}^+(\text{CH}_3)_2\text{NBCl}_3^- \) directly deposited on NaCl plates. Likewise the tentative assignments presented in Table XVIII are a compilation of several spectra. The region from 3400 cm\(^{-1}\) to 2900 cm\(^{-1}\) which encompasses both the \( \text{OH} \) and CH stretching regions showed marked signs of decomposition in the time required to record a spectrum. The first scan resulted in rather broad \( \text{OH} \) and CH stretching absorptions at 3200 cm\(^{-1}\) and 2950 cm\(^{-1}\) respectively. Subsequent scans resulted in a broadening of both peaks, resulting in an envelope centered at 3200 cm\(^{-1}\). Similar behavior was observed in the region centered at 1440 cm\(^{-1}\). The four absorptions at 1495, 1455, 1440, and 1410 cm\(^{-1}\) rapidly became a very broad absorption at 1440 cm\(^{-1}\).
Figure 13. Infrared Spectrum of $\phi_3O^+(CH_3)_2NBOL_3^-$
TABLE XVIII

INFRARED ASSIGNMENT FOR $\tilde{\varphi}_3C^+(\text{CH}_3)_2\text{NBCl}_3^-$

<table>
<thead>
<tr>
<th>Wave Number (cm$^{-1}$)</th>
<th>Description</th>
<th>Assignment (tentative)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3200 vbr (envelope)</td>
<td>$\varphi$H str</td>
<td></td>
</tr>
<tr>
<td>2950 br</td>
<td>CH str</td>
<td></td>
</tr>
<tr>
<td>2120 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2250 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2380 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1495 m</td>
<td>BCl$_3$ str</td>
<td></td>
</tr>
<tr>
<td>1455 m</td>
<td>N-C</td>
<td></td>
</tr>
<tr>
<td>1440 m-sh</td>
<td>CH</td>
<td></td>
</tr>
<tr>
<td>1410 br</td>
<td>$\varphi$H-bend</td>
<td></td>
</tr>
<tr>
<td>1360 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1350 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1222 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1218 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1170 br</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1100 sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1050 m-sh</td>
<td>CH$_3$ rock</td>
<td></td>
</tr>
<tr>
<td>1020 m-sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>920 m-sh</td>
<td>NB str</td>
<td></td>
</tr>
<tr>
<td>830 m-br</td>
<td>CN str</td>
<td></td>
</tr>
<tr>
<td>760 st</td>
<td>$\varnothing$</td>
<td></td>
</tr>
<tr>
<td>720 st-s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>680</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* v=very, br=broad, w=wide, m=medium, sh=shoulder, st=strong, s=sharp
Tentative assignments have been attempted by reference to similar compounds.\textsuperscript{56}

b. Electronic Spectrum

The yellow color of $\text{C}^+(\text{CH}_3)_2\text{NBCl}_3^-$ is due to the presence of the triphenylmethyl cation as is clearly demonstrated by the absorptions at 410 and 430 nm in benzene.\textsuperscript{52}

c. $^1\text{H}$ nmr Spectrum

The spectrum of $\text{C}^+(\text{CH}_3)_2\text{NBCl}_3^-$ in benzene consists of a broad singlet ($\sim 7\text{Hz}$) at -1.4 $\delta$ and a complex multiplet at approximately -7 $\delta$. The singlet is assigned to the methyl resonance and is quite reasonable in light of the ammonium analogy presented on p. 71. Here as with the BF$_3$ adduct solubility and/or stability of $(\text{CH}_3)_2\text{NBCl}_3^-$ limited the choice of solvents. For this reason benzene was used even though it obscured the phenyl region and made the assignment of the chemical shift of the phenyl resonances difficult.

d. X-ray Diffraction

Diffraction patterns of $\text{C}^+(\text{CH}_3)_2\text{NBCl}_3^-$ were taken and the d spacing of the ten most intense peaks are listed in Table XVI. The pattern for this complex prepared from gas-solid reaction and reaction in benzene solution are identical.
e. Physical Properties

1) Melting Point

The BCl₃ adduct did not melt but began to decompose in a sealed capillary tube at approximately 100°.

2) C, H, and N Analyses

The analyses of this compound performed at Galbraith Laboratories gave the following results.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc.</td>
<td>62.3</td>
<td>5.19</td>
<td>3.46</td>
</tr>
<tr>
<td>Found</td>
<td>62.2</td>
<td>5.04</td>
<td>1.54</td>
</tr>
</tbody>
</table>

As with the BF₃ analog N analysis of Ø₃C⁺(CH₃)₂NBCl₃⁻ is disturbingly low and again no definite evidence was obtained to explain this observation. The C and H analyses show the same error often observed in analyses of hygroscopic B-N compounds.

3) Solubility

The solubility of this complex and the attendant difficulties in obtaining a good solvent are identical to those observed with Ø₃C⁺(CH₃)₂NBF₃⁻. The only solvents in which more than slight solubility was observed were benzene and toluene.
E. Reaction of $\text{O}_3\text{CN(CH}_3\text{)}_2$ and $\text{B}_2\text{H}_6$

There is no reaction between $\text{O}_3\text{CN(CH}_3\text{)}_2$ and $\text{B}_2\text{H}_6$ at temperatures between $-25^\circ$ and $-160^\circ$. At least six attempts were made to perform this reaction. While in two of the attempts some decomposition of $\text{B}_2\text{H}_6$ was evidenced by the production of non-reproducible amounts of hydrogen, no uptake of diborane could be detected. The base displacement reaction between $\text{O}_3\text{CN(CH}_3\text{)}_2$ and $\text{Et}_2\text{OBH}_3$ also failed to give reproducible data to indicate the uptake of $\text{BH}_3$ by $\text{O}_3\text{CN(CH}_3\text{)}_2$.

