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STUDIES OF DIMETHYLBORON DERIVATIVES

by

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A THESIS
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FACULTY OF GRADUATE STUDIES

The undersigned hereby certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled

"STUDIES OF DIMETHYLBORON DERIVATIVES"

submitted by GILBERT FRANCIS LANTHIER in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

Various techniques have been applied to the study of boron-oxygen bonding in compounds such as $(CH_3)_2BOCH_3$ and $(CH_3)_2BOB(CH_3)_2$. A convenient synthesis and full characterization of the latter is reported.

The Lewis acid character of boron in these compounds has been investigated using trimethylamine as the reference base. The enthalpies of dissociation of $(CH_3)_2BOB(CH_3)_2 \cdot N(CH_3)_3$ and $(CH_3)_2BOCH_3 \cdot N(CH_3)_3$ are 9.5 kcals. and 6.8 kcals., respectively. The Lewis acidity decreases as the ratio of boron to oxygen decreases. These results indicate that boron-oxygen π-bonding, rather than an inductive effect, is of predominant importance in determining the Lewis acid character of these compounds.

The Lewis base character of oxygen in these compounds has been investigated by an nmr study of the chloroform dilution shift. Values of this shift are a measure of the availability of the oxygen lone pair electrons for hydrogen bonding. The shifts decrease markedly as the ratio of boron to oxygen increases; a result supporting the above interpretation of boron-oxygen bonding.

A barrier to rotation about the boron-oxygen bond in the region _ca_. 9.0 kcals. has been established for these compounds using variable temperature nmr techniques.

This barrier to rotation is considered to result from the interaction of the lone pair electrons on oxygen with the vacant p_z orbital on boron.

The degree of association of $(CH_3)_2BOH$ in solution was observed to range from three to seven in the temperature region -36° to -63°C. Nmr and ir studies established that hydrogen bonding is the source of this association. Correlation of these spectral results with other systems suggest that the enthalpy of dissociation of the hydrogen bond in this compound is 4.7 kcals.

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TABLE OF CONTENTS

Page

Abstract iii

Acknowledgements v

Table of Contents vi

List of Tables viii

List of Figures x

CHAPTER I

INTRODUCTION 1

1. The Nature of the Trivalent Boron Compounds 1

2. The Compounds and Techniques 4

3. The Use of Nmr for Kinetic Studies . . . 5

4. Outline of Study 7

CHAPTER II

APPARATUS, PREPARATIONS AND ANALYSES 8

1. Description of Apparatus 8

2. Infrared Spectra. 10

3. Mass Spectra 10

4. Nmr Spectra 12

5. Preparation of Compounds 14

6. Statistical Treatment of Data 23

CHAPTER III

EXPERIMENTAL RESULTS 27

1. The Characterization of Dimethylboric Anhydride 27

Page

2. Results of Other Preparations 30
3. Complex Formation with Dimethylboric Anhydride 34
4. Ambient Temperature NMR Analyses of the Complexes 43
5. Variable Temperature NMR Studies of Some Dimethylboric Anhydride Systems. . 44
6. Studies of Dimethylmethoxyboron 58
7. Other Systems 69
8. Chloroform Dilution Shift Study 73
9. Study of Dimethylboric Acid 78

CHAPTER IV

DISCUSSION. 86
1. The Characterization of Dimethylboric Anhydride 86
2. Other Compounds Prepared 89
3. Studies on Dimethylboric Anhydride . . 93
4. Dimethylmethoxyboron and Related Compounds 104
5. The Relative Base Strength of Oxygen . 109
6. Dimethylboric Acid. 110

CHAPTER V

CONCLUSIONS 113
BIBLIOGRAPHY 116
APPENDIX A 123
APPENDIX B 124
APPENDIX C 125

LIST OF TABLES

Table		Page
I	Preliminary study of the $(CH_3)_4Sn-BCl_3$ reaction.	15
II	Vapor pressure data for dimethylboric anhydride.	28
III	Mass spectrum of dimethylboric anhydride.	29
IV	Vibrational frequencies and suggested assignments for dimethylboric anhydride.	31
V	Abbreviated mass spectral data for dimethylmethoxyboron.	33
VI	Abbreviated mass spectral data for dimethylpentafluorophenoxyboron.	35
VII	Abbreviated mass spectrum of dimethyl-_t_-butoxyboron.	36
VIII	Saturation pressures of dimethylboric anhydride-trimethylamine.	37
IX	Gas phase dissociation of dimethylboric anhydride-trimethylamine.	39
X	Saturation pressures of dimethylboric anhydride-trimethylphosphine.	42
XI	60 Mc. nmr chemical shifts of some acid-base systems.	45
XII	Results of the variable temperature study on dimethylboric anhydride.	49
XIII	Results of the variable temperature study on the dimethylboric anhydride-trimethylamine system, 1:1 ratio.	52
XIV	Table of chemical shifts for dimethylboric anhydride-trimethylamine systems.	56
XV	Results of the variable temperature study on the dimethylboric anhydride-dimethylboron chloride system.	59

Table		Page
XVI	Saturation pressures of dimethylmethoxyboron-trimethylamine.	61
XVII	Effect of temperature upon the B-methyl resonance of dimethylmethoxyboron.	63
XVIII	Dissociation data for dimethylmethoxyboron-trimethylamine in solution.	70
XIX	Results of the variable temperature study of the trimethylboron-trimethylamine system.	74
XX	List of bulk susceptibility corrected shifts for the chloroform proton relative to the corrected shift of this proton in cyclohexane.	79
XXI	Association of dimethylboric acid in _n_-butane.	80

LIST OF FIGURES

Figure Page

1. Collection device for gas-liquid chromatographic system. Shaded section represents glass wool packing. Trap I is in "bypass" condition, while trap II is in "collecting" condition. 11

