71-12,223

RONAN, Richard Joseph, 1943-
ACCEPTOR STRENGTH OF CO-ORDINATED BORON HALIDES.

University of Hawaii, Ph.D., 1970
Chemistry, inorganic

University Microfilms, A XEROX Company, Ann Arbor, Michigan

THIS DISSERTATION HAS BEEN MICROFILMED EXACTLY AS RECEIVED

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

IN CHEMISTRY

SEPTEMBER 1970

By

Richard Joseph Ronan

Thesis Committee:

John W. Gilje, Chairman
Richard G. Inskeep
Ray L. McDonald
Roger E. Cramer
Thomas H. Roelofs

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 $(CH_3)_2N(BCl_3)(BF_3)^-$ 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 $Ø_3CN(CH_3)_2$ with BX_3 have been employed in their synthesis.

TABLE OF CONTENTS

		Page
ABSTRACT		iii
LIST OF TABLES		ix
LIST OF FIGURES		xi
I.	INTRODUCTION	1
II.	STATEMENT OF THE PROBLEM	7
III.	SUMMARY OF ACID AND BASE THEORIES	8
IV.	DISCUSSION AND RESULTS - PART I BRONSTED BASICITY OF $R_2NBX_3^-$	11
	A. Preparation of $Na(CH_3)_2NBF_3$	11
	B. Characterization of $Na(CH_3)_2NBF_3$	13
	1. Elemental Analyses - Methods	13
	2. Fluorine	14
	3. Boron	14
	4. C, H, and N	15
	5. Melting Point	15
	C. Aqueous Acid-Base Chemistry of $Na(CH_3)_2NBF_3$	15
	D. Non-Aqueous Titrations of Amine-BX_3 Complexes	20
	1. Preparation of Amine-BF_3 Complexes	20
	2. Characterization of Amine-BF_3 Complexes	21
	a. Infrared Spectra of H_3NBF_3, $CH_3H_2NBF_3$, and $(CH_3)_2HNBF_3$	21
	b. NMR Spectra of H_3NBF_3, CH_3HNBF_3, and $(CH_3)_2HNBF_3$	26
	c. Mass Spectra of H_3NBF_3, $CH_3H_2NBF_3$, and $(CH_3)_2HNBF_3$	36
	3. Non-Aqueous Titrations - System	36

Page

a. Solvent 43

b. Titrant 44

c. Electrodes and Electrometer 45

d. Titration of Benzoic Acid 47

4. Non-Aqueous Titrations - HNP Determinations 47

a. Titration of H_3NBF_3, $CH_3H_2NBF_3$, and $(CH_3)_2HNBF_3$ 47

b. Titration of $(CH_3)_2HNBH_3$ 52

5. Non-Aqueous Titrations - Acidity of Amine-BF_3 Complexes 52

V. DISCUSSION AND RESULTS - PART II LEWIS BASICITY OF $R_2NBX_3^-$ 59

A. Introduction 59

B. Preparation and Characterization of $Ø_3CN(CH_3)_2$ 60

1. Preparation 60

2. Characterization 60

a. Mass Spectrum 61

b. IR Spectrum 61

c. ^1H nmr Spectrum 65

d. Physical Properties 65

C. Preparation and Characterization of $Ø_3C^+(CH_3)_2NBF_3^-$ 65

1. Reaction of $Ø_3CN(CH_3)_2$ and BF_3 65

2. Characterization of $Ø_3C^+(CH_3)_2NBF_3^-$ . . . 68

a. IR Spectrum 68

b. Electronic Spectrum 68

Page

c. ^1H nmr Spectrum 68

d. X-ray Diffraction 72

e. Physical Properties 72

D. Preparation and Characterization of $Ø_3C^+(CH_3)_2NBCl_3^-$ 74

1. Reaction of $Ø_3CN(CH_3)_2$ and BCl_3 74

2. Characterization of $Ø_3C^+(CH_3)_2NBCl_3^-$ . . . 75

a. IR Spectrum 75

b. Electronic Spectrum 78

c. ^1H nmr Spectrum 78

d. X-ray Diffraction 78

e. Physical Properties 79

E. Reaction of $Ø_3CNCH_3$ and B_2H_6 80

F. Tensimetric Titrations 80

1. Reaction of BF_3 and $Ø_3CN(CH_3)_2$ 82

2. Reaction of BCl_3 and $Ø_3CN(CH_3)_2$ 85

3. Reaction of BF_3 and $Ø_3C^+(CH_3)_2NBCl_3^-$ . . . 88

4. Lewis Basicity of $(CH_3)_2NBX_3^-$ 89

VI. DISCUSSION AND RESULTS - PART III - SUMMARY . . . 93

VII. EXPERIMENTAL 94

A. Preparation of Amine-BF_3 Complexes 94

1. Preparation of $(CH_3)_2HNBF_3$ 94

2. Preparation of $CH_3H_2NBF_3$ 94

3. Preparation of H_3NBF_3 95

B. Physical Properties of Amine-BF_3 Complexes . . 95

1. Melting Points 95

Page

2. Solubilities 96

C. Reaction of $(CH_3)_2HNBF_3$ with Na in Liquid Ammonia 97

D. Fluorine and Boron Analyses of $Na(CH_3)_2NBF_3$ 98

1. Fluorine 98

2. Boron 98

E. Aqueous Titrations of $Na(CH_3)_2NBF_3$ 99

F. Aqueous Titrations of $(CH_3)_2HNBF_3$ 99

G. Non-Aqueous Titrations 99

1. Preparation of Tetra-N-butylammonium Hydroxide 99

2. Electrodes 100

3. EMF Measurement - Apparatus 101

4. Standardization of TBAH using Benzoic Acid 104

5. Titration of Amine-BF_3 Complexes in Pyridine 105

a. General Method 105

b. Titration of H_3NBF_3, $CH_3H_2NBF_3$, and $(CH_3)_2HNBF_3$ 105

H. Preparation of $Ø_3CN(CH_3)_2$ 106

I. Tensimetric Titrations 107

1. Apparatus 107

2. $Ø_3CN(CH_3)_2$ and BF_3 107

3. $Ø_3CN(CH_3)_2$ and BCl_3 108

4. $Ø_3C^+(CH_3)_2NBCl_3^-$ and BF_3 108

J. General Methods 109

1. Aqueous Titrations 109

Page

2. NMR Technique 109

3. Mass Spectra 110

4. IR Spectra 110

5. Vacuum Line Techniques 110

6. X-ray Diffraction 110

K. Materials 110

1. Preparation of B_2H_6 110

2. Gasses 111

LITERATURE CITED 112

LIST OF TABLES

TABLE		Page
I	Stoichiometry of $(CH_3)_2HNBF_3$ and Na Reaction . .	11
II	C, H, and N Analyses of $Na(CH_3)_2NBF_3$	15
III	Acidity of Substituted Acetic Acids	19
IV	Infrared Assignments for H_3NBF_3	23
V	Infrared Assignments for $CH_3H_2NBF_3$ and $(CH_3)_2HNBF_3$	25
VI	^1H Chemical Shifts and Spin-Spin Coupling Constants for Amine-BF_3 Complexes	28
VII	^{14}N Chemical Shifts and Line Widths for Amine-BX_3 Complexes	35
VIII	Mass Spectrum Compilation for H_3NBF_3	37
IX	Mass Spectrum Compilation for $CH_3H_2NBF_3$	39
X	Mass Spectrum Compilation for $(CH_3)_2HNBF_3$	40
XI	Acidity of Amine-BF_3 Complexes in Pyridine . . .	46
XII	Mass Spectrum Compilation for $Ø_3CN(CH_3)_2$	62
XIII	Infrared Assignments for $Ø_3CN(CH_3)_2$	64
XIV	Infrared Assignments for $Ø_3C^+(CH_3)_2NBF_3^-$	70
XV	Methyl Proton Resonance of Quaternary and Tertiary Nitrogen Compounds	71
XVI	d Spacings for $Ø_3C^+(CH_3)_2NBF_3^-$ and $Ø_3C^+(CH_3)_2NBCl_3^-$	73
XVII	C, H, and N Analyses of $Ø_3C^+(CH_3)_2NBF_3^-$	73
XVIII	Infrared Assignments for $Ø_3C^+(CH_3)_2NBCl_3^-$	77
XIX	C, H, and N Analyses of $Ø_3C^+(CH_3)_2NBCl_3^-$	79
XX	Tensimetric Titrations of $Ø_3CN(CH_3)_2$ and BF_3 . .	83
XXI	Tensimetric Titrations of $Ø_3CN(CH_3)_2$ and BCl_3 . .	86
XXII	Tensimetric Titrations of $Ø_3C^+(CH_3)_2NBCl_3^-$ and BF_3	88

TABLE Page

XXIII Melting Points of Amine-BF_3 Complexes 96

XXIV Qualitative Solubilities of Amine-BX_3 Complexes 96

LIST OF FIGURES

FIGURE		Page
1	Titration of $(CH_3)_2NBF_3^-$ with HCl in Water . . .	17
2	Proton NMR Spectrum of H_3NBF_3	29
3	Proton NMR Spectrum of $CH_3H_2NBF_3$	32
4	Proton NMR Spectrum of $(CH_3)_2HNBF_3$	34
5	Titration of Benzoic Acid with TBAH in Pyridine	48
6	Titration of H_3NBF_3 with TBAH in Pyridine . . .	49
7	Titration of $CH_3H_2NBF_3$ with TBAH in Pyridine	50
8	Titration of $(CH_3)_2HNBF_3$ with TBAH in Pyridine	51
9	Acidity of Amine-BF_3 Complexes in Pyridine . . .	54
10	Trends in ^{14}N Chemical Shifts with Methyl Substitution	55
11	Proton NMR Spectrum of $Ø_3CN(CH_3)_2$	66
12	Infrared Spectrum of $Ø_3C^+(CH_3)_2NBF_3^-$	69
13	Infrared Spectrum of $Ø_3C^+(CH_3)_2NBCl_3^-$	76
14	Tensimetric Titration Apparatus	81
15	Tensimetric Titration of $Ø_3CN(CH_3)_2$ and BF_3 . .	84
16	Tensimetric Titration of $Ø_3CN(CH_3)_2$ and BCl_3 . .	87
17	Op-Amp Follower-Electrometer	102

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 (1.58Å) is of the same magnitude as a C-C bond (1.54Å),[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 (R_3NBH_3), Borazene (R_2NBH_2), and Borazole ($(RNBH)_N$) 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[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.[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.[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 $B_2H_6(NH_3)_2$. A controversy which lasted more than twenty years arose over the structure of this product which was finally identified as $H_2B(NH_3)_2^+BH_4^-$ by R. Parry and co-workers.[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, H_3NBH_3, and postulated that the following reaction took place in ammonia solutions of sodium.

$$H_3NBH_3 + Na \xrightarrow[NH_3]{} Na(H_2NBH_3) + 1/2H_2 \qquad (1)$$

This reaction had been suggested earlier by A. Burg and H. Schlesinger.[10] Neither group, however, isolated or characterized the postulated NaH_2NBH_3. In work previously[11] done in this laboratory, the reduction of $(CH_3)_2HNBH_3$ with sodium was investigated. Dimethylamineborane was chosen because it is more stable than ammoniaborane and is, therefore, easier to handle. Sodium dimethylamidotrihydroborate(III), $Na(CH_3)_2NBH_3$, was prepared from $(CH_3)_2HNBH_3$ according to the following equation:

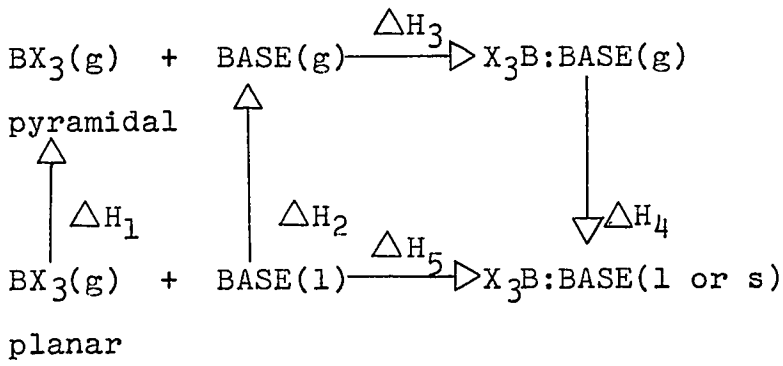
$$(CH_3)_2NHBH_3 + Na \xrightarrow[NH_3]{} 1/2H_2 + Na(CH_3)_2NBH_3 \qquad (2)$$

This compound is still the only well-characterized BH_3 derivative of an amide.

The chemistry of the compound can be interpreted by analogy with the isoelectronic trimethylamine. $Na(CH_3)_2NBH_3$ behaves as the salt of a monoprotic weak acid, $(CH_3)_2HNBH_3$. The acid dissociation constant (Ka) of $(CH_3)_2HNBH_3$ is 4.6×10^{-11}, or somewhat less than the corresponding Ka of 1.7×10^{-10} for trimethylammonium ion. The preparation is similar to the well-known reduction of ammonium ions by sodium,[12] and the borane hydrolysis closely parallels amine hydrolysis. The most important differences in the chemistry between $(CH_3)_2HNBH_3$ and $(CH_3)_3NH^+$ are probably due to the hydrolytic instability of the BH_3 group and the lower electronegativity of BH_3 compared with 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 BX_3 (X=H or halogen) is formally a Lewis acid-base complex, the factors which determine the acidity of the BX_3 group may well be central to the behavior of such compounds. Intuitively one would expect that the acidity of a BX_3 group should increase with increasing electronegativity of the X group. However, even very early thermodynamic studies[13] of these compounds indicate that the order of acidity toward first period reference bases is $BCl_3 > BF_3 > BH_3$. This apparent anomaly has been explained in terms of a

thermochemical cycle.[14]



For example, in the cases of BF_3 and BCl_3 if the reference base is held constant, it is found[13] that Lewis acid-base neutralization of BF_3 is less exothermic (ΔH_5) than the corresponding reaction of BCl_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 ΔH_2 and ΔH_4 are fairly independent of the reference acid. The energy required to reorganize the normally planar BX_3 into the pyramidal form is represented by ΔH_1, and ΔH_3 is the heat of reaction of the reorganized BX_3 with the base. Assuming that ΔH_3 is proportional to the electronegativity of X, then the reversal in ΔH_5 between BCl_3 and BF_3 must be a result of a more positive ΔH_1 for BF_3 than BCl_3. That is, BF_3 is a weaker acid than BCl_3 because more energy is required to reorganize BF_3 from planar to pyramidal form than is required for BCl_3. If the above assumptions and published[15] estimates of ΔH_1 are

employed, the order of acidity of the reorganized boron halide is $BF_3 > BCl_3$ as is expected from inductive effect arguments.

A variety of nmr,[16] ir,[17] and electronic[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. Onyszchuk.[16a]

In addition to the conventional spectroscopic investigations, Swanson, Schriver, and Ibers[14b] have recently reported X-ray structures of acetonitrile-borontrihalides 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 BX_3 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 X_3B:base complexes. Unfortunately, there are no direct measurements of the electron withdrawing ability of the co-ordinated BX_3 groups. Since we had previously demonstrated that differences in Bronsted basicities of nitrogen in the compounds $R_2NBH_3^-$ and R_2NCH_3 may reflect differences in electronegativity between BH_3 and CH_3^+, we felt it was logical to attempt to extend studies on the basicity of $R_2NBX_3^-$ compounds to other compounds containing other X groups. Since the electron donating ability of the nitrogen in $R_2NBX_3^-$ should be directly related to the electronegativity of the co-ordinated BX_3 group, the relative Lewis or Bronsted basicities of a series of such compounds should reflect the relative electronegativities of the respective BX_3 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[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,[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.

$$\underset{\text{acid}}{HA} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{conjugate base}}{A^-} + \underset{\text{conjugate acid}}{H_3O^+} \tag{3}$$

$$Ka = \frac{[A^-][H_3O^+]}{[HA]} \tag{4}$$

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. Lewis[20] 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.

$$\underset{\text{acid}}{A} + \underset{\text{base}}{:B} \rightleftharpoons \underset{\text{addition adduct}}{A:B} \tag{5}$$

$$K = \frac{[A:B]}{[A][:B]} \tag{6}$$

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 BX_3 (X = H, Cl, F) moieties.

IV. DISCUSSION AND RESULTS - PART I

BRONSTED BASICITY OF $R_2NBX_3^-$

A. Preparation of $Na(CH_3)_2NBF_3$

As previously mentioned, the reaction between H_3NBH_3 and Na was studied by several groups[9,10] 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]

$$(CH_3)_2HNBH_3 + Na \xrightarrow[NH_3]{} Na(CH_3)_2NBH_3 + 1/2H \qquad (7)$$

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

The only amine-BF_3 alkali metal reaction which has previously been studied is that between H_3NBF_3 and Na and K. Keenan and McDowell[21] proposed that H_3NBF_3 reacts quite differently with different alkali metals. Specifically, they proposed the net reaction with Na as:

$$2H_3HNBF_3+5Na+2NH_3 \longrightarrow (NH_2)_2B(NHBF(NH_2)+5NaF+2-1/2H_2 \qquad (8)$$

with the reaction proceeding in two steps. In the first reaction 1 mole of Na reacts with 1 mole of H_3NBF_3 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 borontrifluoride reacts smoothly and easily with Na in liquid NH_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

STOICHIOMETRY OF $(CH_3)_2HNBF_3$ AND Na REACTION

$(CH_3)_2HNBF_3$	H_2
2.847 mmoles	1.48 mmoles
3.002 mmoles	1.53 mmoles

These data indicate the reaction to be:

$$(CH_3)_2HNBF_3 + Na \xrightarrow[NH_3]{} Na(CH_3)_2NBF_3 + 1/2H_2 \quad . \qquad (9)$$

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° to -40°. 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 NH_3 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 $Na(CH_3)_2NBF_3$, was handled in a dry box at the dew point of P_2O_5 during all subsequent operations.