F. Tensimetric Titrations

A tensimetric titration is a measurement of a gas-condensed phase equilibrium. The method affords a convenient and precise method of determining stoichiometries of gas-condensed phase reactions and permits subtle interactions which might be missed in "bulk" reactions to be observed.

Tensimetric titrations were performed using an apparatus similar to that shown in Figure 14. A mmolar amount of $\text{O}_3\text{CN(CH}_3\text{)}_2$ was placed in the reaction tube, the entire apparatus affixed to the vacuum line and evacuated. A known amount of gaseous reactant (e.g. $\text{BF}_3$ or $\text{BCl}_3$) was then frozen into the tensimeter which was sealed at point $S$. The portion of the apparatus containing $\text{O}_3\text{CN(CH}_3\text{)}_2$ was then carefully thermostated at an appropriate temperature and
Figure 14. Tensimetric Titration Apparatus
stirred until the system reached equilibrium (several days to weeks). By preparing a number of tubes with differing $\text{BX}_3/\text{O}_3\text{CN(CH}_3)_2$ ratios a complete tensimetric titration, which in fact is nothing more than a gas-solid phase diagram, was obtained. It should be noted that each experimental point is independent of every other point and that the apparatus used insured that the reactive $\text{BX}_3$ could only come in contact with $\text{O}_3\text{CN(CH}_3)_2$, mercury and glass. The all glass construction of the tensimeter eliminated problems of slow gas leakage from the atmosphere.

1. Reaction of $\text{BF}_3$ and $\text{O}_3\text{CN(CH}_3)_2$

The complete data for the tensimetric titration of $\text{BF}_3$ with $\text{O}_3\text{CN(CH}_3)_2$ at $-78^\circ$ is presented in Table XX and the results are represented graphically in Figure 15. At this temperature both stable 1:1 and an unstable 1:2 (decomp $P = 20$ cm) $\text{O}_3\text{CN(CH}_3)_2/\text{BF}_3$ complexes form. In the tensimetric titration reported here runs 1, 2, and 3 showed an incubation period of several days before any yellow solid formed. In fact, as a result of several reactions, it appears that $\text{BF}_3$ is taken up by the $\text{O}_3\text{CN(CH}_3)_2$ and that the reaction mixture remains white if the temperature is maintained below $-78^\circ$ and the ratio of $\text{BF}_3$/amine is less than 0.3. Upon warming or the addition of more $\text{BF}_3$ the mixture takes on the yellow color of $\text{O}_3\text{C}^+$. Attempts to characterize the white solid failed because of its extreme sensitivity to heat and $\text{BF}_3$. However, it is interesting to
TABLE XX
TENSIMETRIC TITRATION OF $\text{O}_3\text{CN(CH}_3\text{)}_2$ AND BF$_3$

<table>
<thead>
<tr>
<th>#</th>
<th>$\text{O}_3\text{CN(CH}_3\text{)}_2$</th>
<th>Calc $P_{mm}\text{BF}_3$</th>
<th>Actual $P_{mm}\text{BF}_3$</th>
<th>Ratio BF$_3$/O$_3$</th>
<th>Equil Press cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.2934</td>
<td>34.12</td>
<td>32.7</td>
<td>.0988</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>.1573</td>
<td>91.41</td>
<td>92.5</td>
<td>.521</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>.1538</td>
<td>160.96</td>
<td>160.5</td>
<td>.927</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>.2581</td>
<td>358.77</td>
<td>365.0</td>
<td>1.346</td>
<td>20.0</td>
</tr>
<tr>
<td>5</td>
<td>.1593</td>
<td>258.87</td>
<td>250.0</td>
<td>1.494</td>
<td>20.3</td>
</tr>
<tr>
<td>6</td>
<td>.1249</td>
<td>257.02</td>
<td>251.3</td>
<td>1.913</td>
<td>20.1</td>
</tr>
<tr>
<td>7</td>
<td>.1183</td>
<td>261.38</td>
<td>263.6</td>
<td>1.975</td>
<td>21.8</td>
</tr>
<tr>
<td>8</td>
<td>.0997</td>
<td>226.76</td>
<td>232.5</td>
<td>2.220</td>
<td>25.0</td>
</tr>
<tr>
<td>9</td>
<td>.1031</td>
<td>297.21</td>
<td>297.5</td>
<td>2.558</td>
<td>29.1</td>
</tr>
</tbody>
</table>
Figure 15. Tensimetric Titration of $\phi_3\text{CN(CH}_3)_2$ and BF$_3$
speculate on the significance of these results to the overall descriptive chemistry of the system. Borontrifluoride is known to complex most amines forming compounds of the type amine:BF$_3$. Perhaps the takeup of BF$_3$ before the formation of the yellow complex represents the initial formation of a normal F$_3$B: amine complex whose C-N bond is only cleaved by warming or additional BF$_3$. The overall reaction sequence would be represented by:

$$
\text{BF}_3 \text{BF}_3 \text{BF}_3
\text{BF}_3 \text{BF}_3 \text{BF}_3
\text{BF}_3 \text{BF}_3 \text{BF}_3
$$