2. Gas phase infrared spectrum of dimethylboric anhydride. Full trace obtained from 16 mm sample pressure; inset from 4 mm sample pressure; cell length 5 cm. 32

3. The variation of the equilibrium constant with temperature for the gas phase dissociation of the dimethylboric anhydride-trimethylamine adduct. 40

4. Schematic representations of nmr spectra of dimethylboric anhydride and dimethylboric anhydride-trimethylamine systems at various temperatures. 46

5. Conformation of dimethylboric anhydride permitting maximum overlap of oxygen lone pairs (shaded) with vacant boron orbitals. 48

6. Temperature dependence of the reorientation rate constant ($1/2\tau$) for dimethylboric anhydride. 50

7. Temperature dependence of the rate constant ($1/2\tau$) for the exchange reaction between dimethylboric anhydride and trimethylamine. 53

Figure | Page

8. Temperature dependence of the rate constant (1/2τ) for the exchange reaction between dimethylboric anhydride and dimethylboron chloride. 60

9. Temperature dependence of the reorientation rate constant (1/2τ) for dimethylmethoxyboron showing combined results of two studies. Circles describe data obtained from a 15% solution in $CFCl_3$ and triangles a 30% solution in $CD_3C_6D_{11}$. 65

10. Temperature dependence of the chemical shifts for the proton resonances in the dimethylmethoxyboron-trimethylamine system in $CFCl_3$ solution. 67

11. Temperature dependence of the equilibrium constant for the dissociation of the dimethylmethoxyboron-trimethylamine adduct in a $CFCl_3$ solution. 71

12. Temperature dependence of the rate constant (1/2τ) for the exchange reaction between trimethylboron and trimethylamine. 75

13. Uncorrected dilution curves for chloroform in (A) $(CH_3)_2BOB(CH_3)_2$ (B) C_6H_{12} (C) $(CH_3)_2$-$BOCH_3$ (D) $CH_3B(OCH_3)_2$ (E) $B(OCH_3)_3$. 77

14. Chemical shift of the OH proton resonance *versus* mole fraction of dimethylboric acid in cyclohexane at 36°C. 82

Figure | Page

15. Chemical shift of the OH proton resonance *versus* temperature for a 1 mole % solution of dimethylboric acid in methylcyclohexane. Shifts relative to cyclohexane are calculated by subtracting 1.44 ppm from the chemical shift relative to tetramethylsilane (TMS). 83

16. Expanded infrared spectra of the OH stretching frequencies in dimethylboric acid. The upper spectrum was obtained from the gas phase; the lower from a 5-10% solution in CCl_4. 85

INTRODUCTION

Chapter 1

This chapter introduces the reader to the problems investigated, the experimental techniques used in this work, and the chemistry to which it is applied.

1. The Nature of the Trivalent Boron Compounds.

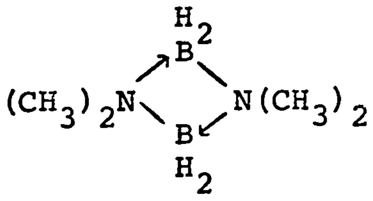
The field of boron chemistry is of such broad scope that only specific aspects will be briefly discussed in this section. The reader is referred to some excellent textbooks and review articles for a more complete description of the fundamentals of boron, its compounds and complexes (1,2,3).

Boron, a first period, group III element, is normally trivalent in its stable compounds, despite the $2s^2 2p$ electronic structure. This is because the total energy released in formation of three bonds in a BX_3 compound exceeds the energy of formation of one bond in a BX compound by more than enough to provide for promotion of boron to a hybridized valence state of the sp^2 type. Typical trivalent boron compounds, BX_3, are planar molecules with the substituents aligned at 120° angles about the central boron atom. In the case where substituents are not equivalent, the bond angles will be somewhat modified to suit the characteristics of the substituents. The B-X σ-bonding electrons are considered to occupy three equivalent sp^2-hybridized orbitals, leaving a vacant $2p_z$ orbital on the boron atom available for interaction with an appropriate electron pair of a donor atom, such as the nitrogen atom of an amine. In such a manner are complexes formed, and this donor-acceptor relationship is referred to as an acid-base reaction in the Lewis definition. It is, of course, recognized that such complexing involves some degree of rehybridization of the boron orbitals, so that the final result may approach sp^3-hybridization of the boron orbitals. An example of this type of complex is $H_3N \cdot BF_3$, first prepared by Gay-Lussac (4), almost 160 years ago. In modern times, interest in the physico-chemical studies of similar complexes has continued (1,2,3).

A second consequence of this vacant orbital on boron, is the formation of "electron deficient" molecules (5), such as B_2H_6, whose structure is considered to contain "three-center" bonds, each of which encloses one of the bridging hydrogen atoms, as well as the two boron atoms (6). Many higher hydrides, which also involve "three-center" bonds, are well characterized (3).

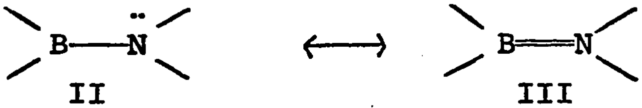
Yet a third manner of filling the vacant boron p_z orbital exists: the formation of inter- or intramolecular dative bonds. A classical example of the former is the compound $(CH_3)_2NBH_2$, which can form a dimer (I) via boron-

I



nitrogen coordinative linkages (7). Intermolecular dative bonds involving oxygen, rather than nitrogen, are known also, as for example in $F_2BOC_2H_5$, which is reported to form a trimer in the liquid phase (8).