B. Characterization of $Na(CH_3)_2NBF_3$

1. Elemental Analyses - Methods

Boron is conventionally determined as boric acid[25] by titration with hydroxide in the presence of mannitol. It has been observed that both nitrogen[23] and fluorine[24] 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 analsis is given below.

1) Hydrolysis of sample . . . addition of conc. HNO_3

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-borontrifluoride complexes is reported elsewhere.[24] 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 $\pm$ .2; this was found to be essential to insure reproducibility of results. The average weight percent determined for fluorine in the known $(CH_3)_2HNBF_3$ 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 $Na(CH_3)_2NBF_3$ 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[25a] 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.[25b] 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

C, H, AND N ANALYSES OF $Na(CH_3)_2NBF_3$

	C	H	N
Calc.	17.8	4.49	10.40
Found	13.5	3.92	9.27

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, $Na(CH_3)_2NBF_3$, does not melt or exhibit any signs of decomposition at temperatures up to 250°.

C. Aqueous Acid-Base Chemistry of $Na(CH_3)_2NBF_3$

$(CH_3)_2NBF_3^-$ and $(CH_3)_2NBH_3^-$ should be nearly isostructural. We have previously demonstrated[11] the following

equilibrium for $(CH_3)_2NBH_3^-$:

$$(CH_3)_2NBH_3^- + H_2O \rightleftharpoons (CH_3)_2HNBH_3 + OH^- \qquad (10)$$

In fact, the $(CH_3)_2NBH_3^-$ anion could be titrated as a salt of a weak acid giving the Ka value for its conjugate acid, $(CH_3)_2HNBH_3$. There was every reason to believe that $(CH_3)_2NBF_3^-$ would undergo a similar hydrolysis allowing the acidity of $(CH_3)_2HNBF_3$ to be determined. The differences in the Ka's of $(CH_3)_2HNBH_3$ and $(CH_3)_2HNBF_3$ would then provide data which hopefully could be related to the electronegativities of BH_3 and BF_3. Further, it was hoped that data on BCl_3 might become available through similar studies on the analogous borontrichloride complexes.

When $(CH_3)_2NBF_3^-$ is dissolved in water, the pH increases to 9, an observation consistent with the postulated equilibrium:

$$(CH_3)_2NBF_3^- + H_2O \rightleftharpoons (CH_3)_2HNBF_3 + OH^- \qquad (11)$$

Further evidence in support of this equilibrium is the formation of $(CH_3)_2HNBF_3$ from $(CH_3)_2NBF_3^-$ either in wet $CHCl_3$ (as detected by nmr) or in moist air. ($(CH_3)_2HNBF_3$ could be separated from $Na(CH_3)_2NBF_3^-$ by sublimation after 10 minutes exposure to the atmosphere.)

Titrations of $(CH_3)_2NBF_3^-$ 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

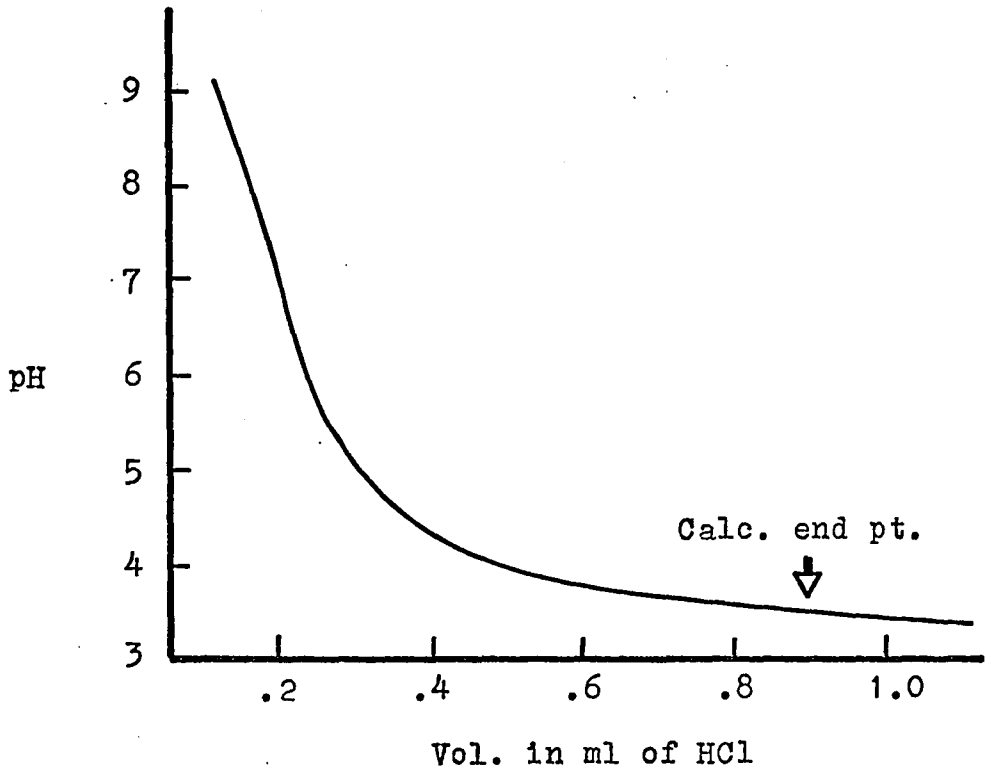


Figure 1. Titration of $(CH_3)_2NBF_3^-$ with HCl in Water

of less than 7 (i.e., Ka $\approx 10^{-7}$). Since an acid with a pKa 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 pKa of the acid must exceed 7. These results indicate that $(CH_3)_2HNBF_3$ has a pKa $\approx$ 7-8 and is thus untitratable either directly as an acid or indirectly as its conjugate base in aqueous solution.

A pKa of 7 for $(CH_3)_2HNBF_3$ might seem surprising since $(CH_3)_2HNBH_3$ has a pKa 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

Acid	K_a
H_3COOH	1.7×10^{-5}
Cl_3COOH	1.1×10^{-1}
F_3COOH	completely dissociated

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-BX_3 Complexes

1. Preparation of Amine-BF_3 Complexes

The literature contains an abundance of methods for the preparation[26,27] and characterization of addition compounds between borontrifluoride 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 Et_2OBX_3. This was suggested by Krause and Brown[26] in 1929 for the preparation of H_3NBF_3, questioned by Laubengayer and Condike[27] 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 H_3NBF_3, $CH_3H_2NBF_3$, and $(CH_3)_2HNBF_3$ were all prepared by addition of the amine to ether solutions of BF_3. For example, the base displacement preparation of H_3NBF_3 is:

$$NH_3 + Et_2OBF_3 \longrightarrow H_3NBF_3 + Et_2O \qquad (12)$$

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

The products were purified by crystallization of H_3NBF_3 (water or acetone) and $CH_3H_2NBF_3$ (isopropyl alcohol) and sublimation of $(CH_3)_2HNBF_3$. The sharp melting points of

163° for H_3NBF_3, 93.5° for $CH_3H_2NBF_3$, and 52° for $(CH_3)_2HNBF_3$ and the spectroscopic data presented in the next section confirm the purity of the crystalline materials.

2. Characterization of Amine-BF_3 Complexes

a. Infrared Spectra of H_3NBF_3, $CH_3H_2NBF_3$, and $(CH_3)_2HNBF_3$

1) IR - H_3NBF_3

The text book example of the compound which contains a co-ordinate covalent bond, H_3NBF_3, has received remarkably little spectroscopic investigation. In 1958 several papers[29,30] appeared detailing its IR and Raman spectra and in 1965 Sawodhy and Goubeau[31] in a review of similar compounds discussed and presented additional data including force constant calculations on H_3NBF_3. In this latter work several discrepancies related to assignment of fundamental modes,[29] as well as large differences[30] in reported frequencies between the results which appeared in the two 1958 papers, were not mentioned. Recently[28] Taylor, Gabelnick, Aida, and Amster reported a study of the isotopic frequencies and force constant calculations for H_3NBF_3 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 H_3NBF_3 exposed to moisture. This statement is particularly significant in that H_3NBF_3 is usually purified by recrystallization[26,27] 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 H_3NBF_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 H_3NBF_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 NBF_3 stretch in the region between 1220 cm^{-1} and 1000 cm^{-1}.

TABLE IV

INFRARED ASSIGNMENTS FOR H_3NBF_3

H_3NBF_3 (cm^{-1})		Assignment[28]
this work	ref 29	
3250 m-br	3285	asym N-H str
3152 m-br	3170	sym N-H str
2900 w	2917	sym NH_3 def (overtone)
2300 w		
1730 m-s	1735	in and out of phase NBF_3 str
1700 m-sh		
1590 st-sh	1596	asym NH_3 def
1440 st-s	1440	
1430 st-br	1420	sym NH_3 def
1220 br	1210	in phase NBF_3 str and asym BF_3 def
1180 bf		sym BF_3 def and NH_3 rock
1140 br	1144	asym BF_3 st
1110 br		
1020 br	1028	^{10}B out of phase NBF_3 str
980 br	982	^{11}B out of phase NBF_3 str
860 m-sh	860	NH_3 rock
	510	
	330	

st=strong, m=medium, w=weak, s=sharp, br=broad, sh=shoulder

2) IR - $CH_3H_2NBF_3$

The observed infrared frequencies of $CH_3H_2NBF_3$ 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_3NBF_3, assigned spectrum of the parent amine and assignments for $(CH_3)_2HNBH_3$.[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 - $(CH_3)_2HNBF_3$

A summary of the observed infrared frequencies of $(CH_3)_2HNBF_3$ 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_3NBF_3, dimethylamine, and the earlier work on $(CH_3)_2HNBH_3$.[33]

TABLE V

INFRARED ASSIGNMENTS FOR
$CH_3H_2NBF_3$ AND $(CH_3)_2HNBF_3$

$CH_3H_2NBF_3$ (cm^{-1})	$(CH_3)_2HNBF_3$ (cm^{-1})	Assignment (tentative)
3597 m	3370 w-sh	
3390 w-s	3300 w-sh	NH str
3263 st-s	3260 st-s	
	3170 m-s	
3190 m-sh	3030 w-s	
3030 w-sh	2975 m-s	CH str
2941 w-sh	2920 m-sh	
2788 w	2790 w	
	2690 w	
	2370 w	
	2292 m-s	
	2258 m-s	
1608 st-s	1650 m-vbr	CH_3 def
1466 st-s		
1387 w-sh	1480 m-sh	BF
1364 st-br	1460 st-s	NH def
1351 st-br	1440 m-s	CH
1325 st-br	1400 br	CN
	1350 s-st	
1193 st-br	1240 sh	
1179 st-br	1220 sh	NBF_3 str
1161 st-br	1160 vb	
1111 m-br	1070 br	CH_3 rock
1058 st-br	1040 br	
1033 st-br	1020 br	
1005 st-br		
966 m-br	930 br	
788 m-s	910 br	NB str
720 m-s	800 w-br	
	700 st-vs	CN str
	570 m-sh	

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_3NBF_3, $CH_3H_2NBF_3$, and $(CH_3)_2HNBF_3$

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 ^1H (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-borontrifluoride were split by the boron as well as the N-H proton. Confirmation of Heitsch's assignment of coupling constants for H_3NBF_3, $CH_3H_2NBF_3$, and $(CH_3)_2HNBF_3$ from spin decoupling of ^1H-^1H and ^1H-^{14}N as well as ^{14}N spectra are presented below.

1) ^{1}H nmr of H_3NBF_3

The chemical shift and coupling constant data for H_3NBF_3 are given in Table VI and the decoupled ^{1}H-^{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:

```
        19F
1 1 1 1
  3 3 3 3        11B
    3 3 3 3
      1 1 1 1
---------------
1 4 7 8 7 4 1
```

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

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

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

$$f(x) = \frac{1}{1+(x+C_1)^2} + \frac{1}{1+(x+C_2)^2} + \ldots \frac{1}{1+(x+C_i)^2} \tag{14}$$

TABLE VI

^1H CHEMICAL SHIFTS* AND SPIN-SPIN COUPLING CONSTANTS FOR AMINE-BF_3 COMPLEXES

Compound	Shift (ppm)	J_{HN}	J_{HcnB}	J_{HncH}	J_{HcnbF}	J_{HnB}	J_{HnbF}
H_3NBF_3	-4.3	42.3	-	-	-	4.1	4.0
$CH_3H_2NBF_3$	-2.5 (CH_3) -4.4 (NH)	**	2.1	6.2	**	-	-
$(CH_3)_2HNBF_3$	-2.5 (CH_3) -4.8 NH	**	1.9	5.8	**	-	-

*relative to tetramethylsilane -δ downfield

**not observed

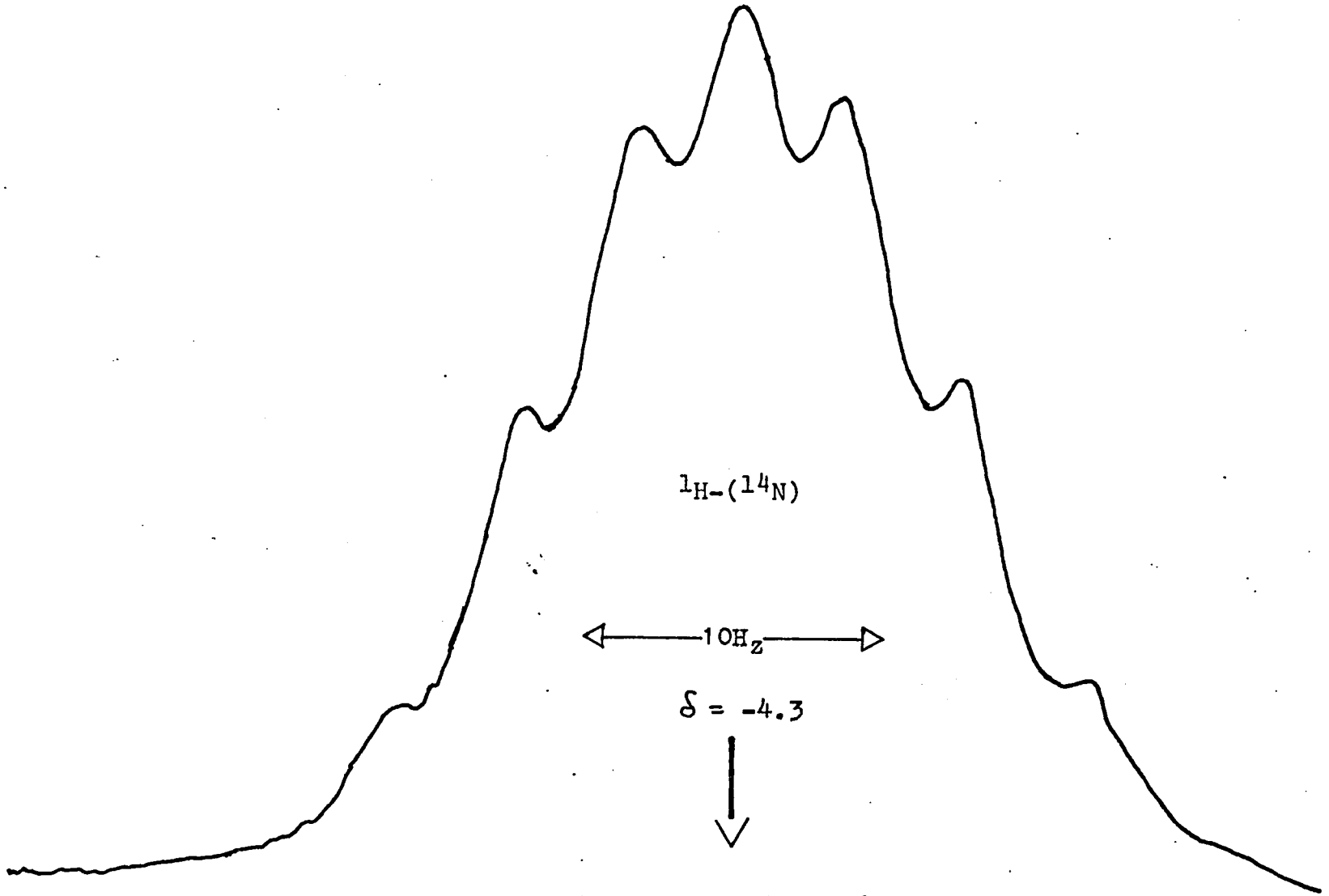


Figure 2. Proton NMR Spectrum of H_3NBF_3

For a quartet arising from splitting by a ^{11}B (I = 3/2), this expression can be rewritten as

$$f(x)=\frac{1}{1+(x-x_o+a)^2}+\frac{1}{1+(x-x_o-a)^2}+\frac{1}{1+(x-x_o+3a)^2}+\frac{1}{1+(x-x_o-3a)^2} \quad (15)$$

where a = 1/2 (coupling constant)

x_o = 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 H_3NBF_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 $x_o = \pm 6, \pm 2$ 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_o and a. In this manner with a = 2 and $x_o = \pm 2, \pm 6$ it was possible to effectively duplicate the observed pattern.