2. Reaction of BC1$_3$ and $\text{O}_3\text{CN(CH}_3\text{)}_2$

The apparatus and techniques employed in the tensimetric titration of $\text{O}_3\text{CN(CH}_3\text{)}_2$ with BC1$_3$ were identical to those in the BF$_3$-$\text{O}_3\text{CN(CH}_3\text{)}_2$ studies. However, it was not possible to conduct these experiments at -78° because of the low vapor pressure of BC1$_3$ (~5 mm) at this temperature. The data for BC1$_3$-$\text{O}_3\text{CN(CH}_3\text{)}_2$ tensimetric titration at 26° is presented in Table XXI and the results are represented graphically in Figure 16. Obviously at 26° BC1$_3$ forms a mono- but not a diadduct. Diadduct formation at low temperature is not ruled out. In the case of BC1$_3$ no induction period of any kind was observed in either the bulk or tensimetric reactions. Therefore, the overall reaction of BC1$_3$ and $\text{O}_3\text{CN(CH}_3\text{)}_2$ is:

$$
\text{O}_3\text{CN(CH}_3\text{)}_2 + \text{BC1}_3 \rightarrow \text{O}_3\text{C}^+(\text{CH}_3)_2\text{NBC1}_3^-
$$
### TABLE XXI

**TENSIMETRIC TITRATION OF $\phi_3$CN(CH$_3$)$_2$ AND BCl$_3$**

<table>
<thead>
<tr>
<th>#</th>
<th>$\phi_3$CN(CH$_3$)$_2$ g</th>
<th>Calc. P$_{mm}$BCl$_3$</th>
<th>Actual P$_{mm}$BCl$_3$</th>
<th>Ratio BF$_3$/Ø</th>
<th>Equil Press cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.2469</td>
<td>26.8</td>
<td>27.0</td>
<td>.103</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>.1911</td>
<td>103.8</td>
<td>103.0</td>
<td>.511</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>.1659</td>
<td>162.2</td>
<td>159.0</td>
<td>.909</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>.2044</td>
<td>244.3</td>
<td>253.0</td>
<td>1.175</td>
<td>16.0</td>
</tr>
<tr>
<td>5</td>
<td>.1683</td>
<td>347.5</td>
<td>342.9</td>
<td>1.932</td>
<td>41.3</td>
</tr>
<tr>
<td>6</td>
<td>.1026</td>
<td>244.1</td>
<td>230.3</td>
<td>2.129</td>
<td>50.6</td>
</tr>
<tr>
<td>7</td>
<td>.1153</td>
<td>331.2</td>
<td>309.7</td>
<td>2.548</td>
<td>57.9</td>
</tr>
</tbody>
</table>
Figure 16. Tensimetric Titration of $\Phi_3\text{CN(\text{CH}_3)_2}$ and $\text{BCl}_3$
3. Reaction of BF₃ and C₃⁺(CH₃)₂NBCl₃⁻

Since (CH₃)₂NBF₃⁻ forms an unstable complex with BF₃, the basicity of (CH₃)₂NBCl₃⁻ toward BF₃ was also of interest. In effect the basicities of the two bases (CH₃)₂NBF₃⁻ and (CH₃)₂NBCl₃⁻ could be compared by determining the dissociation constants for their respective reactions with the reference acid BF₃.

\[
\text{C₃⁺(CH₃)₂NBF₃⁻ + BF₃} \xrightleftharpoons{\text{K}} \text{C₃⁺(CH₃)₂N(BF₃)₂⁻} \quad (24)
\]

\[
\text{C₃⁺(CH₃)₂NBCl₃⁻ + BF₃} \xrightleftharpoons{\text{K}} \text{C₃⁺(CH₃)₂N(BF₃)(BCl₃)⁻} \quad (25)
\]

Tensimetric titrations of both solid C₃⁺(CH₃)₂NBCl₃⁻ and of solutions in toluene were performed. The results are shown in Table XXII, and in no case was the formation of any (CH₃)₂N(BF₃)(BCl₃)⁻ indicated. Thus, if any such complex forms its dissociation pressure must exceed 600 mm. In other words, the complex must be considerably less stable (x3) than C₃⁺(CH₃)₂N(BF₃)₂⁻.

TABLE XXII

TENSIMETRIC TITRATION OF C₃⁺(CH₃)₂NBCl₃⁻ AND BF₃

<table>
<thead>
<tr>
<th>C₃CN(CH₃)₂</th>
<th>Calc P mm</th>
<th>Actual P mm</th>
<th>Ratio</th>
<th>Equil Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>.1483</td>
<td>110.5</td>
<td>111.0</td>
<td>0.7</td>
<td>60.0</td>
</tr>
<tr>
<td>.1687</td>
<td>143.6</td>
<td>136.0</td>
<td>0.8</td>
<td>60.0</td>
</tr>
<tr>
<td>.1524*</td>
<td>146.0</td>
<td>135.0</td>
<td>0.9</td>
<td>60.0</td>
</tr>
</tbody>
</table>

*no solvent
4. Lewis Basicity of $(\text{CH}_3)_2\text{NBX}_3^-$

The strength of a Lewis base, $B$, is a measure of the magnitude of the equilibrium, $K_{eq}$, for the reaction:

$$A + :B \rightleftharpoons A:B$$

If $A$ is a gas and both $:B$ and $A:B$ are solids, then

$$K_{eq} = \frac{1}{P_{\text{diss of AB}}} = \frac{1}{K_{\text{diss of AB}}}$$

Comparing the two anions $(\text{CH}_3)_2\text{NBCl}_3^-$ and $(\text{CH}_3)_2\text{NBF}_3^-$, since $P_{\text{diss}}(\text{CH}_3)_2\text{N(BF}_3)_2 < P_{\text{diss}}(\text{CH}_3)_2\text{N(BF}_3)(\text{BCl}_3)$, the latter is by far the stronger base toward the reference acid $\text{BF}_3$.