Intramolecular dative bonding may arise when a filled hybrid orbital, such as the sp^3-hybridized lone pair of electrons on the nitrogen atom, interacts with the vacant p_z orbital of the boron atom, as in aminoborane compounds (II & III). Several examples of compounds containing this system have been studied using nmr techniques to observe and measure the barrier to internal rotation about the B-N bond (9-10). This barrier to rotation is attributed to boron-nitrogen π-bonding.

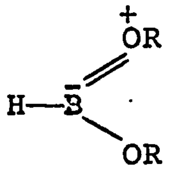


II III

In this thesis we are concerned with intramolecular dative bonding in the boron-oxygen bond. There has been a good deal of evidence in the literature supporting the same type interaction between oxygen and boron in compounds containing a boron-oxygen bond. Lewis and Smyth (13) have discussed the possibility of boron-oxygen π-bonding in the trialkyl borates. The results of their dipole moment studies on $(n\text{-}C_3H_7O)_3B$, $(i\text{-}C_4H_9O)_3B$ and $(s\text{-}C_4H_9O)_3B$ are inconclusive on this particular point, since the results of experiments are compatable with either the absence or presence of restricted rotation due to π-bonding.

Skinner and Smith (14), on the basis of thermochemical experiments on ethoxy-chloroboranes, discuss the results in terms of "π-conjugation" or "back donation" of electrons from oxygen to boron. They report that the "back donating" strength decreases in the series, N>O>>Cl.

Stone (15), in the discussion of $HB(OR)_2$, interprets the non-existence of association in this compound as due to resonance structures of the type (IV).



IV

Coulson and Dingle (16), in an M.O. study of planar boron-oxygen compounds find that the boron-oxygen bond length is well explained in terms of a π bond.

Generally, the existence of this phenomenon is much less firmly established than it is for the boron-nitrogen bond.

2. <u>The Compounds and Techniques.</u> Dimethylboric anhydride, $(CH_3)_2BOB(CH_3)_2$, is particularly interesting when viewed in terms of B-O interaction. The central skeleton of the compound, B-O-B, lends itself well to a study of

B-O π-bonding, since it could conceivably exhibit both Lewis acid or Lewis base character. In the former case, both mono- and di-adducts might be possible.

In this study, dimethylboric anhydride and its derivatives, dimethylalkoxyboron compounds, dimethylboric acid and dimethylboron chloride have been prepared and characterized when necessary. Sensitivity to air and high volatility required standard high vacuum techniques (17) for preparing and handling the compounds studied, while a tensimeter (18) was used for vapor phase equilibrium studies. Spectral methods, namely infrared, mass spectra and nuclear magnetic resonance were used for identification and characterization in this study. Variable temperature proton nmr proved to be a powerful tool in the study of dimethylboric anhydride, its complexes and its derivatives. Several nmr studies involving rate processes, such as exchange and hindered internal rotation, yielded a great deal of information, some of it quite novel.

3. <u>The Use of Nmr for Kinetic Studies.</u> The shape and width of nmr signals are affected by time dependent processes when the lifetime τ, of each species is of the order of $1/\delta\nu$, where $\delta\nu$ is the chemical shift between the interchanging groups. Exchange of the hydroxyl proton in alcohols, cis-trans isomerism in molecules with partial double bond character, and restricted rotation about a

single bond are examples of some rate processes amenable to nmr study. Several textbooks which describe the fundamental aspects and the applications of nmr are available (19,20,21,22).

To study rate processes, it is essential that the nuclei experience different magnetic environments in each species, such that different chemical shifts are observable for each when the interchange is sufficiently slow with respect to the critical rate, $1/\delta\nu$. For rapid processes, the signals then coalesce because of the time-average environment of the nuclei.

It can be shown (21, pp.222-224) that for an intermediate rate of exchange, the lifetime, τ, of a species, is related to the separation of signals under conditions of slow exchange as compared to the separation of the signals during conditions of intermediate exchange. A convenient form of the relation is $1/\tau = \sqrt{2}\pi[(\nu_A{}^\circ-\nu_B{}^\circ)^2-(\nu_A-\nu_B)^2]^{\frac{1}{2}}$, where $(\nu_A{}^\circ-\nu_B{}^\circ)$ represents the maximum separation of the signals under conditions of slow exchange and $(\nu_A-\nu_B)$ the separation at intermediate exchange rates. Thus from measurement of the separation of the signal maxima during intermediate exchange rates, the lifetimes, τ, of the species can be calculated.

The lifetime of a species is related to the rate constant, $k=1/2\tau$; therefore by measuring the temperature dependence of the lifetime, τ, one can apply the Eyring equation (23)

$$\ln k = \ln\left(\frac{\kappa}{h}\, e^{\Delta S^{\ddagger}/R}\right) + \ln T - \frac{\Delta H^{\ddagger}}{RT}$$

where k is the rate constant, κ is the Boltzmann constant, h is Planck's constant, $\Delta S^{\ddagger}$ is the entropy of activation and $\Delta H^{\ddagger}$ is the enthalpy of activation. In practice, the equation is used in the form

$$\log 1/2\pi\tau(\nu_A-\nu_B)T = 10.318/\log\pi(\nu_A^{\circ}-\nu_B^{\circ}) + \Delta S^{\ddagger}/2.3R-\Delta H^{\ddagger}/2.3RT,$$

from which the entropy and enthalpy of activation are readily calculated.

4. <u>Outline of Study.</u> This thesis deals with the preparation and characterization of dimethylboric anhydride, as well as complex formation and spectral studies, since the only reported preparation and characterization (24) proved to be unsatisfactory. Preparations of some derivatives of the anhydride, such as dimethylalkoxyboron compounds, $(CH_3)_2BOR$, and dimethylboric acid, $(CH_3)_2BOH$, are described in detail, as the routes used are different to those reported in the literature (25,26,27).