2) ^1H nmr of $CH_3H_2NBF_3$

The chemical shift and coupling constant data for $CH_3H_2NBF_3$ presented in Table VI agree with values appearing in the literature.[34] The coupling assignments were con-

firmed by proton double resonance and this spectrum along with the single resonance ^{1}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 $J_{HcnH} = 6$ and $J_{HcnB} = 2$ are assumed:

```
      1H2
1  2  1
 1  2  1        11B
  1  2  1
   1  2  1
 ----------
 1113223111
```

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_3C protons with ^{11}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}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}N and no splitting could be reasonably assigned to interaction with this nucleus, any CH_3-^{14}N coupling is probably very small. A lack of ^{14}N coupling is also strongly supported by direct

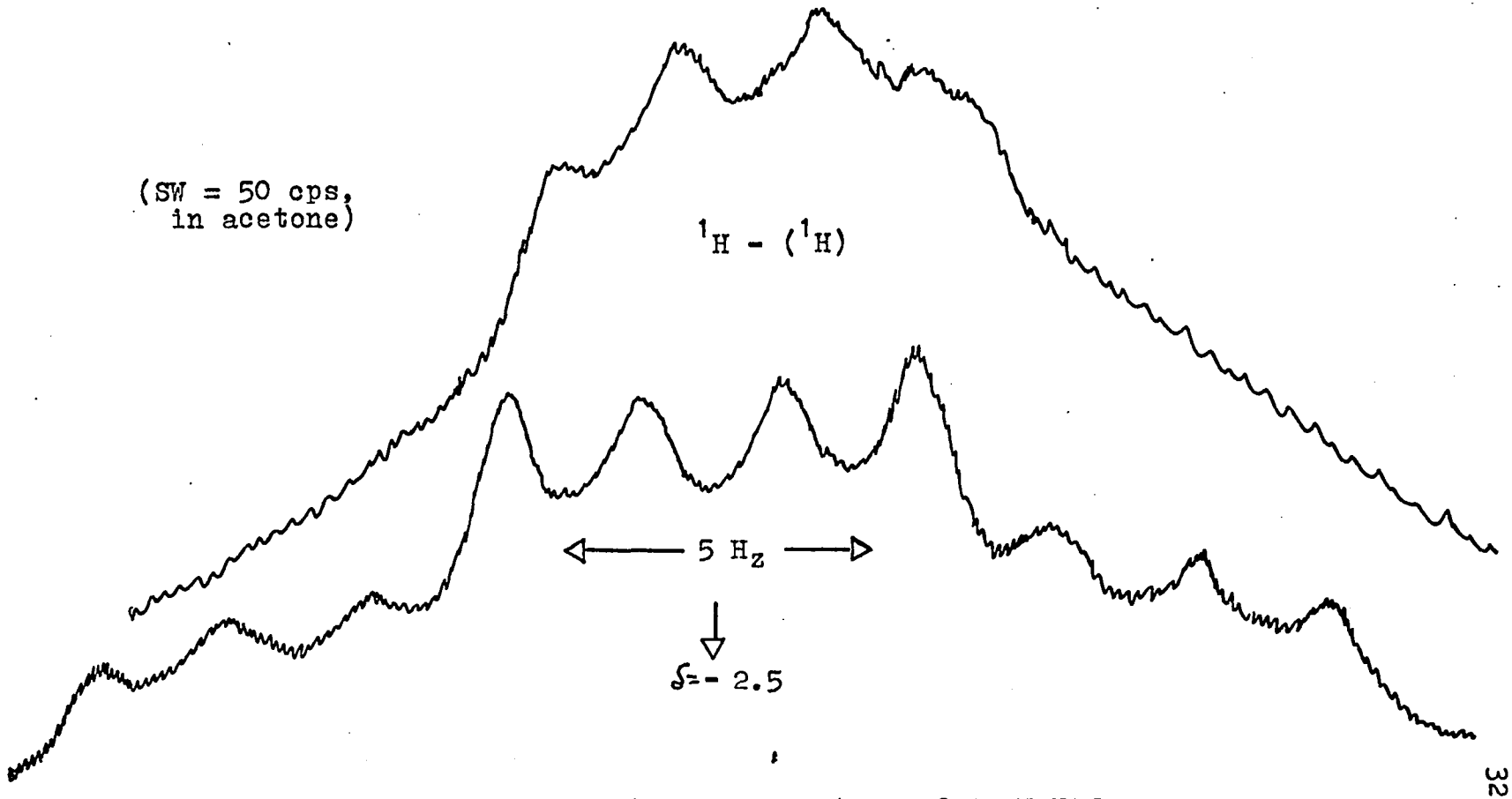


Figure 3. Proton NMR Spectrum of $CH_3H_2NBF_3$

^{14}nmr evidence to be presented below.

3) ^{1}H nmr of $(CH_3)_2HNBF_3$

The relevant chemical shift and coupling constant data for $(CH_3)_2HNBF_3$ are presented in Table VI and agree with the literature.[34] 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:

^{11}B

1 1 1 1
1 1 1 1 ^{1}H

1 1 1 2 1 1 1

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 $x_o = \pm 3$. 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 $CH_3H_2NBF_3$ irradiation of the ^{14}N produces no change in the methyl resonance of $(CH_3)_2HNBF_3$ indicating no ^{14}N coupling, an assumption which is further supported by direct ^{14}N nmr evidence which will be presented below. Irradiation of NH proton collapses the multiplet into a quartet similar to that seen in $CH_3H_2NBF_3$

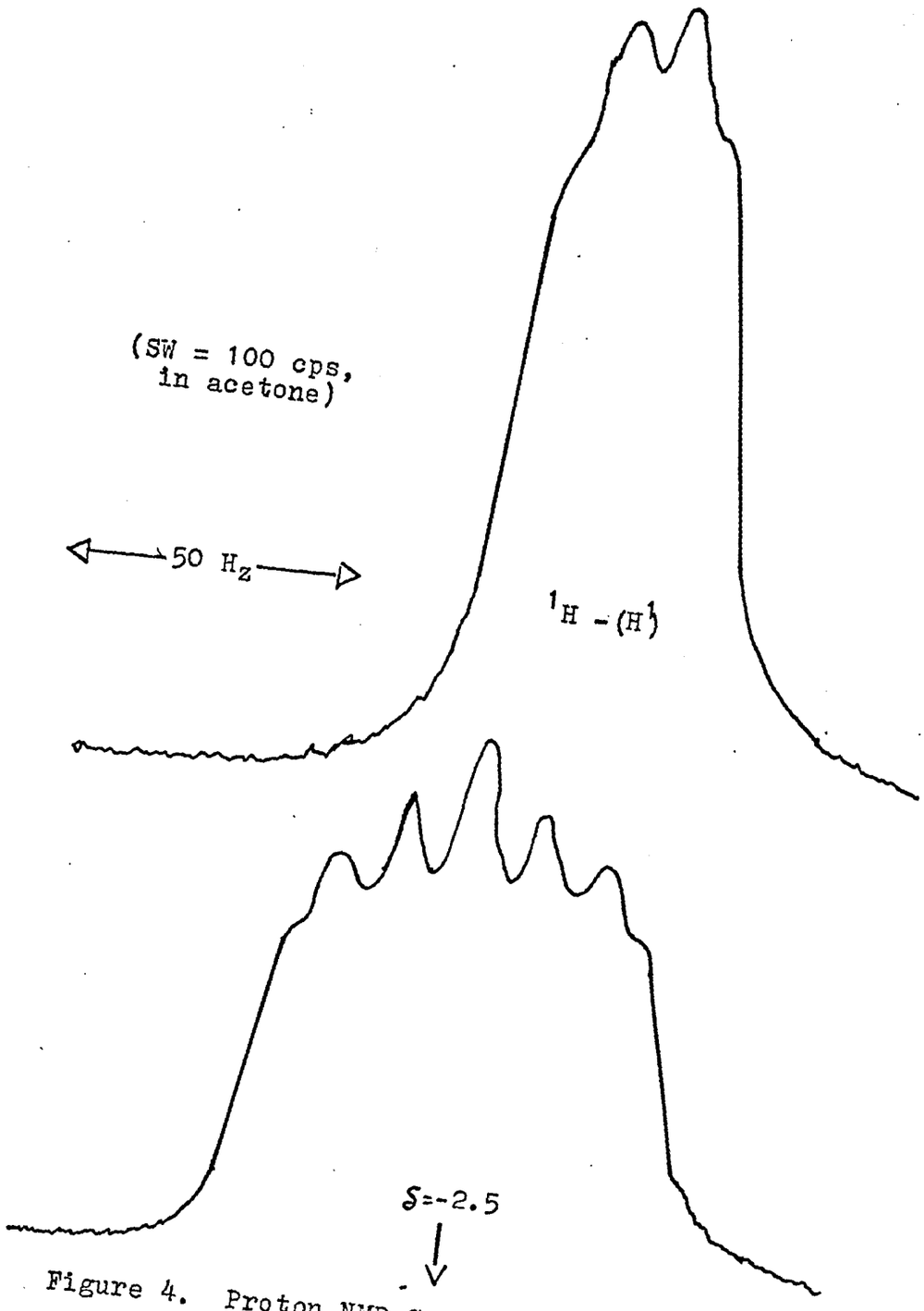


Figure 4. Proton NMR Spectrum of $(CH_3)_2HNBF_3$

upon irradiation of the NH protons. The splitting observed in the $(CH_3)_2HNBF_3$ experiment is also due to coupling of H_3C protons to ^{11}B.

4) ^{14}N nmr of H_3NBF_3, $CH_3H_2NBF_3$, and $(CH_3)_2HNBF_3$

The ^{14}N nmr spectra of the amine-BF_3 complexes were taken in acetone relative to CH_3CN (by sample replacement technique). The chemical shifts and line widths are reported in Table VII. In order to observe coupling of ^{14}N to a proton $J_{HN} \ll \frac{1}{T_2}$. The spin-spin relaxation time, T_2, can be gotten from the observed line width in an nmr experiment.

TABLE VII

^{14}N CHEMICAL SHIFTS* AND LINE WIDTHS FOR AMINE-BX_3 COMPLEXES

Compound	Shift (ppm)	Line Widths (full 1/2 ht)
H_3NBF_3	+219 $\pm$1	350-425 Hz
$CH_3H_2NBF_3$	+218 $\pm$1	350-425 Hz
$(CH_3)_2HNBF_3$	+214 $\pm$1	300-350 Hz
$(CH_3)_2HNBH_3$	+225 $\pm$1	300-350 Hz

*+ppm are upfield from CH_3CN

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-BF_3 complexes fluorine[16c] and boron[16c] 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 $\frac{1}{1800}$ Hz. Both upper and lower limits of T_2 preclude any observable nitrogen coupling in amine-BF_3 complexes.

c. Mass Spectra of H_3NBF_3, $CH_3H_2NBF_3$, and $(CH_3)_2HNBF_3$

The mass spectra of H_3NBF_3, $CH_3H_2NBF_3$, and $(CH_3)_2HNBF_3$ 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.[36] The fragmentation for $CH_3H_2NBF_3$ and $(CH_3)_2HNBF_3$ is quite similar to the patterns observed in methyl- and dimethylamine, specifically in the m/e region centered at 29 and 44 respectively.[36]

3. Non-Aqueous Titrations - System

While $(CH_3)_2HNBF_3$ 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

$$HA + \text{solvent} \rightleftharpoons H^+(\text{solvent}) + A^- \qquad (16)$$

acidity of the acid is increased. The equilibrium constant K_a defines the acidity of the acid HA.

TABLE VIII

MASS SPECTRUM COMPILATION FOR H_3NBF_3

m/e	% I/I_o	Assignment
15	3.6	NH
16	34.5	NH_2
17	42.3	NH_3, OH
18	26	H_2O, NH_4
19	1	
20	3	
27	1	CO, $^{10}B_2H_5$
28	14.5	N_2, $^{11}B_2H_5$
29	1	^{10}BF
30	2.5	^{11}BF
31	1	
32	3.5	
41	1	
42	2	
43	2	
44	3	$HN^{10}BF$, CO_2
45	17.2	$H_2N^{10}BF$, $HN^{11}BF$
46	45.5	$H_3N^{10}BF$, $H_2N^{11}BF$
47	6	$H_3N^{11}BF$
48	23.1	$^{10}BF_2$
49	100	$^{11}BF_2$
64	1	$H_2N^{10}BF_2$
65	20.3	$H_3N^{10}BF_2$, $H_2N^{11}BF_2$

TABLE VIII. (Continued) MASS SPECTRUM COMPILATION FOR H_3NBF_3

m/e	% I/I_o	Assignment
66	73	$H_3N^{11}BF_2$
67	1	
68	3.7	
85	1	H_3NBF_3

TABLE IX

MASS SPECTRUM COMPILATION FOR $CH_3H_2NBF_3$

m/e	% I/I_o	Assignment
15	17	NH, CH_3
18	1	H_2O, NH_4
27	2	$^{10}B_2H_5$
28	18	N_2, $^{11}B_2H_5$
29	3	^{10}BF, CH_3N
30	39	$H^{10}BF$, ^{11}BF, CH_3NH, $(CH_3)_2$
31	20	$H^{11}BF$, CH_3NH_2, $(CH_3)_2H$
45	2	$H_2N^{10}BF$
46	7	$H_2N^{11}BF$
47	2	
48	4	$^{10}BF_2$
49	15	$^{11}BF_2$
57	1	$CH_3H^{10}BF$
58	3	$CH_3H^{11}BF$
59	1	$CH_3H_2N^{10}BF$
60	4	$CH_3H_2N^{11}BF$
76	2	
77	1.5	$CH_3N^{10}BF_2$
78	5.5	$CH_3HN^{10}BF_2$, $CH_3N^{11}BF_2$
79	25.6	$CH_3H_2N^{10}BF_2$, $CH_3HN^{11}BF_2$
80	100	$CH_3H_2N^{11}BF_2$

TABLE X

MASS SPECTRUM COMPILATION FOR $(CH_3)_2HNBF_3$

m/e	% I/I_o	Assignment
14	1.7	N, CH_2
15	10.4	NH, CH_3
18	8.5	H_2O, NH_4
27	2.5	CO, $^{10}B_2H_5$
28	1.5	N_2, $^{11}B_2H_5$
29	1.0	$(CH_3)N$, ^{10}BF
30	4.4	$(CH_3)_2$, CH_3NH, ^{11}BF
31	1.0	
40	2.4	
41	2.5	
42	8.1	C_2H_4N
43	4.6	C_2H_5N, CH_3N_2, CHNO
44	71.0	$(CH_3)_2N$, CO_2, $H_2N^{10}BF$
45	28.0	$(CH_3)_2NH$, $H_2N^{10}BF$, $HN^{11}BF$
46	8	$H_3N^{10}BF$, $H_2N^{11}BF$
47	5.6	$H_3N^{11}BF$
48	11.0	
57	1.2	
58	3.6	
59	1.5	
60	5.6	
74	.6	
75	.9	

TABLE X. (Continued) MASS SPECTRUM COMPILATION FOR $(CH_3)_2HNBF_3$

m/e	% I/I_o	Assignment
76	3.6	
77	5.5	$CH_3N^{10}BF_2$
78	21.8	$CH_3HN^{10}BF_2$, $CH_3N^{11}BF_2$
79	1.0	$(CH_3)HN^{11}BF_2$
90	.5	
91	.8	
92	2.7	$(CH_3)_2N^{10}BF_2$
93	26.8	$(CH_3)_2HN^{10}BF_2$, $(CH_3)\ N^{11}BF_2$
94	100	$(CH_3)_2HN^{11}BF_2$
95	2.8	

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{17}$$

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.[37] 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, $10^{-18} \leqslant a_{H^+} \leqslant 1$). 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_4NCl (or R_4NI) 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 $\pm$.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-BF_3 complexes the titer of the TBAH determined with benzoic acid gives erronious equivalent weights for the borane complexes. For this reason H_3NBF_3 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-BF_3 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 XI

ACIDITY OF AMINE-BF_3 COMPLEXES IN PYRIDINE

Compound	End Point (ml)	Equivalent Wt. theo.	Equivalent Wt. calc.	h.n.p. (mv-ave dev)
H_3NBF_3	0.720	84.8		172 (3)
$CH_3H_2NBF_3$	0.715	98.8	99.0	133 (2)
$(CH_3)_2HNBF_3$	0.720	112.8	113.0	189 (8)

in pyridine is discussed in the literature.[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_3NBF_3, $CH_3H_2NBF_3$, and $(CH_3)_2HNBF_3$

The titrations of methylamine-BF_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