The strength of an electron donor toward a reference acid is determined by the charge density in the region of space where bonding to the acid occurs, the ease by which the donor atom's electron cloud can be polarized, and by steric effects. In an isostuctural series of bases containing the same donor atom, the compound's basicity in general reflects the electron withdrawing or donating characteristics of the group attached to the donor. The basicity of the $R_2\text{NBX}_3^-$ complexes thus should reflect the electron donating properties of the two methyl groups and the co-ordinated $\text{BF}_3$ or $\text{BCl}_3$.

Since $(\text{CH}_3)_2\text{NBF}_3^-$ is definitely a stronger base than $(\text{CH}_3)_2\text{NBCl}_3^-$ the obvious conclusion is that $\text{BCl}_3$ is a more efficient electron withdrawing group than $\text{BF}_3$ provided the
two acids have the same effect on the polarizability of the nitrogen's charge cloud and have similar steric requirements. Probably the effect on the polarizability by BF$_3$ and BCl$_3$ should be about the same, with perhaps the electron cloud in the BCl$_3$ being somewhat more polarizable than the corresponding BF$_3$ complex (an effect that should make R$_2$NBCl$_3^-$ more basic than the BF$_3$ complex). The steric requirement for BCl$_3$ might exceed that of the BF$_3$. However, since the B-N bond length$^{14b}$ in acetonitrile-BCl$_3$ complex is actually less than the B-N bond length in the corresponding BF$_3$ complex, and as space filling molecular models demonstrate that there is ample room to accommodate both BF$_3$ and BCl$_3$ in (CH$_3$)$_2$N(BF$_3$)(BCl$_3$)$^-$, the steric differences between the BX$_3$ groups probably are not dominant factors in determining the basicity of the compounds studied. The conclusion we are left with is that, contrary to intuitive prediction, BF$_3$ is a less efficient electron withdrawing group than is BCl$_3$. This result is in direct contradiction of the ideas originally formulated using the thermodynamic cycle mentioned in the introduction,$^{14}$ but parallel predictions made on the basis of indirect spectroscopic studies.$^{16}$

Intuitively, of course, this result is surprising. However, the charge on the nitrogen calculated via the extended Huckel method$^{58}$ is identical for (CH$_3$)$_2$NBF$_3^-$ (-.302) and (CH$_3$)$_2$NBCl$_3^-$ (-.328) even though the charge on
the boron is some 0.2 of a charge unit higher on the BF$_3$
complex. A large difference in the stability between
(CH$_3$)$_2$N(BF$_3$)$_2$- and (CH$_3$)$_2$N(BF$_3$)(BCl$_3$)- also is indicated by
the extended Huckel calculations which show that the energy
differences for the processes are about 10 ev. more

$$R_2NBX_3^- + BF_3 \rightarrow R_2N(BX_3)BF_3^-$$  (28)

negative for the case where $X = F$ than $X = Cl$. While the
energy differences are clearly much too high (such factors
as the inherent difficulty in performing calculations on
F compounds, as well as steric effects which are not included
in the calculation tend to introduce error) they indicate
that the BF$_3$ complex would be considerably more stable than
the BCl$_3$ complex. Although the calculations may be somewhat
in error, they do underscore the difficulties associated
with utilizing intuitive assumptions concerning group
electronegativities.

It still remains to be rationalized why the electron
withdrawing ability of the BF$_3$ group should be less than
that of BCl$_3$. An answer may be provided by recent CNDO/2
calculations$^{14b}$ on BF$_3$. As BF$_3$ (and presumably any BX$_3$
molecule) is distorted from planarity, the energy of the
lowest unfilled M.O. drops rapidly. Since for Lewis acids
the apparent group electronegativity may be a direct function
of the energy of this orbital,$^{14b}$ the acid with the greatest
electron withdrawing power will be the one in which this
orbital has the lowest energy. Since co-ordinated BF$_3$ has been shown to be less distorted than co-ordinated BCl$_3$ it has been argued that the energy of BCl$_3$'s lowest unfilled M.O. is less than that of BF$_3$; consequently BCl$_3$ should be more electronegative than BF$_3$.$^{14a}$

Brown, Drago, and Bolls$^{63}$ have considered the effect on the C-O stretch in BF$_3$ and BCl$_3$ complexes of ethylacetate. They conclude that BCl$_3$ is a stronger electron pair acceptor than BF$_3$ and explain their results on the basis of extended Huckel calculations on planar and pyramidal BX$_3$. They find that after reorganization BF$_3$ possesses significant $\pi$ character in the $B_2p_z$ orbital and conclude that this residual $\pi$ bonding effectively decreases the ability of BF$_3$ to accept an electron pair.
VI. DISCUSSION AND RESULTS - PART III - SUMMARY

Aqueous, non-aqueous, and tensimetric titrations of basic anions of the type $R_2NBX_3^-$ have been presented in this dissertation. The primary goal of the study is the elucidation of the order of Lewis acidity of co-ordinated $BX_3$. Previous $K_a$ measurements on $R_2NBH_3^-$ in aqueous solution and the current aqueous and non-aqueous acidity determinations in $R_2NBF_3^-$ demonstrate the superiority of $BF_3$ over $BH_3$ as an electron acceptor and indicate another area in which isoelectronic analogies between carbon and boron chemistry can be productively employed. Lastly, the relative acceptor abilities of bonded $BCl_3$ and $BF_3$ have been investigated and $BCl_3$ has been shown to be a stronger Lewis acid than $BF_3$. This conclusion puts the indirect spectroscopic indications of this trend on firm ground. To conclude, on the basis of direct measurements we have shown the order of acceptor ability in bonded boranes to be:

$$BCl_3 > BF_3 > BH_3$$
VII. EXPERIMENTAL

A. Preparation of Amine-BF₃ Complexes

1. Preparation of (CH₃)₂HNBF₃

   In a typical preparation approximately 0.1 mole of BF₃ was distilled on the vacuum line into 25 ml of dry diethyl-ether held at -196° in a standard 50 ml reaction flask. As the flask was warmed the pressure increased as the BF₃ began to vaporize, but dropped when the diethylether began to melt and F₃BO(C₂H₅)₂ began to form. Additional diethylether was then frozen upon the sides of the reaction flask to insure complete etherate formation. Next, approximately 30 ml (0.44 mmoles) of dimethylamine was distilled into the flask at -196°. The flask was slowly warmed to room temperature to insure complete reaction and the mixture swirled with a pyrex covered magnetic spin bar for an hour. The reaction mixture was cooled to 0° and the diethylether and excess dimethylamine were distilled out of the reaction flask. After one hour at 0°C the temperature was raised to ambient and pumping continued for 24 hours. The crystalline (CH₃)₂HNBF₃ remaining in the reaction flask was purified by sublimation in a standard vacuum sublimator to a -78° cold finger.

2. Preparation of CH₃H₂NBF₃

   The preparation of this complex was carried out in a manner analogous to the preparation used for (CH₃)₂HNBF₃.
The crude product, however, was purified by crystallization from isopropyl alcohol. In a typical crystallization 3.5925 g was dissolved in 10 ml of isopropyl alcohol with a yield of 1.7913 g or 50.0%. No second crop was collected. The excess solvent was removed over a 12 hour period on the vacuum line.

3. Preparation of H₃NBF₃

The preparation of this complex was done in a manner analogous to the synthesis described for (CH₃)₂HNBF₃. The product was then purified by crystallization either from water or acetone. In a typical crystallization 4.7286 g (41.88 mmoles) was dissolved in 25 ml of water with a yield of 2.7200 g or 59.8%. A second crop was grown by condensing the filtrate. This H₃NBF₃ could be stored at 0°C in aqueous solution for at least two months with no noticeable change in the ir spectrum, indicating little or no decomposition in the solvent used in its purification. The excess water was removed from the crystalline product by pumping on the material overnight.

B. Physical Properties of Amine-BF₃ Complexes

1. Melting Points

Melting points were determined to the nearest degree on a Fisher-Jones melting point block and capillaries suspended in a conventional melting point flask. The melting points (uncorrected) are listed in Table XXIII.
TABLE XXIII
MELTING POINTS OF AMINE-BF₃ COMPLEXES

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P. in °C</th>
<th>Literature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)₂HNBF₃</td>
<td>52.4</td>
<td>53.0</td>
<td>62</td>
</tr>
<tr>
<td>(CH₃)H₂NBF₃</td>
<td>93.5</td>
<td>93.5</td>
<td>1</td>
</tr>
<tr>
<td>H₃NBF₃</td>
<td>163</td>
<td>163</td>
<td>26</td>
</tr>
</tbody>
</table>

2. Solubilities

Qualitative solubility data were obtained by placing approximately equivalent amounts of complex in a test tube, adding equal amounts of dry solvent and visually observing the relative solubility after maximum dissolution had occurred. These very qualitative data are presented in Table XXIV.

TABLE XXIV
QUALITATIVE SOLUBILITIES OF AMINE-BX₃ COMPLEXES

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(CH₃)₂HNBF₃</th>
<th>CH₃H₂NBF₃</th>
<th>H₃NBF₃</th>
<th>(CH₃)₂HNBH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl₃</td>
<td>sol</td>
<td>insol</td>
<td>insol</td>
<td>sol</td>
</tr>
<tr>
<td>CDC1₃</td>
<td>sol</td>
<td>insol</td>
<td>insol</td>
<td>sol</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>sol</td>
<td>insol</td>
<td>insol</td>
<td>sol</td>
</tr>
<tr>
<td>DMF</td>
<td>very sol</td>
<td>sol</td>
<td>sol</td>
<td>very sol</td>
</tr>
<tr>
<td>Pyridine</td>
<td>very sol</td>
<td>sol</td>
<td>sol</td>
<td>very sol</td>
</tr>
<tr>
<td>Acetone</td>
<td>very sol</td>
<td>very sol</td>
<td>sol</td>
<td>very sol</td>
</tr>
</tbody>
</table>
C. Reaction of \((\text{CH}_3)_2\text{HNBF}_3\) with Na in Liquid Ammonia

In a representative run 321.2 mg (2.84 mmoles) of \((\text{CH}_3)_2\text{HNBF}_3\) was placed in a reaction tube with 331. mg (14.4 mmoles) of Na which was encased in a glass capsule. Approximately 10 ml of anhydrous \text{NH}_3, previously stored over Na, was distilled into the reaction tube at \(-196^\circ\). The tube was slowly warmed and the temperature maintained between \(-110^\circ\) and \(-40^\circ\) as indicated by the vapor pressure of the solvent ammonia. The glass capsule containing the Na was then broken with a glass covered magnetic hammer, the breakage of which was followed by rapid evolution of gas and the formation of a blue color, due to dissolved Na, in the upper portion of the reaction solution. The solution was maintained at \(-78^\circ\) and periodically mixed until the blue color persisted throughout the solution. The reaction was apparently complete in 30 minutes. At this time the reaction mixture was cooled to \(-196^\circ\) and the non-condensible gas pumped through four \(-196^\circ\) traps into a gas burette by means of a Toepler pump. The reaction mixture was warmed to \(-78^\circ\) and the reaction allowed to continue for 72 hours. The excess sodium in the reaction tube was then amalgamated with mercury. After amalgamation was completed additional non-condensible gas (about 10% of the total) was observed and collected. For the entire reaction a total of 1.48 mmoles of \text{H}_2 (identified by mass spectroscopy) was thus collected. The ratio of moles of \text{H}_2 produced to moles of
(CH$_3$)$_2$HNBF$_3$ used equals 0.516 in this run.