Experimental work was directed towards elucidating the interaction of oxygen lone pair electrons with the vacant p_z orbital on the boron atom, and the results are discussed in terms of this interaction, which, for convenience, will be referred to as partial π-bonding or simply "π-bonding".

APPARATUS, PREPARATIONS AND ANALYSES

Chapter II

This chapter describes the apparatus, the preparation of compounds, the spectroscopic methods and the statistical analysis used to present the results of the following chapter.

1. Description of Apparatus. All syntheses, purifications and characterizations were carried out using high vacuum techniques. The high vacuum apparatus and technical methods used in this work were essentially the same as those described by Stock (17), except for the tensimeter and the gas-liquid chromatography system which shall be described in full detail.

Various sections of the vacuum system, used for measuring the volumes of gaseous samples, were calibrated with chlorotrifluoroethylene, which was chosen for its relatively high molecular weight (116.48) and the large vapor pressure at 25°C (2.47 atm.). Calibration was effected by weighing a quantity of this gas in a Pyrex vessel of accurately known volume followed by introducing the gas into the various sections of the system to be calibrated, then measuring the pressure manometrically in each case. Volume corrections for the variation of the mercury level in the manometer were made on the basis of the known internal diameter of the manometer tubing.

The tensimeter and its uses have been described in detail by Burg and Schlesinger (18). In this work, the tensimeter was connected to the high vacuum system *via* a mercury float valve. The volume of the tensimeter was measured in the manner described previously.

Low temperature vapor pressure studies of various systems involved the use of appropriate slush baths. Temperatures above the ambient were attained by means of an insulated water bath controlled with a Sargent Thermonitor, Model T, with two 250 watt blade-type heating elements, and a Sargent medium range thermistor, S-81625, with a temperature range from +40° to +130°C. The insulated water bath contained plate glass windows so that the levels of the mercury could be measured with a cathetometer which could be read to 0.01 mm. Temperature control was accurate to within ±0.5°C between +40° and +80°C, the limits used in this work.

The gas-liquid chromatography system comprised a Gow-Mac stainless steel gas-density thermistor detector Model #140, used in conjunction with a Gow-Mac power supply #9999 and a Sargent recorder, model SR. The sample introduction system, connected to the high vacuum apparatus by means of a Fischer and Porter Teflon valve, was operated by a pair of 3-way valves (Hoke, C-415K). Nitrogen carrier gas was rerouted through the introduction system by simultaneously closing a by-pass 2-way valve (Hoke, C-413K) and opening both 3-way valves. Good separation characteristics were found for a 10-foot, 7-mm i.d. column, packed with 30-60 mesh Celite and containing 20% by weight of Fisher paraffin oil. Purified samples were collected in two U-traps lightly packed with glass wool, through which the effluent gases could be directed by means of 3-way stopcocks, and frozen out at liquid nitrogen temperatures. (See Figure 1). The nitrogen carrier gas flow rate was 80 ml/minute for the carrier stream and 100 ml/minute for the reference stream, operating at 20 psi.

The use of the gas density balance for determining molecular weights and % compositions of mixtures has been adequately described in the literature (28,29,30,31), therefore no details on the use are offered.

2. <u>Infrared Spectra.</u> All infrared measurements were done on a Perkin-Elmer Model 421 grating spectrophotometer operating at ambient temperature. A 5-cm gas cell having potassium bromide windows was used with pressures ranging between 4 and 50 mm. For solution spectra, a standard 0.1 mm solution cell was used.

3. <u>Mass Spectra</u>. All mass spectra were recorded on AEI MS-2 or MS-9 instruments operating at ionizing voltages of

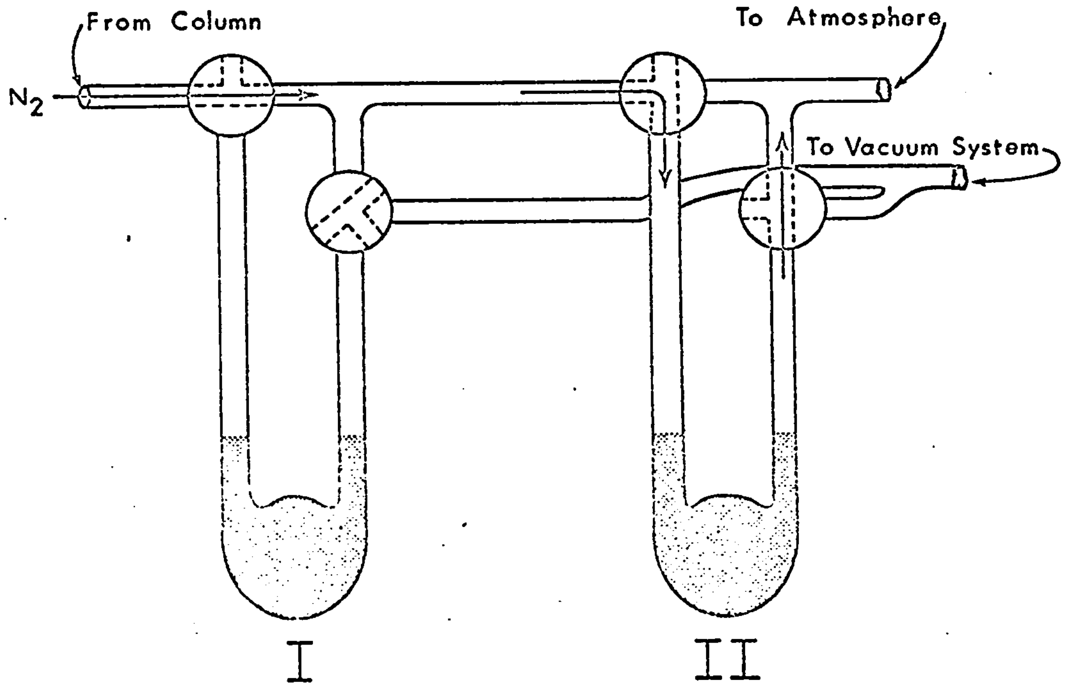


FIGURE 1 Collection device for gas-liquid chromatographic system. Shaded section represents glass wool packing. Trap I is in "bypass" condition, while trap II is in "collecting" condition.