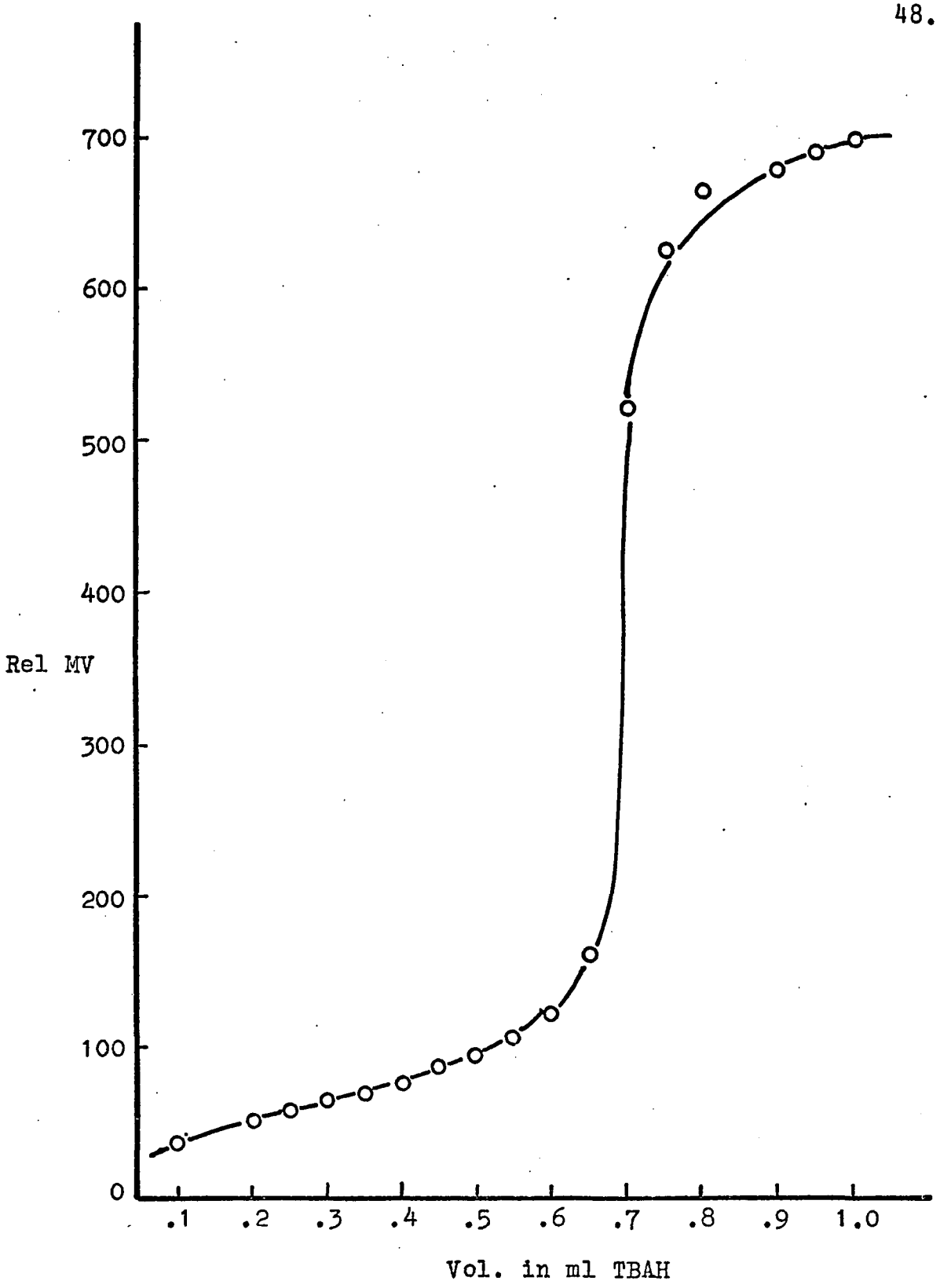


Figure 5. Titration of Benzoic Acid with TBAH in Pyridine

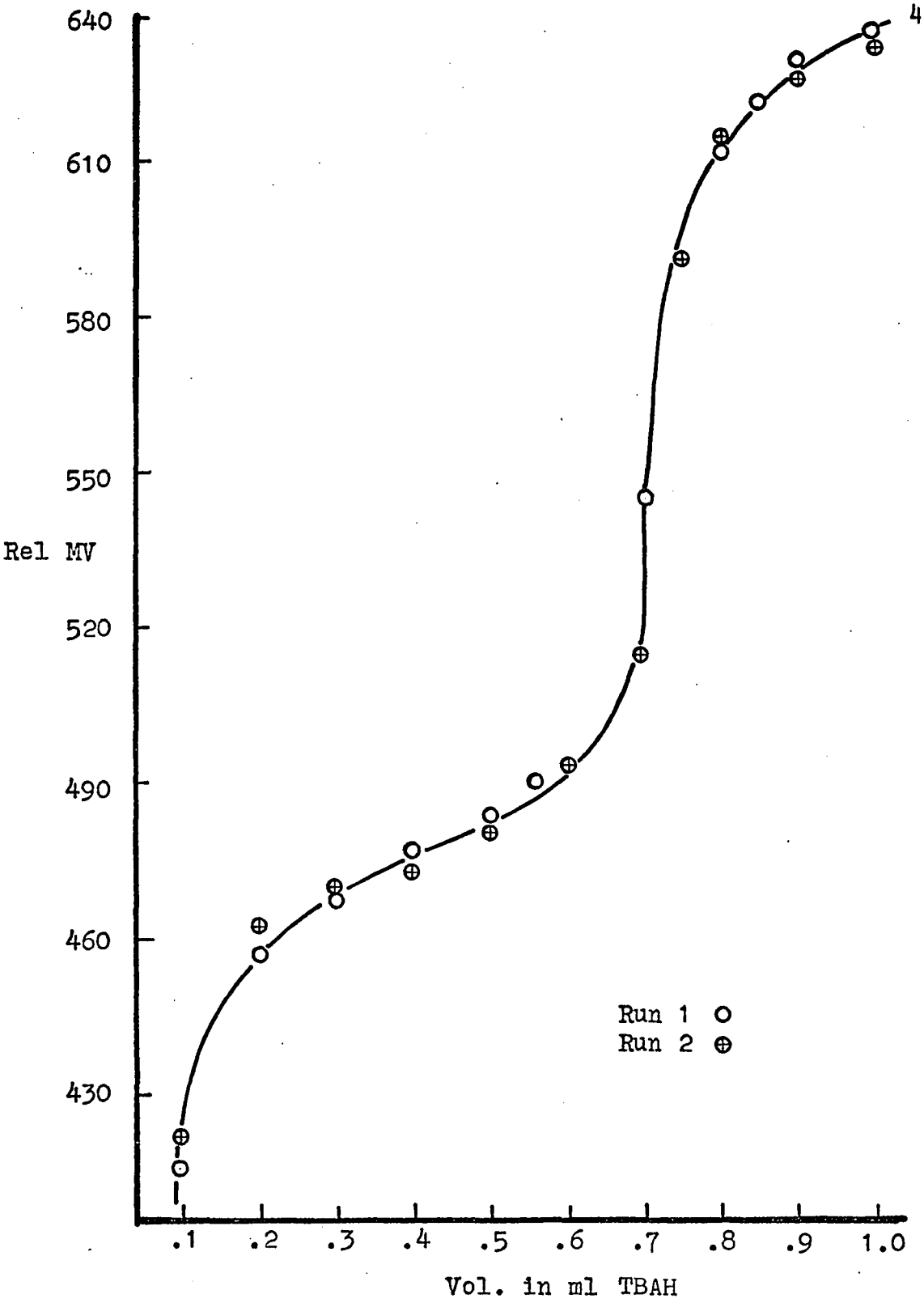


Figure 6. Titration of H_3NBF_3 with TBAH in Pyridine

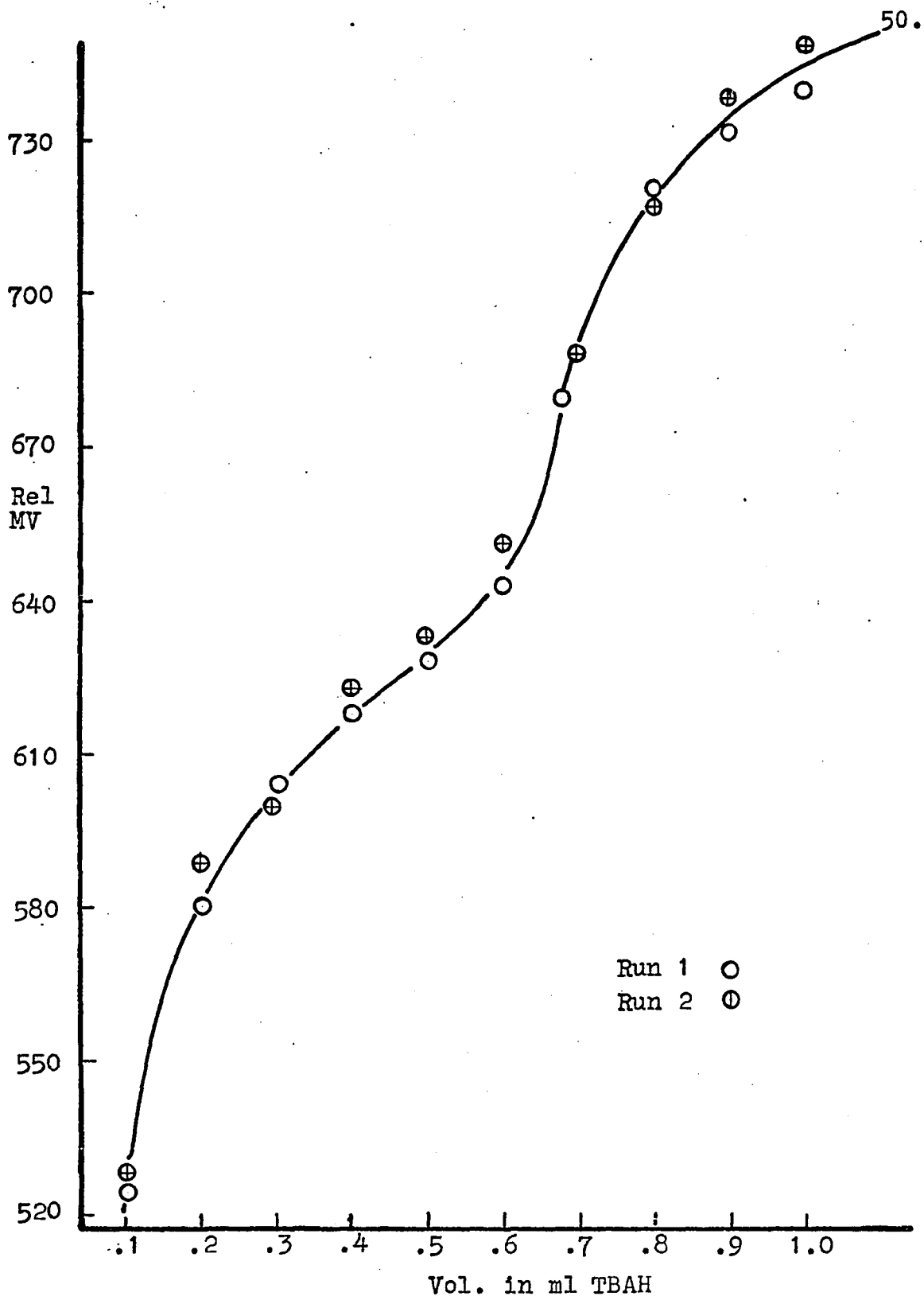


Figure 7. Titration of $CH_3H_2NBF_3$ with TBAH in Pyridine

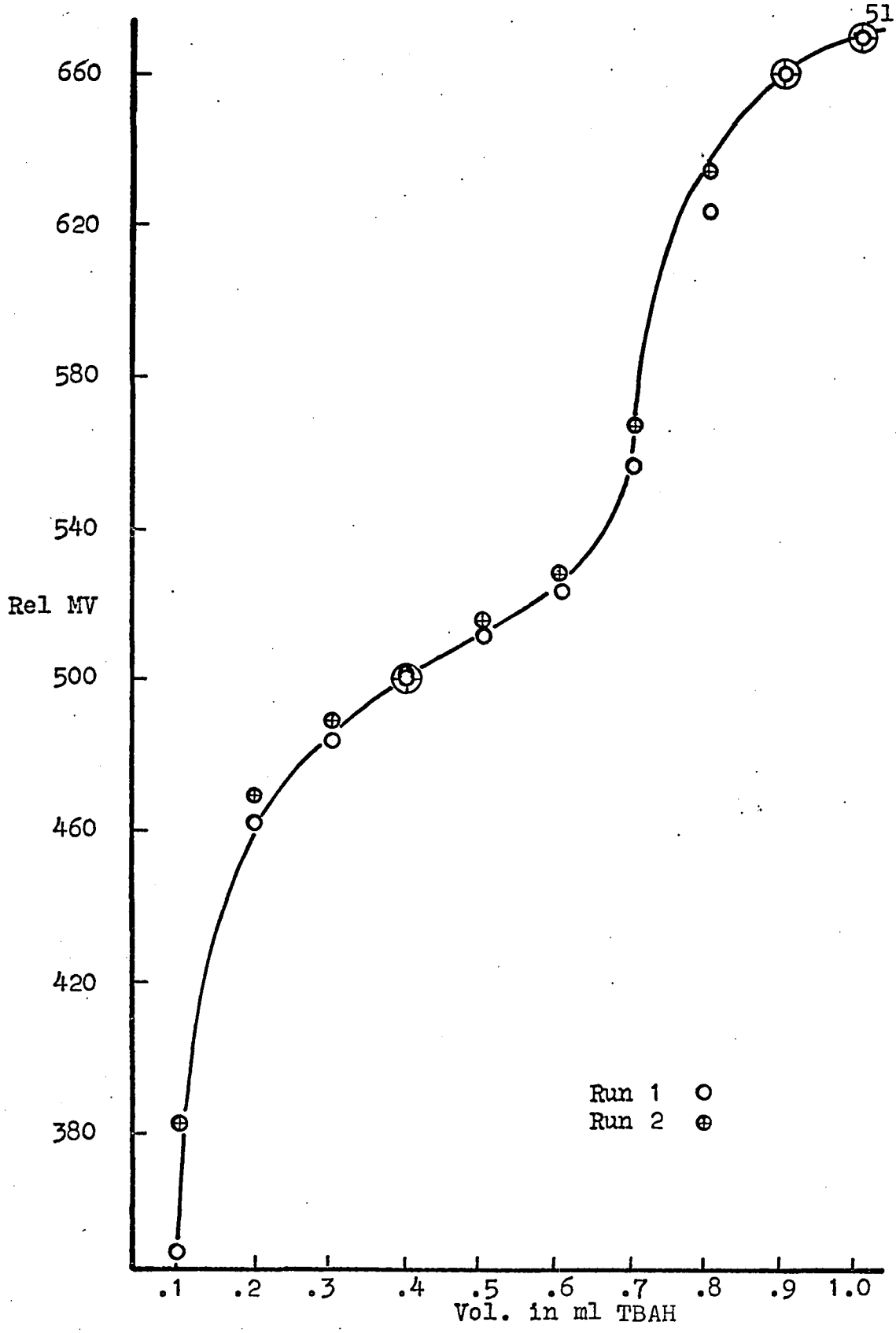


Figure 8. Titration of $(CH_3)_2HNBF_3$ with TBAH in Pyridine

full titration curves for H_3N-, CH_3H_2-, and $(CH_3)_2HNBF_3$ are given with the data being summarized in Table XI.

b. Titration of $(CH_3)_2HNBH_3$

Attempts to titrate $(CH_3)_2HNBH_3$ in pyridine proved unsuccessful; the addition of 0.1 ml of TBAH to $(CH_3)_2HNBH_3$ immediately brought the solvent to its basic potential. In retrospect this is not surprising since the pKa of $(CH_3)_2HNBH_3$ in water is known to be 10.3,[11] which is close to the lower limit of pKa's ($\sim$11) which can be determined in pyridine.[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 BCl_3 adducts were not attempted since most simple amine-BCl_3 complexes intramolecularly eliminate HCl[1] preventing comparisons of acidity between simple amine-BCl_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 BCl_3 amine adducts, was not ralized in these non-aqueous titrations, an interesting trend in the acidity of the amine-BF_3 complexes was observed. The effect of successive replacement 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 $CH_3H_2NBF_3$. While at first glance this trend may appear unique, it finds a close parallel in the acidity of the analogous ammonium ions (e.g. $H_3NCH_3^+$, $H_2N(CH_3)_2^+$ and $HN(CH_3)_2^+$) in which the acidity is a minimum for $(CH_3)_2NH_2^+$.

It is of interest also to compare the trends observed in the acidity of these complexes with the ^{14}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}N chemical shifts of amine-BF_3 complexes do not accurately reflect the acidity of these adducts.