The product was separated from the mercury-sodium amalgam using standard vacuum filtration techniques. The solution was clear and after removal of solvent ammonia, a fluffy white material remained. Na(CH$_3$)$_2$NBF$_3$ is very hygroscopic and all handling was done in the dry box at the dew point of P$_2$O$_5$.

D. Fluorine and Boron Analyses of Na(CH$_3$)$_2$NBF$_3$

1. Fluorine

In a typical analysis 83.1 mg (0.6164 mmoles) of Na(CH$_3$)$_2$NBF$_3$ was hydrolyzed with 10 ml of concentrated HNO$_3$ in a weighed screw capped centrifuge tube. The tube was then warmed to 40° for 15 minutes. The pH was then adjusted to 6.5 with 12 N NaOH and 2 ml of 0.1 N Ca$^{+2}$ anion solution was added to precipitate the fluoride. The white precipitate was digested in a water bath at 50° for four hours. The precipitate was then cooled and the CaF$_2$ was separated by centrifugation. The CaF$_2$ was dried overnight at 120° in glass centrifuge tubes which were used in the determination. The percent iron found was 44.7 which compares favorably with the calculated value of 42.3.

2. Boron

The supernatent liquid from the above fluoride analysis was used to determine boron. To this solution was added several drops of Fe$^{+3}$ solution (sat. Fe$_2$(SO$_4$)$_3$) to insure
complete elimination of any remaining fluoride ions. The pH was then adjusted to 6.8, the solution saturated with mannitol and titrated with 0.1000 N NaOH. The end point of pH = 6.8 was taken as the end point from the titration curve. The percent boron found from this analysis was 7.8 compared to the calculated 8.0.

E. Aqueous Titration of Na(CH₃)₂NBF₃

In the one attempt of an aqueous titration of Na(CH₃)₂NBF₃, 22.3 mg (6.03 mmoles) was dissolved in a 25 ml volumetric flask with deionized water (20°). From this stock solution 5 ml aliquots were titrated with 0.1000 N HCl. In the two runs made, the pH dropped from 9 to 4 before one-third of the calculated equivalent volume had been added. The net shape of the complete titration curve resembled the titration of a salt of weak acid with a pKa of greater than 7.

F. Aqueous Titration of (CH₃)₂HNBF₃

In one of several attempts 31.7 mg (0.283 mmoles) of (CH₃)₂HNBF₃ was dissolved in a 25 ml volumetric flask with deionized water (20°). From this stock solution 5 ml aliquots were titrated with 0.1000 N NaOH. The resulting solution had a pH of approximately 7 and, therefore, it is untitratable in aqueous solution.

G. Non-Aqueous Titrations

1. Preparation of Tetra-N-butylammonium Hydroxide
Tetra-N-butylammonium hydroxide (TBAH) was prepared by ion-exchange on Dowex IRA 400 column of 2.5 cm x 60 cm. The resin was converted into the basic alcoholic form by eluting the column with 1 liter of aqueous KOH, followed by 5 liters of H$_2$O (100 ml/32 sec) to remove the excess KOH, and finally by 2 liters of isopropyl alcohol (100 ml/2273 sec) to displace the H$_2$O. The resin was then removed from the column and shaken vigorously with two successive 1 liter volumes of 95% ethanol, followed by three successive 1 liter volumes of absolute ethanol. The flask was affixed to the vacuum line and all solvent was removed by pumping overnight and the column remade and rinsed with 2 liters of isopropyl alcohol (100 ml/172 sec). To the basic alcoholic column was added 10.15 g of tetra-N-butylammonium iodide (TBAI) in 150 ml of isopropyl alcohol. The first 50 ml, the dead volume of the column, was discarded and the next 100 ml plus three successive 50 ml rinses were collected. The maximum concentration of TBAH which could be prepared by this method is therefore 0.1099 N, compared with the observed normality of 0.1030 N (determined by titration of benzoic acid). This represents a 95% conversion of the TBAI to the hydroxide (TBAH).

2. Electrodes

A normal glass electrode (Sargent S-30050-15C) as the pH sensitive electrode, and for the reference electrode a commercial calomel electrode (Sargent S-30080-15C) in which
the usual aqueous KCl supporting electrolyte had been replaced by a saturated methanolic KCl solution were used in titrations in pyridine. The modification of the calomel electrode has been shown elsewhere to be appropriate for use in the titration of weak acids in pyridine. The calomel salt bridge was made fresh daily and the reference electrode stored in saturated KCl-methanol solution. The glass electrode was stored in water and between all determinations was rinsed with water and wiped dry.

3. EMF Measurements - Apparatus

The measurements were made with the electrometer shown in Figure 17, which is basically an operational amplifier (op-amp) follower circuit. The QFT-2 (Philbrick-Nexus Research) op-amp was specifically chosen because of its operational characteristics, the most important being its fixed input impedance of $10^{11}$ ohms. The second op-amp, SQ 10a (Philbrick-Nexus Research), was added to convert the basic follower circuit into an electrometer with the capability of expanding any potential range between +15V and -15V to any precision which these particular experiments demanded.