70 ev. Precise mass measurements were carried out at high resolution on the MS-9 instrument. Since the compounds studied are gaseous, or at least quite volatile, a room temperature inlet was used, the samples having been prepared in a sealed tube under vacuum.

4. <u>Nmr Spectra.</u> Three instruments, a Varian A-60, a Varian A-56/60 and a Varian HA-100 were used in this study; the latter two instruments were equipped with variable temperature probes.

Samples were prepared under vacuum by distilling measured gas volumes of the sample, the reference, and the solvent into nmr tubes, which were then sealed off. All samples involved the use of 5 mm o.d. medium wall sample tubes which were lightly flamed to remove water.

Due to difficulties involving solubilities, freezing points, overlapping resonances and association of sample and solvent, it was necessary to use a variety of solvents and references in this study. However, all line positions will be reported in parts per million (ppm), relative to a specific internal standard, or when more convenient, in cycles per second (cps), as in the case of peak separation in exchange studies.

The low temperature system on the 100 Mc instrument comprised a V-4333 variable temperature probe used in conjunction with a V-6040 controller. This system is designed to control the temperature variation at any given setting to ± 1°C (32). The temperature of the samples was monitored by means of a capillary of methanol enclosed in the sample tube. The variation of the chemical shift difference between the OH resonance and the CH_3 provided the means of temperature measurement (33).

In low temperature studies used for calculating activation data, all chemical shifts were measured with a Hewlitt-Packard Electronic Counter, Model 3735 A.

The 60 Mc instrument was used for ambient temperature spectra because of the convenience of operation. The HA system "locks" on to an external reference (water), so that only one sweep is necessary for each spectrum. The signal positions are then measured with respect to the internal reference signal. All 60 Mc spectra were run by the technical staff of the Department of Chemistry with the exception of some which were run by Dr. M. G. Hogben and Mr. Andrew J. Oliver.

Temperature studies were carried out on the 100 Mc instrument operating on HA frequency sweep mode. In this case, the spectra were scanned on fast sweep to locate the signals, then the circuit was "locked" onto the internal reference signal. Best resolution was found by "shimming" with the fine tune controls until a maximum signal was observed. In variable temperature studies, it was found that a fifteen minute interval was required for the instrument to stabilize after the temperature was changed. Varying sweep widths and sweep times were utilized to obtain maximum accuracy. This instrument was operated by the author.

5. Preparation of Compounds. Preliminary experiments for the preparation of dimethylboron chloride involved reacting tetramethyltin and boron trichloride, in varying ratios, for two hours at 100°C in a 1000 cc Pyrex vessel. On cooling, the gaseous products were distilled into the

$$(CH_3)_4Sn + BCl_3 \rightarrow (CH_3)_{4-n}SnCl_n + (CH_3)_nBCl_{3-n}$$

vacuum system and analyzed, using chromatographic techniques (28,29,30,31). The tin-containing materials remaining in the vessel were dissolved in carbon tetrachloride and analyzed using nmr techniques. The results are listed in Table I. As previous reports indicated (34,35), in no cases did tin lose more than two methyl groups. Under more vigorous conditions, e.g. 140°C for 12 hours, this was also found to be the case.

Dimethylboron chloride, the basic starting material for the compounds studied in this work, was prepared by reacting equimolar quantities of boron trichloride (Matheson of Canada, Ltd. C.P. grade) with tetramethyltin (M and T Chemicals, Inc.) in a stainless steel Hoke cylinder at 140°C for 12 to 15 hours. While this method of preparation of alkyl

TABLE I

Preliminary Study of the $(CH_3)_4Sn$-BCl_3 Reaction

Reaction Conditions	Reagents (millimoles)		Products [a] (millimoles)						
	$(CH_3)_4Sn$	BCl_3	HCl	$(CH_3)_3B$	$(CH_3)_2BCl$	CH_3BCl_2	$(CH_3)_4Sn$	$(CH_3)_3SnCl$	$(CH_3)_2SnCl_2$
1000 cc Pyrex Vessel 100°C 2 Hours	5.10	5.08	0.58	----	1.18	3.69	----	0.92	4.17
	7.33	3.71	0.47	----	2.54	1.10	0.96	6.37	----
	11.15	3.71	0.31	0.05	3.35	----	3.46	7.70	----
300 cc Stainless Steel Cylinder 120°C 9 Hours	3.46	3.45	<0.02	<0.02	3.40	----	----	----	3.46[b]

[a] The dashes represent yields of less than 0.01 millimoles.

[b] The product was not weighed. Nmr showed only $(CH_3)_2SnCl_2$ to be present, and the yield is considered to be *ca* 100%.

boron halides was first reported in 1960 by Brinckman and Stone (34), there are no reports in the literature using these reaction conditions which give improved yields.

The typical experiment was carried out in a 300 ml stainless steel Hoke cylinder using quantities in the order of 35 millimoles of each reactant. The products were distilled into the vacuum system and analyzed, using chromatography. The crude gaseous product contained, on the average, 95% dimethylboron chloride with the remainder being varying quantities of trimethylboron, methylboron dichloride and some hydrogen chloride. Purification by standard trap to trap distillation was not very effective because of the similarity in vapor pressures of the three boron-containing compounds. Chromatography and collection of crude dimethylboron chloride gave on the average a 75% yield of chromatographically pure product which exhibited a vapor pressure of 684 mm at 0°C. (Literature (36) 685 mm at 0°C). The material was then kept in a 2-liter Pyrex storage vessel until required. Due to the possibility of exchange, the purity was always checked chromatographically before use and, if necessary the compound was purified again.