The existence of a minimum in acidity of ammonium ions and amine-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-BF_3 complexes. The nature of the two factors have been postulated to be largely solvent effects[44]

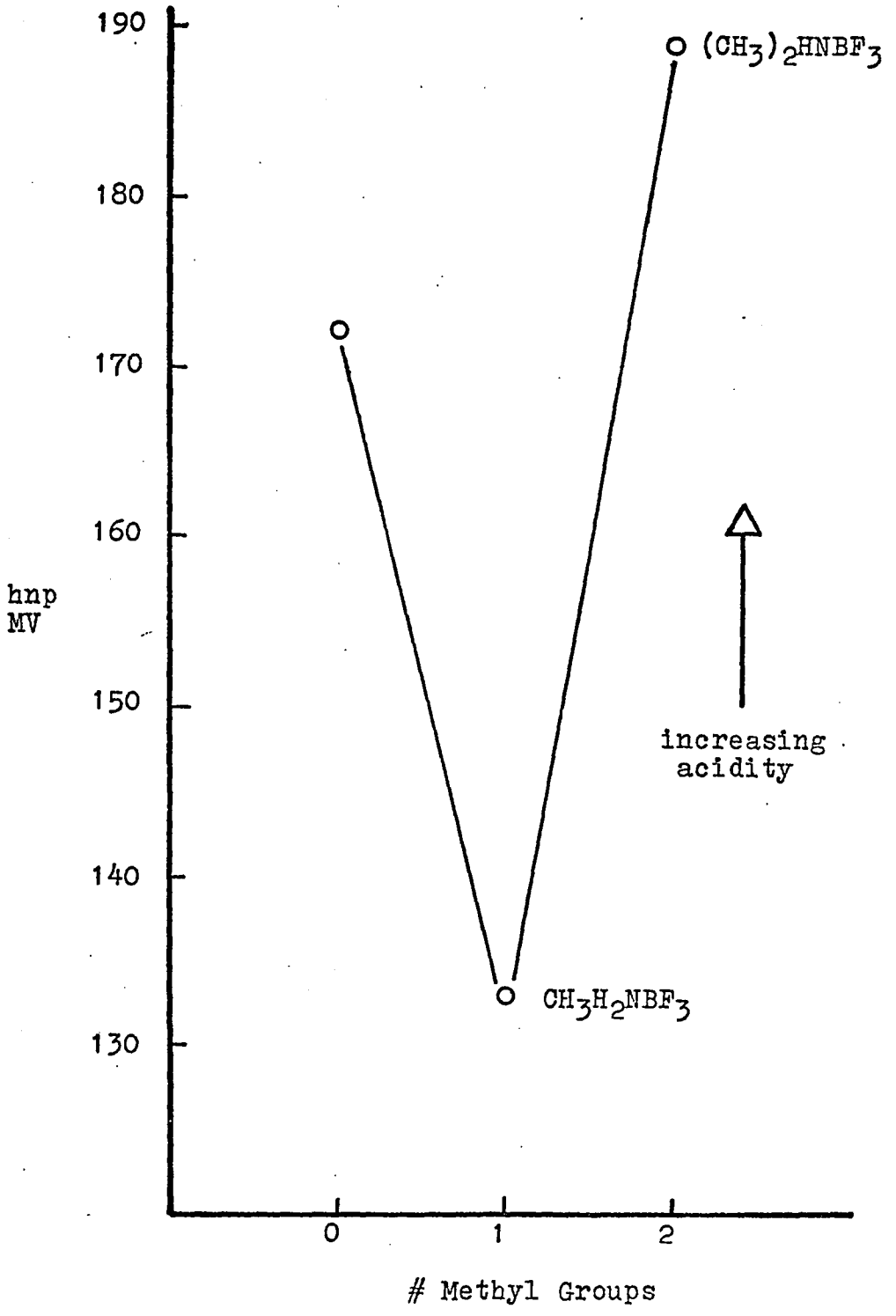


Figure 9. Acidity of Amine-BF_3 Complexes in Pyridine

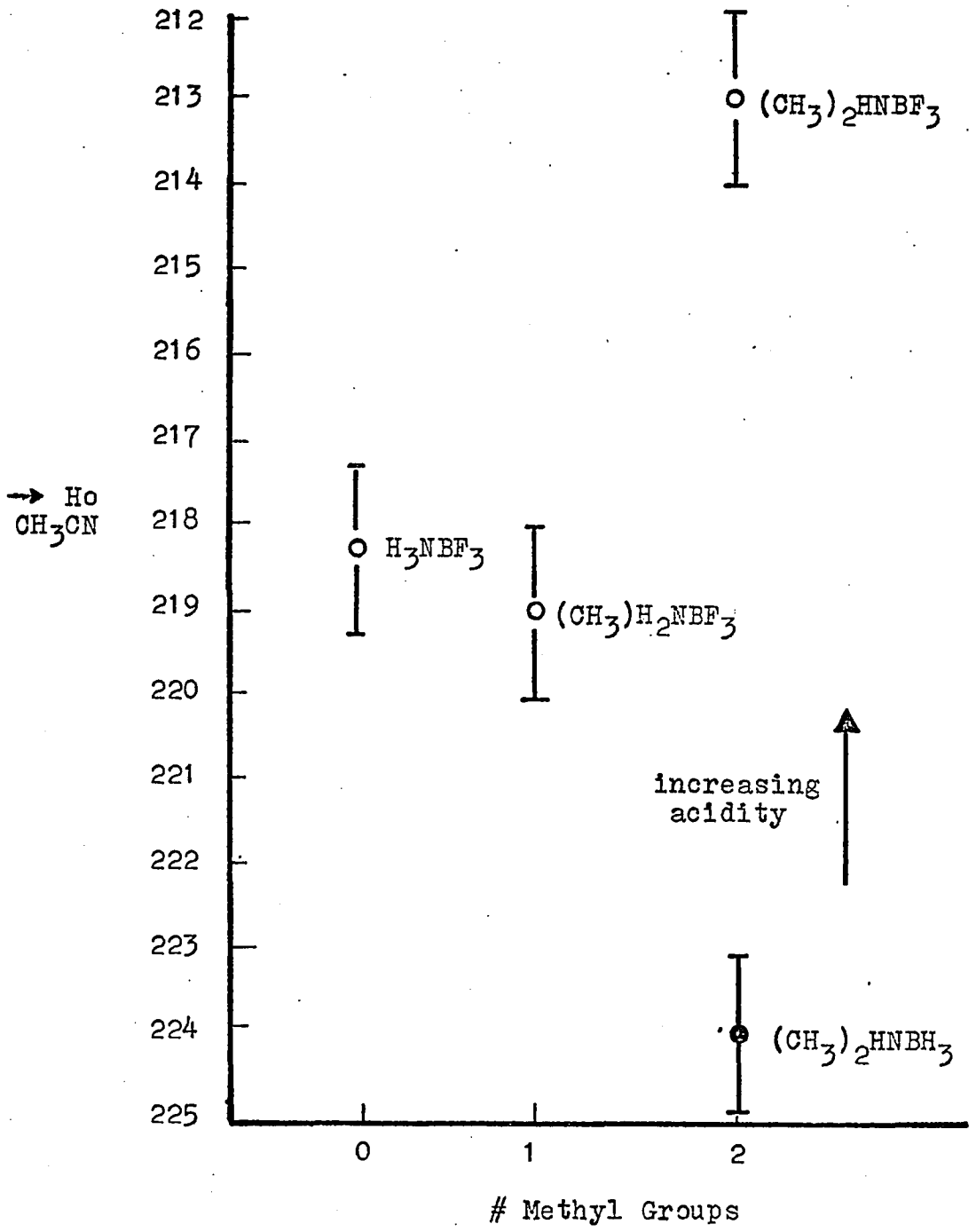


Figure 10. Trends in ^{14}N Chemical Shifts with Methyl Substitution

or, alternatively, as intrinsic electronic interactions within the molecules.[45]

Solvent arguments are concerned with general non-specific interactions as well as specific solvent-solute interac-actions. 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. $RNH_2 > R_2NH \gg R_3N$). 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_3) since the order of basicities of the ammonium ions is invariant (e.g. $NH_3 < RNH_2 \approx R_2NH > R_3N$) in benzene,[46] chloro-benzene,[47] acetonitrile,[48] nitrobenzene,[49] chloroform,[50] carbon tetrachloride,[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.[18]

These acidity trends in amines (and the amine-BF_3 complexes) can also be rationalized considering only the intrinsic electrical nature of the complexes using either a polarization[45] or a hybridization model.[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[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 CH_3^+ for a 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 $R_2NBX_3^-$

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-BX_3 complexes, an alternative method of determining the basicity of $R_2NBX_3^-$ toward a reference acid was attempted. Specifically, the interaction of $R_2NBX_3^-$ with BF_3 was studied. The advantage of this method is that since BF_3 is a gas, the dissociation pressure of its complexes give the dissociation constant, K_d, directly. The synthesis of $(CH_3)_2NBH_3^-$ and $(CH_3)_2NBF_3^-$ 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 $(CH_3)_2NBX_3^-$ an alternative preparative route was sought.

In 1967 Shriver and Biallas reported that the bifunctional Lewis acid $F_2BCH_2CH_2BF_2$ reacts with triphenylmethyl ethers,[52] and triphenylmethyl amines[53] to form $Ø_3C^+RO(F_2BCH_3)_2^-$ and $Ø_3C^+R_3N(F_2BCH_3)_2^-$. In both cases $F_2BCH_3CH_3BF_2$ behaves as a bidentate Lewis acid; i.e. both boron atoms bonded to the base. He further observed[54] that BF_3 reacts with $Ø_3CN(CH_3)_2$, apparently cleaving to the

$Ø_3C$-N bond, and forming what might be a 1:1 complex, which was not characterized. In hopes of obtaining a general synthetic route to $R_2NBX_3^-$ compounds, we further investigated the reaction between $Ø_3CNR_2$ and boranes. Indeed with BF_3 and BCl_3 the desired anion could be formed by the direct reaction

$$Ø_3CN(CH_3)_2 + BX_3 \longrightarrow Ø_3C^+(CH_3)_2NBX_3^- \qquad (18)$$

The description of the preparation and characterization of these compounds plus determinations of the Lewis basicities of $R_2NBX_3^-$ follow.

B. Preparation and Characterization of $Ø_3CN(CH_3)_2$

1. Preparation

The preparation of N, N-dimethyltriphenylmethylamine in $(CH_3)_2CO$ has been reported.[55] Biallas[54] has found that the direct reaction of $Ø_3CCl$ with dimethylamine more

$$Ø_3CCl + (CH_3)_2NH \longrightarrow Ø_3CN(CH_3)_2 + (CH_3)_2NH_2^+Cl^- \qquad (19)$$

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

2. Characterization

$Ø_3CN(CH_3)_2$ 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 $Ø_3CN(CH_3)_2$ 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.[36] The presence of $Ø_3CH^+$, which arises from $Ø_3C$-N bond cleavage and proton migration, as the most abundant ion may imply that the $Ø_3C$-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.[36] Little if any trace can be found of $Ø_3CCl$, 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 $Ø_3CN(CH_3)_2$ are presented in Table XIII. The phenyl envelope (normally observed at 3100 cm^{-1})[56] was centered at 3035 cm^{-1} and was composed of five sharp absorptions at 3085, 3060, 3035, 3030, and 3000 cm^{-1}. The four absorptions of 2945, 2850, 2885, and 2795 cm^{-1} are assigned to the CH stretch which normally occurs[56] in this region. The remainder of the absorptions were assigned by reference to published data on phenylamines.[56] As in the mass spectra

TABLE XII

MASS SPECTRUM COMPILATION FOR $Ø_3CN(CH_3)_2$

m/e	% I/I_o	Assignment
15	1	CH_3^+
18	1	H_2O
22	2	
39	1	
42	2	C_2H_4N
43	1	C_2H_5N
44	1	$(CH_3)_2N$
51	2	
65	1	
77	5.9	Ø
89	1	ØC
91	3.7	$ØCH_2$, ØN
105	3.4	$ØCH_2N$
116	3.0	ØCNCH
118	4.6	$ØCNCH_3$
139	1.7	
152	2.2	$Ø_2(-2H)$
154	1	$Ø_2$
162	1.9	$Ø_2C(-2H)$
163	2.6	$Ø_2C(-1H)$
165	48	$Ø_2C$
166	9.4	$Ø_2CH$, $Ø_2C(^{13}C,D)$
167	3.4	$Ø_2CH_2$

TABLE XII. (Continued) MASS SPECTRUM COMPILATION FOR $Ø_3CN(CH_3)_2$

m/e	% I/I_o	Assignment
183	2.7	$Ø_2C_2H_5$
202	2	
210	9.2	$Ø_2CNC_2H_5$
211	1	$Ø_2CNC_2H_6$
213	1	$Ø_2CNC_2H_7$
215	3.2	
226	1	Ø(-5H)
227	1	$Ø_3$(-4H)
228	5.4	$Ø_3$(-3H)
229	1	$Ø_3$(-2H)
240	5.6	$Ø_3C$(-3H)
241	2	$Ø_3C$(-2H)
242	5.0	$Ø_3C$(-1H)
243	5.0	$Ø_3C$
244	100	$Ø_3C$(+H)
245	25.9	$Ø_3C$(+2H), $Ø_3CH(^{13}C,D)$
260	1	
287	1.7	$Ø_3CN(CH_3)_2$
288	1	

TABLE XIII

INFRARED ASSIGNMENT FOR $Ø_3CN(CH_3)_2$

$Ø_3CN(CH_3)_2$ (cm^{-1})	Assignment (tentative)	$Ø_3CN(CH_3)_2$ (cm^{-1})	Assignment (tentative)
3085 ms		985 w-sh	
3060 ms	ØH str	935 w-sh	CH_2 Wag
3035 ms		903 vst-s	
3030 ms			
3000 ms		855 vm	C-N
2945 st-s		772 st-s	
2850 st-s	CH_3 str	760 st-br	
2885 st-s		745 st-br	Ø
2795 st-s		705 vst-vbr	Ø
		643 m-s	Ø
1965 w-br	overtones &	639 w-sh	Ø
1915 w-br	combinations	629 m-s	Ø
1822 w-br			
1780 vw-br		572 m-s	Ø
		540 m-s	
1592 st-s			
		482 m-s	
1490 st-br	ØH-def	435 m-s	
1475 w-sh			
1460 st-s	CH_3-def		
1445 st-br	Ø-def		
1319 m-s	Ø-def		
1250 w-s	CH_3-def		
1208 st-s	CH_3 rock		
1180 w-sh	Ø		
1175 st-s			
1157 st-s	Ø		
1147 m-sh	Ø		
1092 w-s			
1082 m-s	Ø		
1070 vw-sh	C-C str		
1042 m-s	C-H wag		
1030 st-s	$Ø_3$		
1005 st-br	C-C str		

st=strong, m=medium, w=weak, s=sharp, br-broad, sh=shoulder, v=very

no evidence to indicate the presence of any $Ø_3CCl$ was observed.

c. ^1H nmr Spectrum

The proton nmr spectrum in CH_2Cl_2 taken at 100 MH_z is presented in Figure 11. The nmr consists of a singlet at -1.8 δ due to the methyl protons and a complex multiplet at -6.9 δ 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 $Ø_3CN(CH_3)_2$ 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 $Ø_3C^+(CH_3)_2NBF_3^-$

1. Reaction of $Ø_3CN(CH_3)_2$ and BF_3

The overall reaction of $Ø_3CN(CH_3)_2$ and BF_3 at room temperature is:

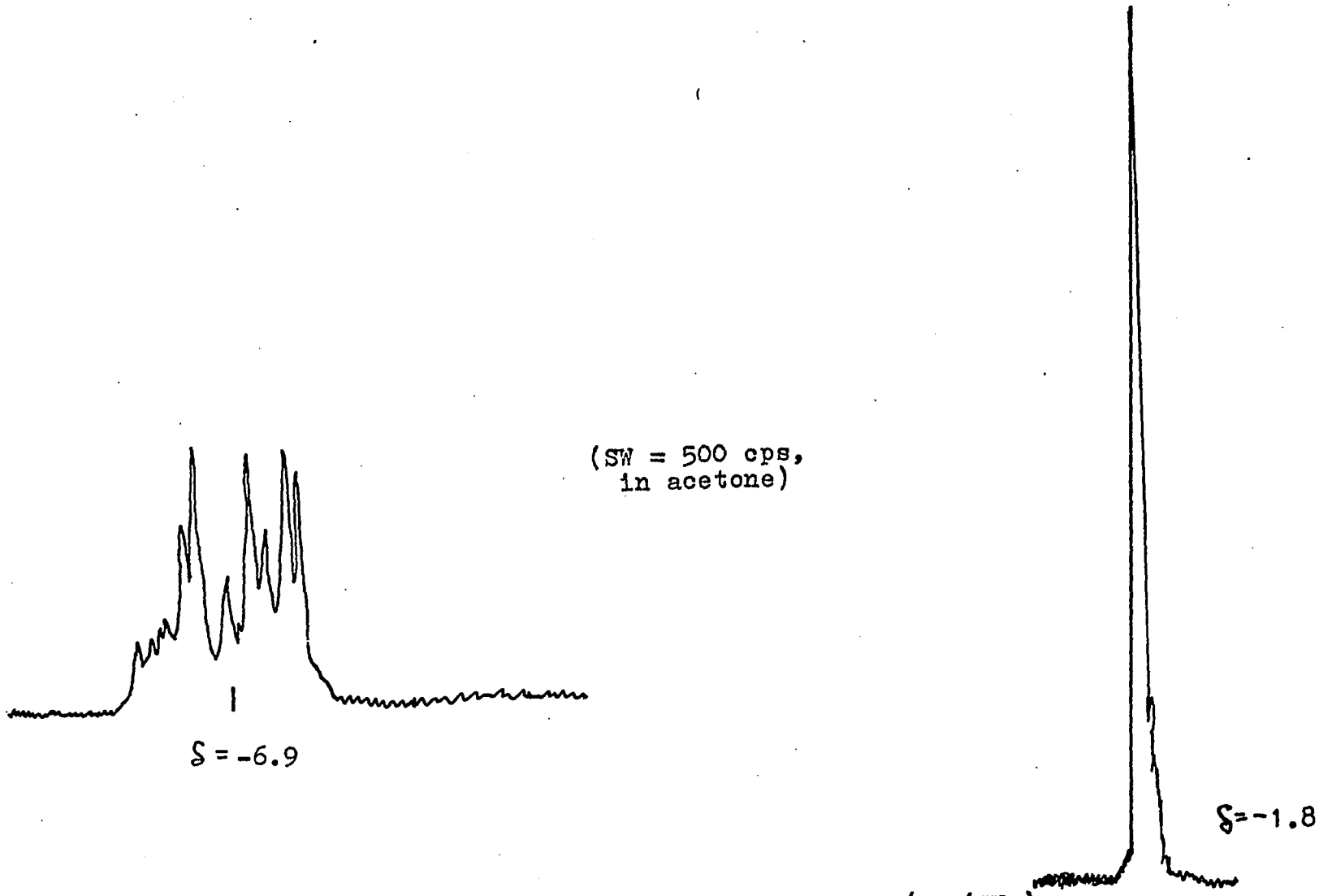


Figure 11. Proton NMR Spectrum of $\emptyset_3CN(CH_3)_2$

$$\emptyset_3CN(CH_3)_2 + BF_3 \longrightarrow \emptyset_3C^+(CH_3)_2NBF_3^- \qquad (20)$$

Gas solid and solution reactions in CH_2Cl_2, benzene and toluene were investigated. At ambient temperatures the $\emptyset_3C$-N bond was instantly cleaved by BF_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_3-$\emptyset_3CN(CH_3)_2$ mixture remained white for several days at -78°. This apparent induction period may be quite significant to the overall descriptive chemistry of the $\emptyset_3CNR_2$-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_2Cl_2, benzene, and toluene were not reproducible. Some of the problems encountered with the solution reactions were proton extraction from CH_2Cl_2 by $(CH_3)_2NBF_3^-$ to form $(CH_3)_2HNBF_3$ and an uncharacterized interaction of BF_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

$Ø_3CNCH_3$ with BF_3 in benzene.

2. Characterization of $Ø_3C^+(CH_3)_2NBF_3^-$

a. IR Spectrum

The infrared spectrum of $Ø_3C^+(CH_3)_2NBF_3^-$ 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 $Ø_3C^+(CH_3)_2NBF_3^-$ 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 pehnyl deformation modes are also usually seen in this region[56a] the assignment of these peaks is difficult. The C-H and Ø-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 $Ø_3C^+(CH_3)_2NBF_3^-$ in benzene exhibits twin absorption maxima at 410 and 430 nm which is characteristic of the triphenylmethyl cation.[52]

c. ^1H nmr Spectrum

The methyl resonance of $Ø_3C^+(CH_3)_2NBF_3^-$ in benzene is a

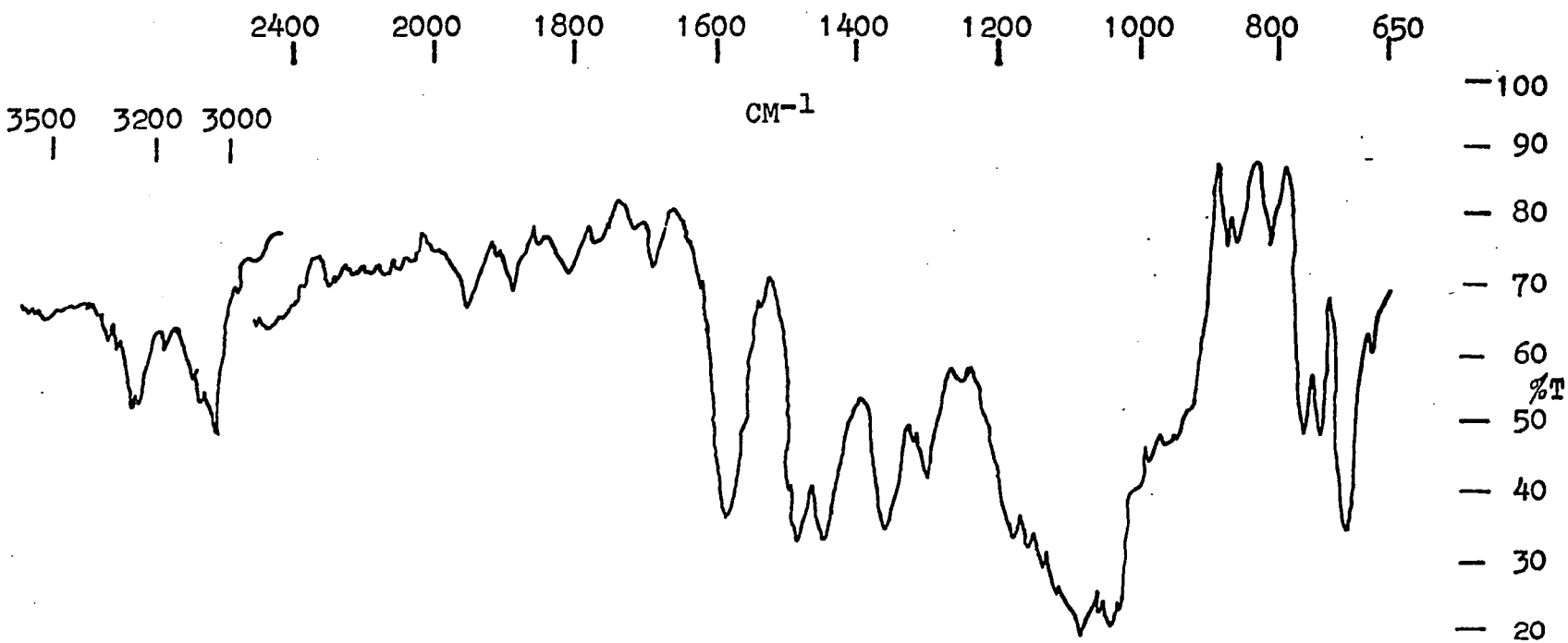


Figure 12. Infrared Spectrum of $\emptyset_3C^+(CH_3)_2NBF_3^-$

TABLE XIV

INFRARED ASSIGNMENT FOR $Ø_3C^+(CH_3)_2NBF_3^-$

$Ø_3C^+(CH_3)_2NBF_3^-$ (cm^{-1})	Assignment (tentative)
3260 env	ØH str
3050 env	CH str
1960 m-br	
1890 m-br	comb
1820 m-br	
1590 st-s	
1490 st-s	ØH def
1450 st-s	CH_3-def
1380 st-s	CH_3 rock
1210 m-s	
1100 vbr	C-C str, $Ø_3$-def, BF str
860	C-N str
820	
765	
745	
710	

env=envelope, m=medium, br=broad, st=strong, s=sharp, v=very

broad singlet approximately 7Hz at half peak height occurring at -1.3δ. In terms of the analogy developed in the introduction between the X_3B amine complexes and the methyl ammonium ions, the methyl resonance of $(CH_3)_2NBF_3^-$ should be shifted relative to $(CH_3)_2HNBF_3$ in the same direction and by approximately the same magnitude as the corresponding resonance in $(CH_3)_2NCH_3$ is shifted relative to that of $(CH_3)_2HNCH_3^+$. 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 $(CH_3)_2HNBF_3$ and $(CH_3)_2NBF_3^-$ 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

Quaternary (ppm)	Tertiary (ppm)	Difference	Reference
$(CH_3)_2HNCH_3^+$	$(CH_3)_2NCH_3$	.7	54
-2.9	-2.2		
$(CH_3)_2HNBH_3$	$(CH_3)_2NBH_3^-$	1.3	11
-2.5	-1.2		
$(CH_3)_2HNBF_3$	$(CH_3)_2NBF_3^-$	1.3	--
-2.6	-1.3		

The methyl resonances of the borane systems occur at a higher field than those in the $(CH_3)_3N$-$(CH_3)_3NH^+$ system. This agrees with the premise that CH_3^+ is a more efficient electron withdrawing group than BH_3 or 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 $Ø_3C^+(CH_3)_2NBF_3^-$ seemed to be either benzene or toluene, the phenyl region of $Ø_3C^+(CH_3)_2NBF_3^-$ could not be examined in any detail. Only a tentative chemical shift assignment of -7δ 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 $Ø_3C^+(CH_3)_2NBF_3^-$ 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 $Ø_3C^+(CH_3)_2NBF_3^-$ 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

$Ø_3C^+(CH_3)_2NBF_3^-$ is a very hygroscopic material which darkens and begins to decompose at approximately 100° in a

sealed tube.

TABLE XVI

d SPACINGS FOR $Ø_3C^+(CH_3)_2NBF_3^-$ AND $Ø_3C^+(CH_3)_2NBCl_3^-$

$Ø_3C^+(CH_3)_2NBF_3^-$	$Ø_3C^+(CH_3)_2NBCl_3^-$
1.05 Å	1.01 Å
1.28	1.51
1.20	1.28
1.13	1.16
2.25	1.11
0.933	0.822
0.863	2.16
0.826	0.916
1.61	0.868
0.796	0.798

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 $Ø_3C^+(CH_3)_2NBF_3^-$

	C	H	N
Calc.	70.90	5.91	3.94
Found	72.36	6.32	1.78

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 $Ø_3C^+(CH_3)_2NBF_3^-$ was markedly soluble. Its solubility in benzene and toluene, estimated from ^1H 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 $Ø_3C^+$. The solvents investigated include 1,2-dimethoxyethane, 2-methoxydiethyl ether, formamide, and N, N-dimethylformamide in which the compound was at most only slightly soluble.

D. Preparation and Characterization of $Ø_3C^+(CH_3)_2NBCl_3^-$

1. Reaction of $Ø_3CN(CH_3)_2$ and BCl_3

The interaction of BCl_3 with $Ø_3CN(CH_3)_2$ is represented by the equation:

$$Ø_3CN(CH_3)_2 + BCl_3 \longrightarrow Ø_3C^+(CH_3)_2NBCl_3^- \qquad (21)$$

Reactions run in benzene and toluene solution, as well as gas-solid reactions, were investigated. In all determinations, instantaneous rupture of the $Ø_3C$-N bond was noted by the formation of the yellow triphenylmethyl cation immediately upon contact of the BCl_3 with $Ø_3CN(CH_3)_2$. Unlike the 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 BCl_3 and $Ø_3CN(CH_3)_2$ 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 $Ø_3C^+(CH_3)_2NBCl_3^-$ were prepared in benzene for characterization of the adduct.

2. Characterization of $Ø_3C^+(CH_3)_2NBCl_3^-$

a. IR Spectrum

The ir spectrum presented in Figure 13 is a compilation of several spectra of suspensions of $Ø_3C^+(CH_3)_2NBCl_3^-$ taken in KBr, nujol and solid $Ø_3C^+(CH_3)_2NBCl_3^-$ 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 ØH and CH stretching regions showed marked signs of decomposition in the time required to record a spectrum. The first scan resulted in rather broad ØH 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}.

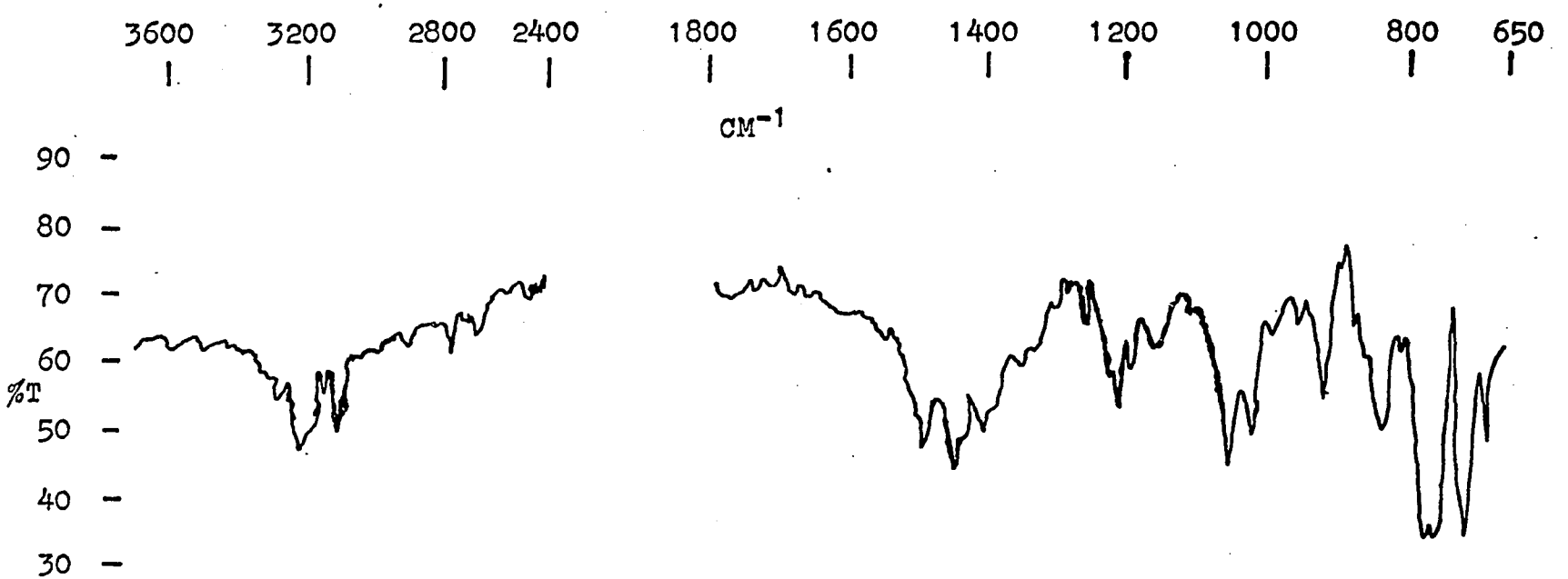


Figure 13. Infrared Spectrum of $\emptyset_3C^+(CH_3)_2NBCl_3^-$

TABLE XVIII

INFRARED ASSIGNMENT FOR $Ø_3C^+(CH_3)_2NBCl_3^-$

$Ø_3C^+(CH_3)_2NBCl_3^-$ (cm^{-1})	Assignment (tentative)
3200 vbr (envelope)	ØH str
2950 br	CH str
2120 w	
2250 w	
2380 w	
1495 m	BCl_3 str
1455 m	N-C
1440 m-sh	CH
1410 br	ØH-bend
1360 w	
1350 w	
1222 m	
1218 m	
1170 br	
1100 sh	
1050 m-sh	CH_3 rock
1020 m-sh	
920 m-sh	NB str
830 m-br	CN str
760 st	Ø
720 st-s	
680	

v=very, br=broad, w=wide, m=medium, sh=shoulder, st=strong, s=sharp

Tentative assignments have been attempted by reference to similar compounds.[56]

b. Electronic Spectrum

The yellow color of $Ø_3C^+(CH_3)_2NBCl_3^-$ is due to the presence of the triphenylmethyl cation as is clearly demonstrated by the absorptions at 410 and 430 nm in benzene.[52]

c. ^1H nmr Spectrum

The spectrum of $Ø_3C^+(CH_3)_2NBCl_3^-$ in benzene consists of a broad singlet ($\sim$ 7Hz) at -1.4 δ and a complex multiplet at approximately -7 δ. 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 $(CH_3)_2NBCl_3^-$ 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 $Ø_3C^+(CH_3)_2NBCl_3^-$ 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 BCl_3 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 XIX

C, H, AND N ANALYSES OF $Ø_3C^+(CH_3)_2NBCl_3^-$

	C	H	N
Calc.	62.3	5.19	3.46
Found	62.2	5.04	1.54

As with the BF_3 analog N analysis of $Ø_3C^+(CH_3)_2NBCl_3^-$ 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 $Ø_3C^+(CH_3)_2NBF_3^-$. The only solvents in which more than slight solubility was observed were benzene and toluene.

E. Reaction of $Ø_3CN(CH_3)_2$ and B_2H_6

There is no reaction between $Ø_3CN(CH_3)_2$ and B_2H_6 at temperatures between -25° and -160°. At least six attempts were made to perform this reaction. While in two of the attempts some decomposition of B_2H_6 was evidenced by the production of non-reproducible amounts of hydrogen, no uptake of diborane could be detected. The base displacement reaction between $Ø_3CN(CH_3)_2$ and Et_2OBH_3 also failed to give reproducible data to indicate the uptake of BH_3 by $Ø_3CN(CH_3)_2$.