A simple voltage divider ($X_1, 0.5, 0.2, 0.1, 0.05$), not shown in Figure 17, was incorporated into the instrument to allow the complete potential range of an experiment to be quickly surveyed. The voltage divider was not used in any actual determinations because greater uncertainty in the
Figure 17. Op-Amp Follower-Electrometer

\[ E_o = E_{in} \frac{R_f}{10^3} \]

\[ \pm15V \]

\[ 4.5K \]

\[ 1K(R_f) \]

\[ 100K \]

\[ 10K \]

\[ 1K \]

\[ 100 \]

\[ \text{Ref} \]

\[ \text{Glass} \]

\[ \text{QFT-2} \]

\[ \text{SQ-10a} \]
measurements would result from any error introduced by the divider.

The characteristics of the complete instrument, the electrodes, the standard chemical system and the chemical system of interest were determined using a Hewlett Packard electronic counter (5245L) equipped with a digital voltmeter (5265A) which allowed direct potential measurements to ±0.1 mv. In several cases the intrinsic potential change of a given experiment was much less than ±0.1 mv and, therefore, a Beckman 10 inch t-y recorder, which has a sensitivity of 10 uv/div, was used. The operating characteristics of the complete instrument were determined by shorting the input. In this zero position the noise was no greater than ±5 mv and the drift less than ±20 uv/hour. In order to evaluate the stability of drifts of the electrode pair to be used in pyridine, a standard combination electrode (Beckman 39142) in an aqueous buffer of pH = 4 was used to evaluate the shielding of the follower in a real potential measuring experiment of known stability. The noise of the combination electrode was less than ±0.05 mv and the drift less than ±0.3 mv/hour, compared with the glass-calomel saturated CH₃OH-KCl noise of less than ±0.05 mv and a drift of less than ±0.5 mv/hour. The characteristics of both instrument and electrodes are acceptable for the non-aqueous determinations of interest in this work in that the drift of the instrumental set-up is at least an order of magnitude
less than the intrinsic precision of these hnp determinations.

4. Standardization of TBAH using Benzoic Acid

In one standardization of TBAH solution, 223.8 mg (1.83 mmoles) of benzoic acid was weighed into a 25.0 ml volumetric flask and dry pyridine was added to the mark. Five separate 1.00 ml aliquots of the benzoic acid stock solution were then titrated with TBAH. Great care had to be taken to insure that all solutions were as close to 20° as possible since small temperature variations caused large differences in observed hnp's. All titrations were carried out in a water bath at 20.0 ±0.05°. The bath was maintained at this temperature using a Sargent Thermonitor (Model S-W). In each of the titrations a 1.00 ml aliquot of benzoic acid standard solution was added to a 150 ml tall form beaker to which 50.0 ml of pyridine was then added. A rubber stopper fitted with electrodes, entry port for titrant and N₂ flush-stirring apparatus (0.5 cm fine frit) was quickly placed on the tall form beaker. The first 0.10 ml of TBAH was added and the potential recorded. The solution was stirred by slowly bubbling N₂ gas which also kept the system relatively free of atmospheric moisture. A titration was then taken by successive addition of TBAH. The reference point in this titration curve used to determine the hnp was taken at the point where exactly 1.00 ml of TBAH had been
added. In this manner the half neutralization potential of benzoic acid was shown to be reproducible to ±2 mv and the concentration of TBAH titrant to be 0.1030 N.

5. Titration of Amine-BF$_3$ Complexes in Pyridine
a. General Method

Procedures identical to the standardization of benzoic acid were used in all borane titrations. One additional type of measurement was made. After a pair of titration determinations were performed and the exact equivalent volume determined, the following experiment was performed. To a 1 ml aliquot sample of borane was added exactly one half the equivalent volume and the potential recorded, after which sufficient titrant was added to reach the reference point in that determination and again the potential was recorded. For example, the equivalent volume for H$_3$NBF$_3$ in the determination given below is 0.700 ml and, therefore, a volume of 0.350 ml was added and the potential recorded and the additional 0.650 ml was added and the potential recorded. The difference of these data is the half-neutralization potential of interest. The advantage of this method is that the entire experiment is completed in less than ten minutes, and the sensitive membrane of the glass electrode is not likely to become dehydrated.

b. Titrations of H$_3$NBF$_3$, CH$_3$H$_2$NBF$_3$, and (CH$_3$)$_2$HNBF$_3$

In a representative run 153.5 mg (1.809 mmoles) of
H2NBF3, 179.2 mg (1.831 mmoles) of CH3H2NBF3, and 205.0 mg (1.816 mmoles) of (CH3)2HNBF3 were dissolved in three 25.00 ml volumetric flasks. One ml aliquots of this stock solution were titrated with TBAH at 20.0 ±0.5°. Three titrations and 5 two point hnp determinations were made. The procedure outlined in the standardization of benzoic acid and in the previous section was employed in the titrations of these compounds.