A similar preparation was used for <u>trimethylboron</u>; in this case three moles of tetramethyltin reacted with two moles of boron trichloride. The crude gaseous products

$$3(CH_3)_4Sn + 2BCl_3 \rightarrow 3(CH_3)_2SnCl_2 + 2(CH_3)_3B$$

contained more than 95% trimethylboron; the remainder was dimethylboron chloride and small quantities of HCl (≃ 1%). Again, purification was carried out chromatographically. The purified material exhibited at vapor pressure of 85.5 mm at -63.5°C (Literature (37) 85.6 mm at -63.5°C).

Repeating McKennon's (24) preparation of dimethylboric anhydride, which involved the dehydration of dimethylboric acid with phosphorus pentoxide, yielded gaseous

$$2(CH_3)_2BOH + P_2O_5 \rightarrow (CH_3)_2BOB(CH_3)_2 + 2HPO_3$$

products which exhibited vapor pressures ranging from 100 to 140 mm at 0°C. (McKennon, 118 mm at 0°C). In only one experiment did the vapor pressure of the product, 119 mm at 0°C, agree with McKennon's work. In all experiments, chromatography showed two major products. Infrared spectra revealed the presence of dimethylboric acid as the contaminant. A method used for the preparation of diphenylboric anhydride (38) and di-n-butylboric anhydride (39) involving the limited hydrolysis of dimethylboron chloride,

$$2(CH_3)_2BCl + H_2O \rightarrow (CH_3)_2BOB(CH_3)_2 + 2HCl$$

was successful and reproducible.

An appropriate quantity of water was placed in a Pyrex reaction vessel using a syringe. The vessel was then cooled to -196° with liquid nitrogen, and evacuated. Dimethylboron chloride was distilled in, and upon warming, the materials reacted. Repeated condensation and re-warming facilitated complete mixing of the two phases. Purification was best carried out by initial trap to trap distillation through a -78.5°C trap to remove hydrogen chloride, followed by sublimation of the material from a cold trap (allowed to warm from -196°C to room temperature by simply removing the liquid nitrogen) into a -78.5° trap, through which traces of more volatile materials readily passed. This procedure yielded a gaseous product, of molecular weight 97.5 as determined by the gas density method, having a vapor pressure of 150 mm at 0°C. The yield of both hydrogen chloride and dimethylboric anhydride was essentially quantitative; however, after rigorous purification, a yield of ca 85% was realized. The material was identified by mass spectra, nmr, ir and molecular weight determination.

Dimethylboric acid has been prepared by the hydrolysis of dimethyldiborane (40) and by the hydrolysis of trimethylboron at 200°C (27). Rather than use these elaborate methods, dimethylboric acid was prepared by hydrolyzing dimethylboron chloride, or dimethylboric anhydride. In

$$(CH_3)_2BCl + H_2O \rightarrow (CH_3)_2BOH + HCl$$

$$(CH_3)_2BOB(CH_3)_2 + H_2O \rightarrow 2(CH_3)_2BOH$$

either case, a stoichiometric quantity of water was placed in a Pyrex vessel. The vessel was then cooled to -196°C and evacuated, after which the chloride or anhydride was distilled in. Upon warming, the reaction went rapidly to completion. In the first instance, the products were hydrogen chloride and dimethylboric acid; in the second instance, only the acid was present. Purification, in both cases was effected by distillation through traps at -45°, -78° and -196°C. The pure dimethylboric acid, exhibiting a vapor pressure of 36 mm at 0°C (Literature (41), 36 mm at 0.4°C), was retained at -78°C. The identity of the compound was confirmed by the infrared spectra.

Dimethylmethoxyboron has been prepared by several routes (25,26,44). The method used in this study, the methanolysis of dimethylboron chloride, has not been

$$(CH_3)_2BCl + CH_3OH \rightarrow (CH_3)_2BOCH_3 + HCl$$

reported, although the method has been applied to diphenyl- and di-n-butylboron chlorides (38,39). The techniques used in the preparation of dimethylmethoxyboron were similar to those mentioned for hydrolysis of dimethylboron chloride, except that methanol was substituted for water. Chromatography showed the presence of two components in the reaction products, identified as hydrogen chloride and dimethylmethoxyboron, indicating completion of the reaction. Purification was carried out by chromatography affording a product exhibiting a vapor pressure of 90.8 mm at -22.4°C (Literature 89.0 mm at -22.4°C (42), 94.4 mm at-22.4°C (43) in yields of ca 75%. The molecular weight was determined to be 70.8 (calculated, 71.91) using the gas density method. Identification of the compound involved mass spectra, nmr, vapor pressure measurement and the molecular weight determination.

Dimethylpentafluorophenoxyboron was prepared by reacting pentafluorophenol and dimethylboron chloride in a Pyrex vessel. Pentafluorophenol (4.0 millimoles) was

$$(CH_3)_2BCl + C_6F_5OH \rightarrow (CH_3)_2BOC_6F_5 + HCl$$

weighed, and transferred to a 50 ml heavy walled Pyrex vessel. After cooling to -196°C, the vessel was evacuated and dimethylboron chloride (4.0 millimoles) was added. The vessel was closed and allowed to come to room temperature, then warmed to 50°C for 5 minutes. The vessel was then opened to the vacuum system and the products distilled through -78° into a -196°C trap, while a viscous liquid remained in the reaction vessel. The -196°C fraction contained 4.0 millimoles of hydrogen chloride indicating completion of the reaction. The -78°C fraction was distilled into a -22°C trap where it was completely retained. A mass spectrum of the compound showed molecular ions at 223 and 224 m/e (Intensity 6.5 and 27.3% of base peak at 41 m/e) whose ratio of intensities was close to the ratio of abundances found at 10 and 11 m/e for B^{10} and B^{11}. A microanalysis (A. Bernhardt 15522/67) of the compound showed 42.8% carbon and 3.10% hydrogen (calculated for $C_8H_6F_5BO$: C, 42.91; H, 2.70). The yield of this reaction is estimated to be in the order of 50 to 70%. The viscous material remaining in the reaction vessel was not identified.