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 $Ø_3CN(CH_3)_2$ was placed in the reaction tube, the entire apparatus affixed to the vacuum line and evacuated. A known amount of gaseous reactant (e.g. BF_3 or BCl_3) was then frozen into the tensimeter which was sealed at point S. The portion of the apparatus containing $Ø_3CN(CH_3)_2$ was then carefully thermostated at an appropriate temperature and

TENSIMETER

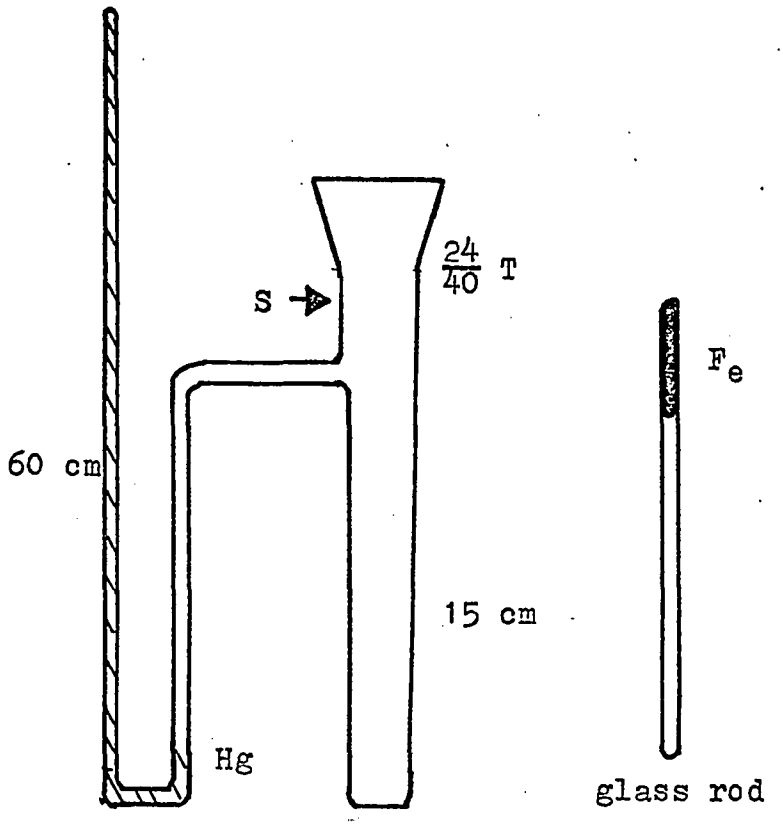


Figure 14. Tensimetric Titration Apparatus

stirred until the system reached equilibrium (several days to weeks). By preparing a number of tubes with differing $BX_3/Ø_3CN(CH_3)_2$ 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 BX_3 could only come in contact with $Ø_3CN(CH_3)_2$, mercury and glass. The all glass construction of the tensimeter eliminated problems of slow gas leakage from the atmosphere.

1. Reaction of BF_3 and $Ø_3CN(CH_3)_2$

The complete data for the tensimetric titration of BF_3 with $Ø_3CN(CH_3)_2$ at -78° 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) $Ø_3CN(CH_3)_2/BF_3$ 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 BF_3 is taken up by the $Ø_3CN(CH_3)_2$ and that the reaction mixture remains white if the temperature is maintained below -78° and the ratio of BF_3/amine is less than 0.3. Upon warming or the addition of more BF_3 the mixture takes on the yellow color of $Ø_3C^+$. Attempts to characterize the white solid failed because of its extreme sensitivity to heat and BF_3. However, it is interesting to

TABLE XX

TENSIMETRIC TITRATION OF $Ø_3CN(CH_3)_2$ AND BF_3

#	$Ø_3CN(CH_3)_2$ g	Calc $P_{mm}BF_3$	Actual $P_{mm}BF_3$	Ratio $BF_3/Ø_3$ actual	Equil Press cm
1	.2934	34.12	32.7	.0988	0.0
2	.1573	91.41	92.5	.521	0.0
3	.1538	160.96	160.5	.927	0.0
4	.2581	358.77	365.0	1.346	20.0
5	.1593	258.87	250.0	1.494	20.3
6	.1249	257.02	251.3	1.913	20.1
7	.1183	261.38	263.6	1.975	21.8
8	.0997	226.76	232.5	2.220	25.0
9	.1031	297.21	297.5	2.558	29.1

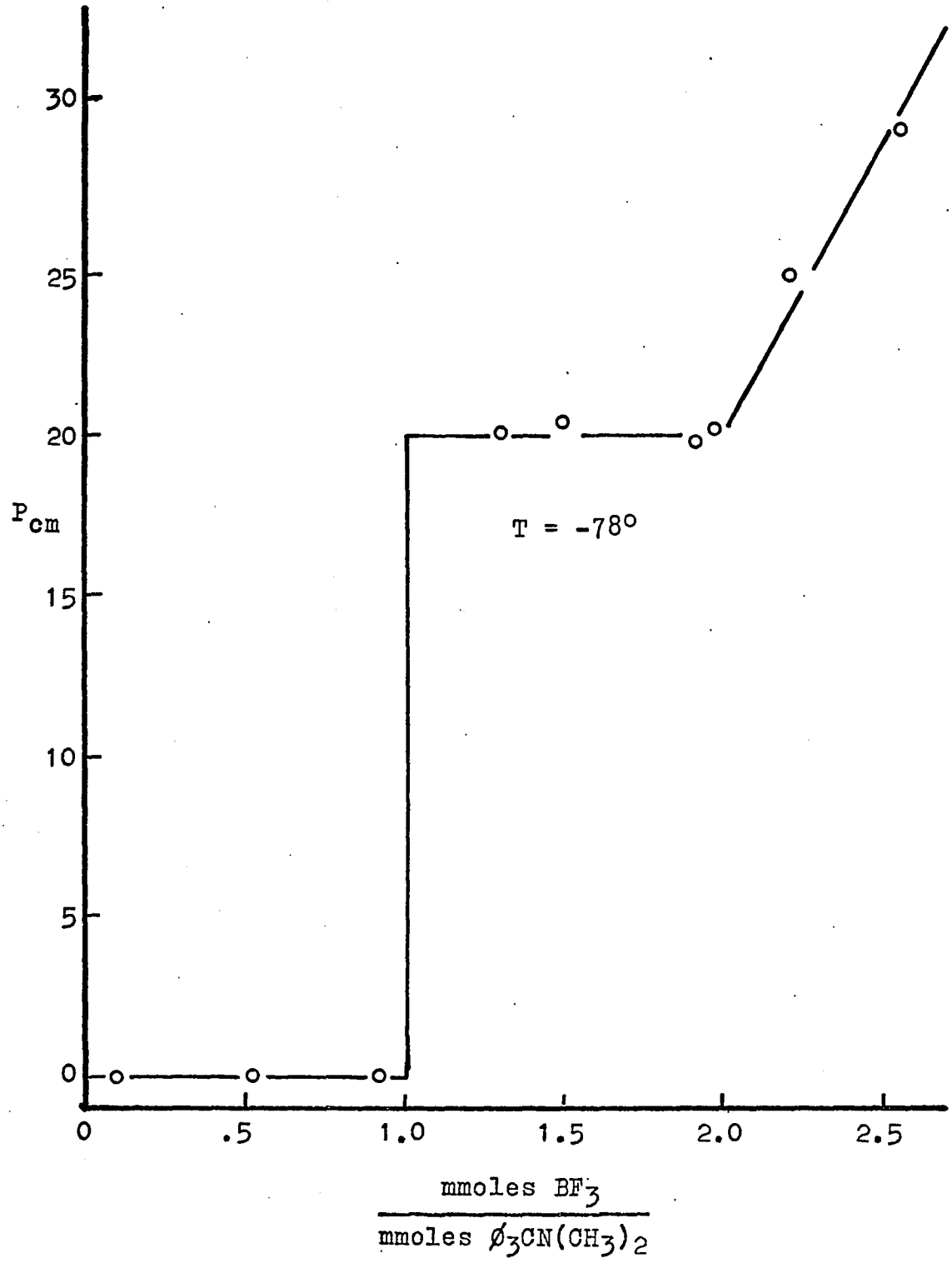


Figure 15. Tensimetric Titration of $\emptyset_3CN(CH_3)_2$ and BF_3

speculate on the significance of these results to the overall descriptive chemistry of the system. Borontrifluoride is known to complex most amines[1] 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_3B: amine complex whose C-N bond is only cleaved by warming or additional BF_3. The overall reaction sequence would be represented by:

$$\emptyset_3CN(CH_3)_2 \xrightarrow{BF_3} \emptyset_3C\underset{\underset{BF_3}{|}}{N}(CH_3)_2 \rightarrow \emptyset_3C^+\underset{\underset{BF_3}{|}}{N}(CH_3)_2^- \xrightleftharpoons{BF_3} \emptyset_3C^+\overset{\overset{BF_3}{|}}{\underset{\underset{BF_3}{|}}{N}}(CH_3)_2^- \qquad (22)$$

2. Reaction of BCl_3 and $\emptyset_3CN(CH_3)_2$

The apparatus and techniques employed in the tensimetric titration of $\emptyset_3CN(CH_3)_2$ with BCl_3 were identical to those in the BF_3-$\emptyset_3CN(CH_3)_2$ studies. However, it was not possible to conduct these experiments at -78° because of the low vapor pressure of BCl_3 ($\sim$5 mm) at this temperature. The data for BCl_3-$\emptyset_3CN(CH_3)_2$ tensimetric titration at 26° is presented in Table XXI and the results are represented graphically in Figure 16. Obviously at 26° BCl_3 forms a mono- but not a diadduct. Diadduct formation at low temperature is not ruled out. In the case of BCl_3 no induction period of any kind was observed in either the bulk or tensimetric reactions. Therefore, the overall reaction of BCl_3 and $\emptyset_3CN(CH_3)_2$ is:

$$\emptyset_3CN(CH_3)_2 + BCl_3 \longrightarrow \emptyset_3C^+(CH_3)_2NBCl_3^- \qquad (23)$$

TABLE XXI

TENSIMETRIC TITRATION OF $Ø_3CN(CH_3)_2$ AND BCl_3

#	$Ø_3CN(CH_3)_2$ g	Calc. $P_{mm}BCl_3$	Actual $P_{mm}BCl_3$	Ratio $BF_3/Ø_3$	Equil Press cm
1	.2469	26.8	27.0	.103	0.0
2	.1911	103.8	103.0	.511	0.0
3	.1659	162.2	159.0	.909	0.0
4	.2044	244.3	253.0	1.175	16.0
5	.1683	347.5	342.9	1.932	41.3
6	.1026	244.1	230.3	2.129	50.6
7	.1153	331.2	309.7	2.548	57.9

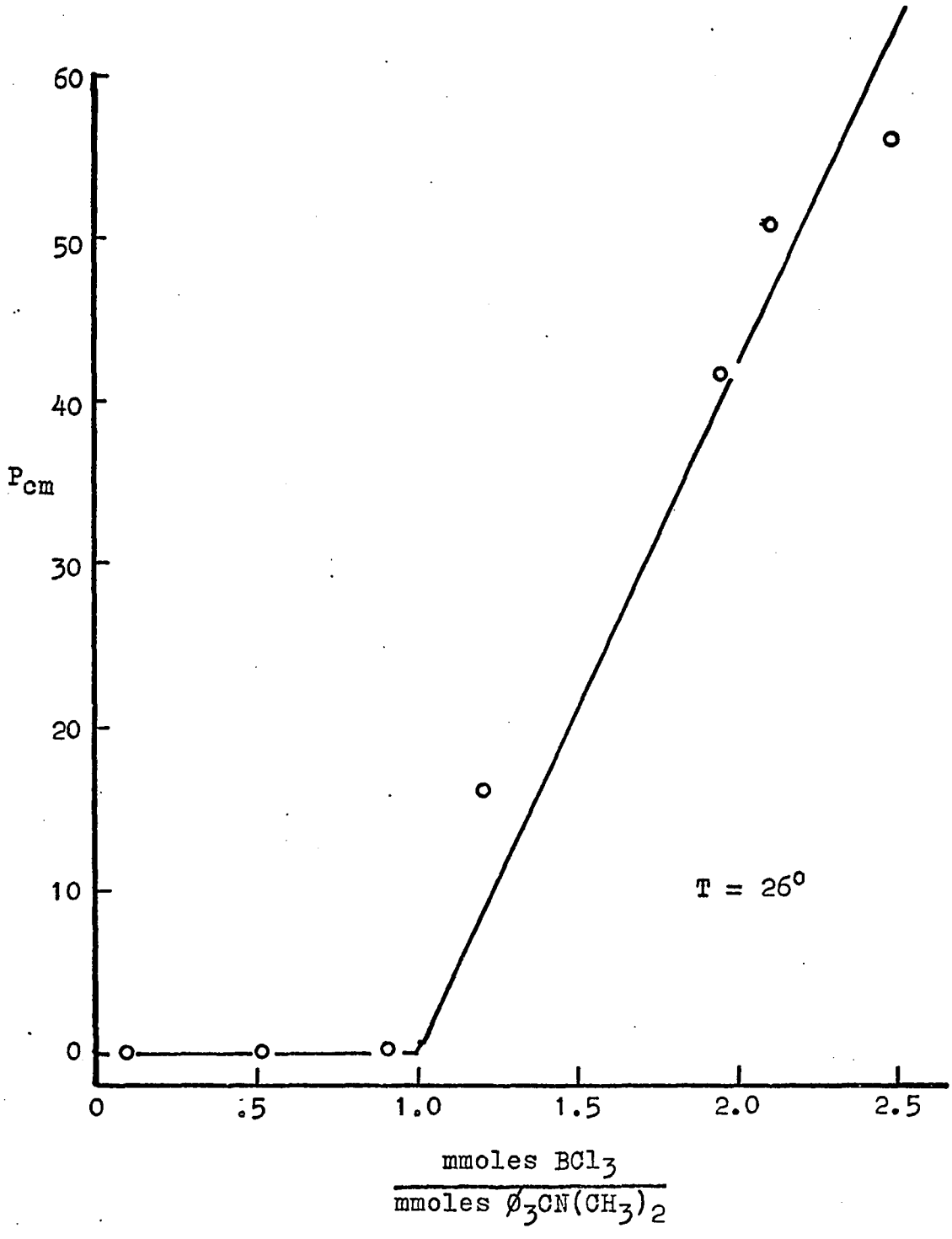


Figure 16. Tensimetric Titration of $\emptyset_3CN(CH_3)_2$ and BCl_3

3. Reaction of BF_3 and $Ø_3C^+(CH_3)_2NBCl_3^-$

Since $(CH_3)_2NBF_3^-$ forms an unstable complex with BF_3, the basicity of $(CH_3)_2NBCl_3^-$ toward BF_3 was also of interest. In effect the basicities of the two bases $(CH_3)_2NBF_3^-$ and $(CH_3)_2NBCl_3^-$ could be compared by determining the dissociation constants for their respective reactions with the reference acid BF_3.

$$Ø_3C^+(CH_3)_2NBF_3^- + BF_3 \rightleftharpoons Ø_3C^+(CH_3)_2N(BF_3)_2^- \quad (24)$$

$$Ø_3C^+(CH_3)_2NBCl_3^- + BF_3 \rightleftharpoons Ø_3C^+(CH_3)_2N(BF_3)(BCl_3)^- \quad (25)$$

Tensimetric titrations of both solid $Ø_3C^+(CH_3)_2NBCl_3^-$ and of solutions in toluene were performed. The results are shown in Table XXII, and in no case was the formation of any $(CH_3)_2N(BF_3)(BCl_3)^-$ 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 $Ø_3C^+(CH_3)_2N(BF_3)_2^-$.

TABLE XXII

TENSIMETRIC TITRATION OF $Ø_3C^+(CH_3)_2NBCl_3^-$ AND BF_3

$Ø_3CN(CH_3)_2$ g	Calc P_{mm} BF_3	Actual P_{mm} BF_3	Ratio $BF_3/Ø_3$	Equil Press
.1483	110.5	111.0	.7	60.0
.1687	143.6	136.0	.8	60.0
.1524*	146.0	135.0	.9	60.0

*no solvent

4. Lewis Basicity of $(CH_3)_2NBX_3^-$

The strength of a Lewis base, B, is a measure of the magnitude of the equilibrium, Keq, for the reaction:

$$A + :B \rightleftharpoons A:B \tag{26}$$

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

$$Keq = \frac{1}{P_{diss\ of\ AB}} = \frac{1}{K_{diss\ of\ AB}} \tag{27}$$

Comparing the two anions $(CH_3)_2NBCl_3^-$ and $(CH_3)_2NBF_3^-$, since $P_{diss}(CH_3)_2N(BF_3)_2 < P_{diss}(CH_3)_2N(BF_3)(BCl_3)^-$, the latter is by far the stronger base toward the reference acid 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 isostructural 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.[57] The basicity of the $R_2NBX_3^-$ complexes thus should reflect the electron donating properties of the two methyl groups and the co-ordinated BF_3 or BCl_3.