H. Preparation of Ø3CN(CH3)2

Approximately 10 g amounts of triphenyldimethylamine were prepared by the direct reaction of Ø3CCI with excess (CH3)2HN.

\[ Ø3CCI + (CH3)2HN \rightarrow Ø3CN(CH3)2 + (CH3)2NH2^+Cl^- \]  

(excess)

In a typical preparation 19.1 g (68.5 mmoles) of Ø3CCI was weighed in the dry box and transferred in this inert nitrogen atmosphere into a 200 ml flask with a 25 cm dewar encased neck and fitted with a standard 24/40 M joint. This flask was quickly placed on the vacuum line and evacuated. Approximately 100 ml of (CH3)2HN was then frozen into the flask at -196°. The dewar containing the nitrogen was then replaced by a beaker filled with water at 0° which was held in place by a magnetic stirrer. The dewared neck was filled with an ice-NaCl mixture and the temperature was maintained...
between -5° and -10° for the 5-6 hours which insured complete reaction. In this experimental set-up the resultant vapor pressure of the excess (CH₃)₂HN remained between 50-70 mm. At the end of the reaction the excess reactant was carefully removed to a trap and vented in a fume hood. The mixture of dissolved triphenylamine and methylammonium salt was filtered and washed with excess pentane (≈300 ml) through a fine frit. The insoluble dimethylammonium chloride was discarded and the soluble triphenylmethylidimethylamine was allowed to crystallize from this solution. The yield obtained after two crystallizations from pentane was 7.88 g or 40%.

I. Tensimetric Titrations

1. Apparatus

A diagram of the all glass tensimeter used is shown in Figure 14. The design is conventional and quite similar to those described by Schriver. Reactants were stirred by a glass stirrer containing an Fe rod. The stirrer was raised magnetically by means of a solenoid (Bendix 0969).

2. Ø₃CN(CH₃)₂ and BF₃

In a typical experiment 0.1573 g (0.5473 mmoles) of Ø₃CN(CH₃)₂ was placed in the reaction tube of the tensimeter and 0.2854 mmoles (32.7 mm in 61.13 ml gas weighing bulb at 26°) of BF₃ was frozen into the tensimeter (at -196°) which was then sealed. The reaction tube was then immersed in a
dry ice acetone bath (-78°) and the pressure recorded until equilibrium was established. For this tube, equilibrium was achieved in approximately three weeks at which time the pressure at -78° was 0.0 mm.

3. \( \text{C}^+\text{N(CH}_3\text{)}_2 \text{BCl}_3 \)

The preparation of reaction tubes for this reaction is identical with Section 2 above except that the reaction was thermostated at 26°. The complete data is presented in Table XXI.

4. \( \text{C}^+\text{N(CH}_3\text{)}_2 \text{BF}_3 \)

Into the reaction tube of a tensimeter was placed 0.1483 g (0.5160 mmoles) of \( \text{C}^+\text{N(CH}_3\text{)}_2 \). The phenyl amine was then dissolved in approximately 1 ml of dry toluene (frozen in at -196°) and 10 mmoles of BCl₃ frozen into the solution at -196°. The solution was carefully warmed and the reaction was allowed to proceed, with solenoid stirring, overnight at T = 25-27°. The excess BCl₃ and solvent was removed at 26°. The \( \text{C}^+\text{N(CH}_3\text{)}_2 \text{BF}_3 \) was then partially dissolved in 1 ml of toluene which was frozen in at -196°. A measured aliquot of BF₃ corresponding to (0.7)(0.5160) mmoles of \( \text{C}^+\text{N(CH}_3\text{)}_2 \text{BF}_3 \) was then quantitatively transferred into the reaction tube of the tensimeter. The reaction tube was cooled to -196°, sealed, and transferred to a -78° bath. The resultant pressure in the apparatus was greater than 60 cm and remained so for over one month.
The identical procedure for the gas-solid reaction of \( \Phi_3C^+(CH_3)_2NBCl_3^- \) and \( BF_3 \) was used. After reaction with \( BCl_3 \) all solvent and excess gas were removed and no additional solvent added prior to addition of \( BF_3 \).

J. General Method

1. Aqueous Titrations

   All pH measurements were made on a Beckman Expandomatic pH meter using a pair of Sargent electrodes. The glass electrode (S-30050-15C) had a 0-14 pH range. The calomel reference electrode (S-30080-15C) was used in the conventional manner in aqueous titrations. All pH readings were made to ±0.01 pH units and buffered with standard Beckman buffers (pH 4, 7, 10, 12) with an absolute pH uncertainty of ±0.01 pH units.

   The temperature in the analysis was held constant to ±0.05° by a Sargent thermonitor and monitored with a Beckman thermometer.

2. NMR Technique

   All nmr spectra were taken on either a Varian HA 60 or HA 100, both having variable temperature probes. The solvents were all of spectral quality and were dried with molecular sieves (Linde type 3A or 4A) or by the use of chemical scavengers (Na or CaH or LiAlH₄) depending on the nature of the solvent.
3. Mass Spectra

All mass spectra were run as solids or gases by Sister Mary Rogers on a Hitachi Perkin-Elmer RMU-6E Mass Spectrometer.

4. IR Spectra

The IR spectra were taken on both a Beckman IR5 or IR10 and Perkin-Elmer 700. The KBr used in pellets was dried at 700°F and stored in a dry box, at the dew point of P₂O₅, where all handling was performed. Pellets were prepared using both the conventional die and the Wilks "Minipress." Mulls were dried and stored over sodium before use.

5. Vacuum Line Techniques

The vacuum line techniques employed follow standard procedures discussed elsewhere. 59,60

6. X-ray Diffraction

All diffraction patterns were obtained by the powder method using a 57.3 mm camera and Ni filtered Cu K radiation from a General Electric XRD-5 unit.

K. Materials

1. Preparation of B₂H₆

Diborane was prepared by the addition of reagent grade NaBH₄ (ICN grade) to concentrated H₂SO₄ (Dupont). Diborane was produced in a yield of about 70-80%. The details of
2. Gases

Reagent grade boron trifluoride, borontrichloride, and dimethylamine were purchased from Matheson and Co. The amine was dried over sodium, the boron trifluoride purified by reaction with NaF and the borontrichloride was used without further purification.
LITERATURE CITED

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