Dimethyl-t-butoxyboron was prepared by reacting the dimethylboron chloride-trimethylamine adduct with t-butanol in the solvent xylene. A Pyrex reaction vessel, capacity

$$(CH_3)_2ClB\cdot N(CH_3)_2 + (CH_3)_3COH \xrightarrow{\text{solvent}} (CH_3)_2BOC(CH_3)_3 + (CH_3)_3NH^+Cl^-$$

50 ml containing ca 7 ml of xylene and 11.7 millimoles (0.868 gms) of t-butanol was cooled to -196° and evacuated, after which 11.7 millimoles of dimethylboron chloride and the same quantity of trimethylamine were distilled in. Upon warming, the dimethylboron chloride-trimethylamine adduct formed, as evidenced by a white, lumpy, insoluble powder on the walls of the vessel. On warming to 50° and shaking, the appearance changed suddenly. The white, lumpy powder on the walls became a very finely divided suspension in the solvent. The vessel was then opened to the vacuum system. A white powder was left behind in the reaction vessel. The volatile products were distilled through a -22°C trap to remove the xylene solvent, the more volatile materials being collected at -196°C. Chromatography showed the presence of four materials. The products were separated chromatographically and identified by ir, nmr and molecular weight determinations. The com-

ponents were identified as isobutylene (M.W. Found, 56.8, Calculated, 56.1), t-butyl chloride (M.W. Found, 92.8, Calculated, 92.6), dimethylboric acid (identified by ir), and dimethyl-t-butoxyboron (identified by mass spectrum and nmr). The separation of these components by chromatography was poor, therefore it was necessary to re-chromatograph the collected components to ensure purity, particularly the dimethyl-t-butoxyboron. The final yield of pure dimethyl-t-butoxyboron was ca 15%. Due to the small amount obtained, no vapor pressure studies were carried out.

Trimethylphosphine was prepared and purified as described by Thomas and Eriks (45). The purified compound exhibited a vapor pressure of 158 mm at 0°C (Literature (45) 158.5 mm at 0°C). All commercially available compounds used in this study were purified by either chromatography or trap-to-trap distillation, where applicable. Aside from chromatography, vapor pressure measurements were used as an index of purity and the measured values agreed well with values reported in the literature. As an indication of purity of the compounds used in this work, the vapor pressures at specific temperatures are listed, along with the literature values: trimethylamine, 681 mm at 0°C (Literature (46) 681.7 at 0°C); dimethyl ether, 33.8 mm at -78.5°C (Literature (47) 34.4 mm at -78.5°C); and dimethyl sulfide, 166.8 mm at 0°C (Literature (48) 167 mm at 0°C).

6. <u>Statistical Treatment of Data</u>. The sets of data obtained from experimental results were subjected to a simple regression treatment using a computer program (49). The program is reproduced in Appendix A. This program treats one variable as being determinable to so high a degree of precision that its uncertainty can be ignored; in this work that variable was taken to be the reciprocal of the temperature, 1/T. The data are fitted to the straight line $y=A + Bx$ where A is the intercept and B is the slope, or coefficient of regression of y on x. The procedure fits the best straight line to the data by the method of least squares (50). The deviation from the line is measured in the y-direction, since the error of x is insignificant. Three quantities are reported for each least mean square analysis, which determine, <u>statistically,</u> the validity of the data.

The "coefficient of correlation", r, is defined by Spiegel as "the ratio of the explained variation to the total variation" (51). STATPACK 1 determines r from the relation

$$r = \frac{\Sigma(x-\bar{x})(y-\bar{y})}{[\Sigma(x-\bar{x})^2\Sigma(y-\bar{y})^2]^{\frac{1}{2}}}$$

which is known as the product-moment formula. As the standard texts in statistical analysis (50,51,52,53) show, the correlation coefficient will range from plus or minus unity, the value for a perfect straight line, to zero, the value if there is no correlation whatsoever. In this work, r^2 will be quoted since departure from unity is then more noticeable.

The correlation coefficient is useful since tables are available (Appendix B) whereby for a given number of observations, the probability can be calculated that this correlation coefficient could have been derived in a random manner. If the probability is under 1%, then the trend is highly significant.

The "standard error of estimate", $s_{y,x}$, determined by the relation

$$s_{y,x} = \left(\frac{N}{N-2}\right)^{\frac{1}{2}} s_y (1-r^2)^{\frac{1}{2}}$$

which is a modified version for small samples (54). The standard error of estimate is sometimes referred to as a <u>confidence level</u> (55), and has properties analogous to those of the standard deviation. The standard error of estimate is a value, in the same units as the y-coordinate (in this work), which describes the plus or minus limits from the regression line, in which we would expect to find 68% of the sample points, provided N, the sample size, were large enough. Therefore, $s_{y,x}$ is indicative of the amount of scatter in the observed points, which is directly related to the precision.

In keeping with present literature the data will be reported to a confidence level of 95%. To rephrase, we are 95% confident that the values for $\Delta H°$ and $\Delta H^{\ddagger}$, which are calculated from the regression coefficient B, lie within the reported limits.