Since $(CH_3)_2NBF_3^-$ is definitely a stronger base than $(CH_3)_2NBCl_3^-$ the obvious conclusion is that BCl_3 is a more efficient electron withdrawing group than 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 $R_2NBCl_3^-$ 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 $(CH_3)_2N(BF_3)(BCl_3)^-$, 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 $(CH_3)_2NBF_3^-$ (-.302) and $(CH_3)_2NBCl_3^-$ (-.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 $(CH_3)_2N(BF_3)_2^-$ and $(CH_3)_2N(BF_3)(BCl_3)^-$ also is indicated by the extended Huckel calculations which show that the energy differences for the processes are about 10 ev. more

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

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 π character in the B_{2pz} orbital and conclude that this residual π 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-BF_3 Complexes

1. Preparation of $(CH_3)_2HNBF_3$

In a typical preparation approximately 0.1 mole of BF_3 was distilled on the vacuum line into 25 ml of dry diethylether held at -196° in a standard 50 ml reaction flask. As the flask was warmed the pressure increased as the BF_3 began to vaporize, but dropped when the diethylether began to melt and $F_3BO(C_2H_5)_2$ 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 $(CH_3)_2HNBF_3$ remaining in the reaction flask was purified by sublimation in a standard vacuum sublimator to a -78° cold finger.

2. Preparation of $CH_3H_2NBF_3$

The preparation of this complex was carried out in a manner analogous to the preparation used for $(CH_3)_2HNBF_3$.

The crude product, however, was purified by cyrstallization 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 H_3NBF_3

The preparation of this complex was done in a manner analogous to the synthesis described for $(CH_3)_2HNBF_3$. 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 H_3NBF_3 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-BF_3 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-BF_3 COMPLEXES

Compound	M.P. in C°	Literature	Reference
$(CH_3)_2HNBF_3$	52.4	53.0	62
$(CH_3)H_2NBF_3$	93.5	93.5	1
H_3NBF_3	163	163	26

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-BX_3 COMPLEXES

Solvent	$(CH_3)_2HNBF_3$	$CH_3H_2NBF_3$	H_3NBF_3	$(CH_3)_2HNBH_3$
$CHCl_3$	sol	insol	insol	sol
$CDCl_3$	sol	insol	insol	sol
C_2H_6	sol	insol	insol	sol
DMF	very sol	sol	sol	very sol
Pyridine	very sol	sol	sol	very sol
Acetone	very sol	very sol	sol	very sol

C. Reaction of $(CH_3)_2HNBF_3$ with Na in Liquid Ammonia

In a representative run 321.2 mg (2.84 mmoles) of $(CH_3)_2HNBF_3$ 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 NH_3, previously stored over Na, was distilled into the reaction tube at -196°. The tube was slowly warmed and the temperature maintained between -110° and -40° 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° 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° and the non-condensible gas pumped through four -196° traps into a gas burette by means of a Toepler pump. The reaction mixture was warmed to -78° 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 H_2 (identified by mass spectroscopy) was thus collected. The ratio of moles of H_2 produced to moles of

$(CH_3)_2HNBF_3$ used equals 0.516 in this run.

The product was separated from the mercury-sodium amalgum using standard vacuum filtration techniques. The solution was clear and after removal of solvent ammonia, a fluffy white material remained. $Na(CH_3)_2NBF_3$ is very hygroscopic and all handling was done in the dry box at the dew point of P_2O_5.

D. Fluorine and Boron Analyses of $Na(CH_3)_2NBF_3$

1. Fluorine

In a typical analysis 83.1 mg (0.6164 mmoles) of $Na(CH_3)_2NBF_3$ 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 $Na(CH_3)_2NBF_3$

In the one attempt of an aqueous titration of $Na(CH_3)_2NBF_3$, 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 $(CH_3)_2HNBF_3$

In one of several attempts 31.7 mg (0.283 mmoles) of $(CH_3)_2HNBF_3$ 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_2O (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_2O. 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.[43] 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 (X1, 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

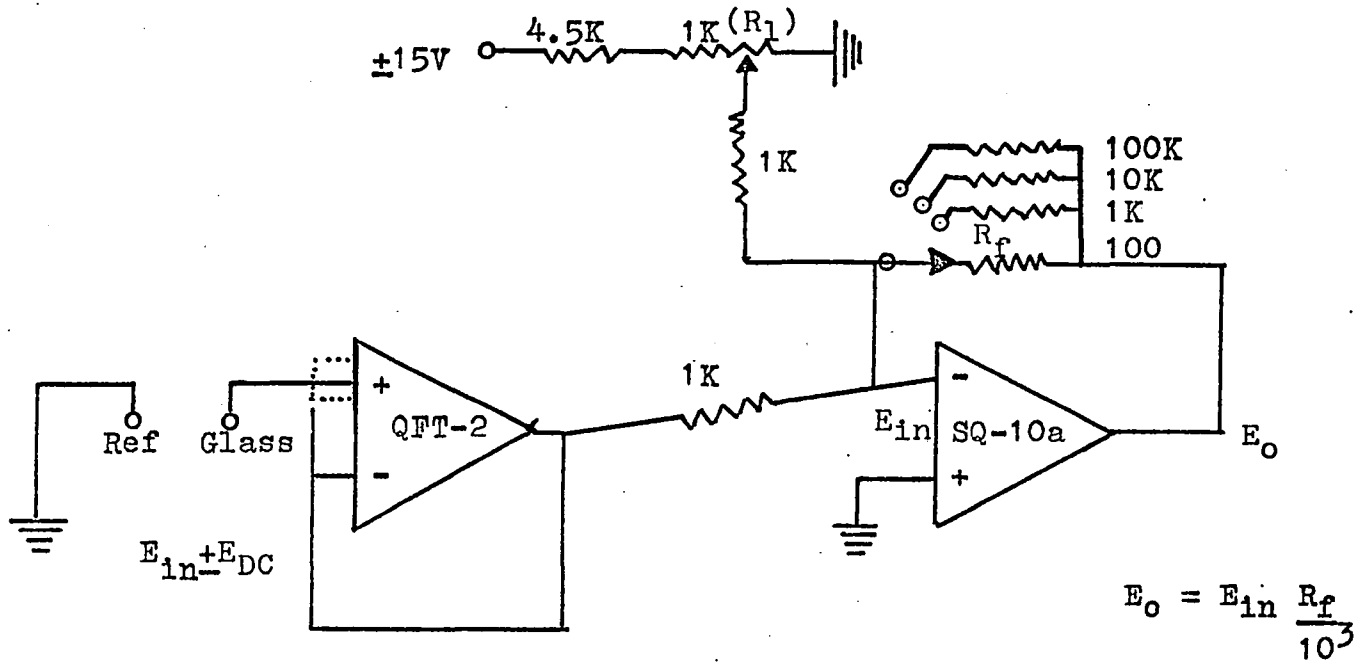


Figure 17. Op-Amp Follower-Electrometer

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 CH_3OH-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 $\pm$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 N_2 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 N_2 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_3NBF_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_3NBF_3, $CH_3H_2NBF_3$, and $(CH_3)_2HNBF_3$

In a representative run 153.5 mg (1.809 mmoles) of

H_3NBF_3, 179.2 mg (1.831 mmoles) of $CH_3H_2NBF_3$, and 205.0 mg (1.816 mmoles) of $(CH_3)_2HNBF_3$ were dissolved in three 25.00 ml volumetric flasks. One ml aliquots of this stock solution were titrated with TBAH at 20.0 $\pm$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 $Ø_3CN(CH_3)_2$

Approximately 10 g amounts of triphenyldimethylamine were prepared by the direct reaction of $Ø_3CCl$ with excess $(CH_3)_2HN$.

$$Ø_3CCl + \underset{\text{(excess)}}{(CH_3)_2HN} \longrightarrow Ø_3CN(CH_3)_2 + (CH_3)_2NH_2^+Cl^- \qquad (29)$$

In a typical preparation 19.1 g (68.5 mmoles) of $Ø_3CCl$ 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 $(CH_3)_2HN$ 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 $(CH_3)_2HN$ 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 ($\sim$300 ml) through a fine frit. The insoluble dimethylammonium chloride was discarded and the soluble triphenylmethyldimethylamine 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.[59] Reactants were stirred by a glass stirrer containing an Fe rod. The stirrer was raised magnetically by means of a solenoid (Bendix 0969).

2. $Ø_3CN(CH_3)_2$ and BF_3

In a typical experiment 0.1573 g (0.5473 mmoles) of $Ø_3CN(CH_3)_2$ 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 BF_3 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. $Ø_3CN(CH_3)_2$ and 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. $Ø_3C^+(CH_3)_2NBCl_3^-$ and BF_3

Into the reaction tube of a tensimeter was placed 0.1483 g (0.5160 mmoles) of $Ø_3CN(CH_3)_2$. The phenyl amine was then dissolved in approximately 1 ml of dry toluene (frozen in at -196°) and 10 mmoles of BCl_3 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 BCl_3 and solvent was removed at 26°. The $Ø_3C^+(CH_3)_2NBCl_3^-$ was then partially dissolved in 1 ml of toluene which was frozen in at -196°. A measured aliquot of BF_3 corresponding to (0.7)(0.5160) mmoles of $Ø_3C^+(CH_3)_2NBCl_3^-$ 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 $Ø_3C^+(CH_3)_2NBCl_3^-$ 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 $\pm$0.01 pH units and buffered with standard Beckman buffers (pH 4, 7, 10, 12) with an absolute pH uncertainty of $\pm$0.01 pH units.

The temperature in the analysis was held constant to $\pm$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 $LiAlH_4$) 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 P_2O_5, 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 diffration 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 B_2H_6

Diborane was prepared by the addition of reagent grade $NaBH_4$ (ICN grade) to concentrated H_2SO_4 (Dupont). Diborane was produced in a yield of about 70-80%. The details of

this procedure were developed by H. Weiss and I. Shapiro.[61]

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

1. K. Neidenzu and J. W. Dawson, "Boron-Nitrogen Compounds," Springer-Verlag, Berlin, 1965, pp. 1-4.

2. A. Stock, "The Hydrides of Boron and Silicone," Cornell University Press, Ithaca, N. Y., 1937, pp. 173-207.

3. A. Stock and E. Pohland, Ber. dtsch. Chem. Ges., 59, 2215 (1926).

4. E. Wiberg, Naturwissenschaften, 35, 182, 212 (1948).

5. Chem. Engng. News, 32, 1441 (1954).

6. Ibid., 34, 560 (1956).

7. Inorg. Chem., 7, 1945 (1968).

8. G. Kodama and R. W. Parry, Inorg. Chem., 4, 410 (1965).

9a. R. W. Parry, D. R. Schultz, and P. R. Girardot, J. Am. Chem. Soc., 80, 1 (1958).

b. D. R. Schultz and R. W. Parry, ibid., 80, 4 (1958).

c. S. G. Shore and R. W. Parry, ibid., 80, 8-12 (1958).

d. R. W. Parry and S. G. Shore, ibid., 80, 15 (1958).

e. S. G. Shore, R. P. Girardot, and R. W. Parry, ibid., 80, 20 (1958).

f. R. W. Parry, G. Kodama, and D. R. Schultz, ibid., 80, 24 (1958).

g. R. C. Taylor, D. R. Schultz, and A. R. Emery, ibid., 80, 27 (1958).

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

11. J. W. Gilje and R. J. Ronan, Inorg. Chem., 7, 1248 (1968).

12. G. W. Watt, Chem. Rev., 46, 289 (1950).

13a. A. W. Laubengayer and D. S. Sears, J. Am. Chem. Soc., 67, 164 (1945).

b. H. C. Brown and R. R. Holmes, ibid., 78, 2173 (1956).

14a. F. G. A. Stone, Chem. Rev., 58, 101 (1958).

b. B. Swanson, D. F. Shriver and J. A. Ibers, Inorg. Chem., 8, 2182 (1969).

15. F. A. Cotton and J. R. Leto, J. Chem. Phys., 30, 933 (1959), and references therein.

16a. J. M. Miller and M. Onyszchuk, Can. J. Chem., 44, 899 (1966).

b. R. G. Pews, Y. Tsuno, and R. W. Taft, J. Am. Chem. Soc., 89, 2391 (1967).

c. P. H. Clippard and R. C. Taylor, Inorg. Chem, 8, 2802 (1969).

17. D. F. Shriver and J. Posner, J. Am. Chem. Soc., 88, 1672 (1966).

18. I. Gynes, "Titrations in Non-Aqueous Media," Iliffe Books Ltd., London, 1967.

19. J. N. Bronsted, Rec. Trav. Chim., 42, 718 (1923); J. Phys. Chem., 30, 777 (1926); Chem. Rev., 5, 1231 (1928).

20. G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chem. Catalog Co., New York, 1923.

21. W. J. McDowell and C. W. Keenan, J. Am. Chem. Soc., 78, 2065 (1956).

22. I. G. Ryss and N. G. Parkhomeuke, Zh. Neorg. Khim., 11, 2052 (1966).

23. H. Steinberg, "Organoboron Chemistry," Vol. 2, Interscience, N. Y., 1966, p. 3.

24. V. D. Aftandilian, H. C. Miller, and E. L. Mutterties, J. Am. Chem. Soc., 83, 2471 (1961).

25a. F. J. Foote, Ind. Eng. Chem. Anal. Ed., 4, 39 (1932).

b. H. W. Dodger and G. K. Rollefson, J. Am. Chem. Soc., 71, 2600 (1949).

26. A. Krauss and H. C. Brown, J. Am. Chem. Soc., 51, 2690 (1929),

27. A. W. Laubengayer and G. F. Condike, ibid., 70, 2274 (1948).

28. R. C. Taylor, H. S. Gabelnick, K. Aida, and R. L. Amster, Inorg. Chem., 8, 605 (1969).

29. J. Goubeau and J. Mitschelen, Z. Physik. Chem., 14, 61 (1958).

30. A. A. Babuskin, J. F. Kovalev, and V. M. Emil'yamova, Opt. i Sektoskopiya, 4, 486 (1958).

31. W. Sawodhy and J. Goubeau, Z. Physik. Chem., 44, 227 (1965).

32. S. Geller and J. L. Hoard, Acta. Cryst., 3, 121 (1950).

33. R. C. Taylor, "Infrared Spectra of Inorg. Compounds Containing Bridge and Co-ordinate Bonds," Department of Chemistry, University of Michigan publication 2963.

34. C. W. Heitsch, Inorg. Chem., 4, 1019 (1965).

35. J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Company, N. Y., 1959.

36a. A. Cornu and R. Massot, "Compilation of Mass Spectra Data," Aexden and Son Limited, London, 1966.

b. R. S. Gohlke and F. W. McLafferty, Anal. Chem., 34, 1281 (1962).

37. W. Huber, "Titrations in Non-Aqueous Solvents," Academic Press, N. Y., 1967.

38. L. G. Chatten and L. E. Harris, Anal. Chem., 34, 1495 (1962).

39. J. Kucharsky and L. Safarik, "Titrations in Non-Aqueous Solvents," Elsener Publishing Co., Amsterdam, 1965.

40. H. B. van der Heijde, Anal. Chem. Acta, 17, 512 (1957).

41. G. A. Harlow, Anal. Chem., 34, 1483 (1962).

42a. W. Leland, L. W. Marpel, J. S. Fritz, ibid., p 796.

b. G. A. Harlow, ibid., p. 148.

43. R. H. Cundiff and P. C. Markunas, ibid., 28, 792 (1956).

44. R. S. Drago and N. A. Matwiyoff, "Acids and Bases," D. C. Heath and Co., Lexington, Mass., 1968.

45. R. Weaver and R. W. Parry, Inorg. Chem., 5, 718 (1966).

46. Davis and Hetzer, J. Res. Nat. Bur. Stand., 48, 381 (1952).

47. R. P. Bell and J. W. Balyes, J. Chem. Soc., 1518 (1952).

48. J. S. Fritz, Anal. Chem., 25, 407 (1953).

49. I. M. Kolthoff, D. Stocesoca, and T. S. Lee, J. Am. Chem. Soc., 75, 1834 (1953).

50. F. Becker, Ber., 86, 1150 (1953).

51. H. Yoneda, Bull. Chem. Soc. Japan, 31, 703 (1958).

52. D. F. Schriver and M. J. Biallas, J. Am. Chem. Soc., 89, 1078 (1967).

53. M. J. Biallas, ibid., 91, 7290 (1969).

54. M. J. Biallas, personal communication.

55. E. H. Varga and K. Nador, Arzheim. Forsch., 17, 409 (1967).

56a. N. B. Colthup, L. H. Daly and Stephen E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, N. Y., 1964.

b. J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentic-Hall, Inc., Englewood Cliffs, N. J., 1965.

57. K. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, N. Y., 1964.

58. R. Hoffmann, J. Chem. Phys., 39, 1397 (1963).

59. D. F. Shriver, "The Manipulation of Air-sensitive Compounds," McGraw-Hill Book Co., N. Y., 1969.

60. R. S. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, N. Y., 1948.

61. H. Weiss and I. Shapiro, J. Am. Chem. Soc., 81, 6167 (1959).

62. J. Goubeau, Doctoral Dissertation, Munich, (1942).

63. D. G. Brown, R. S. Drago, and T. F. Bolls, J. Am. Chem. Soc., 90, 5708 (1968).