The calculation involves the "Student t distribution" (56). By applying the relation

$$\varepsilon_b = \pm \frac{t}{(N-2)^{\frac{1}{2}}} \left(\frac{s_{y,x}}{s_x}\right)$$

(where ε_b are the appropriate limits to be calculated, N is the number of observations, $s_{y,x}$ is the standard error of estimate, s_x is the standard deviation of the independent variable (1/T), and t is a coefficient dependent upon the number of observations and the confidence limits required), we obtain values which represent the required 95% confidence limits. Tables are available (Appendix C) whereby for a given number of observations and a given confidence level, the coefficient, t, can be found.

It is well to remind the reader that statistical treatment can be applied only to random errors, those errors which cause a lowering of reproducibility. These errors are brought about by the effects of uncontrolled variables, and are as likely to cause high results as low results.

Determinate errors, those assigned to definite causes, are usually unidirectional. In this study, the most serious source of a determinate error would arise from incomplete equilibration of the sample after a temperature change had been carried out. To counteract this possibility, the data were collected in two series, one with increasing and the other with decreasing temperature. Other sources include the reading of manometers, measuring nmr signal separations and in general, observational information. These errors cause a loss of accuracy, therefore efforts were made to avoid personal bias when undertaking measurements.

EXPERIMENTAL RESULTS

Chapter III

This chapter describes, in detail, the experiments and the experimental results. The data compiled will be discussed in the following chapter.

1. The Characterization of Dimethylboric Anhydride. Dimethylboric anhydride as prepared and purified in this study was found to have a molecular weight of 97.5 using the gas density method (calculated 97.72). The vapor pressure of the liquid was measured at several temperatures between -20.2°C and +10.0°C, with results as given in Table II. Values calculated using the least square equation $\log P_{liq} = 8.459 - 1718/T$ are also given in Table II. From the equation, the heat of vaporization is calculated as 7.86 kcals., the boiling point +34.8°C, and the Trouton constant 25.5. The melting point is -21.2°C using the magnetic plunger method of Stock (17). The vapor pressure of the solid material was determined at three temperatures as shown in Table II. These values determine the equation $\log P_{solid} = 13.63 - 3028/T$, from which the heat of sublimation is calculated to be 13.9 kcals.

Mass spectral data are reported in Table III. While the molecular ion is too weak for a mass determination at high resolution, the fragment at 83 m/e was shown in this

TABLE II

Vapor Pressure Data for Dimethylboric Anhydride

	Liquid							Solid		
Temp. °C.	+10.0	+8.0	+5.5	0.0	-7.0	-15.0	-20.2	-22.9	-35.0	-45.3
Press. (obs.) mm.	244.0	224.6	195.9	150.0	102.4	63.2	46.3	33.6	8.0	2.3
Press. (calc.) mm.	247.2	223.9	197.2	148.3	101.2	63.8	46.6	34.2	8.3	2.2

TABLE III

Mass Spectrum of Dimethylboric Anhydride[a]

m/e	Ion	I,%[b]	m/e	Ion	I,%[b]
10	B^{10}	0.3	40	$C_2H_6B^{10}$	27.0
11	B^{11}	1.1	41	$C_2H_6B^{11}$	85.0
13	CH	1.3	42	$CH_4B^{10}O$	31.3
15	CH_3	5.8	43[c]	$CH_4B^{11}O$	100
25	CH_2B^{11}	1.1	44	$C^{13}H_4B^{11}O$	1.6
26	$C_2H_2,B^{10}O$	1.8	51	$CH_3B^{10}B^{10}O$	0.3
26.5[e]	$CH_3B^{11}B^{11}O$	0.1	52	$CH_3B^{10}B^{11}O$	0.5
27	$B^{10}OH,B^{11}O,$	2.8	53	$CH_3B^{11}B^{11}O$	1.1
28	$B^{11}OH$	3.3	57	$C_2H_7B^{10}O$	0.4
29	C_2H_5	4.0	58	$C_2H_7B^{11}O$	1.6
33[e]	$C_2H_6B^{10}B^{10}O$	1.3	81	$C_3H_9B^{10}B^{10}O$	3.0
33.5[e]	$C_2H_6B^{10}B^{11}O$	4.0	82	$C_3H_9B^{10}B^{11}O$	21.3
34[e]	$C_2H_6B^{11}B^{11}O$	4.2	83[d]	$C_3H_9B^{11}B^{11}O$	42.3
34.5[e]	$C^{13}CH_6B^{11}B^{11}O$	0.1	84	$C^{13}C_2H_9B^{11}B^{11}O$	1.5
36	$C_2H_2B^{10}$	1.2	96	$C_4H_{12}B^{10}B^{10}O$	≈0
37	$C_2H_2B^{11}$	3.8	97	$C_4H_{12}B^{10}B^{11}O$	≈0
38	$CB^{10}O,$	2.5	98	$C_4H_{12}B^{10}B^{11}O$	0.1
39	$CB^{11}O$	8.3			

[a] Peaks of less than 1% of the base peak are not listed unless considered pertinent.

[b] % intensity relative to the base peak.

[c] Exact mass calcd, 43.0355; found, 43.0351

[d] Exact mass calcd, 83.0839; found, 83.0840.

[e] Doubly charged ion.

way to be $C_3H_9B_2{}^{11}O$. The observed and calculated masses differ by less than 1 ppm.

Infrared data are reported in Table IV, where tentative assignments have been made as discussed later. Figure 2 is a reproduction of the spectrum.

The ambient temperature proton nmr spectrum of dimethylboric anhydride in CS_2, $CHCl_3$, $CFCl_3$ and C_7D_{14} consisted of a single broad resonance (half width ca 3.5 cps) 0.43 ppm downfield from TMS. Varying the concentration between 2 and 20 mole % did not affect the chemical shift.

2. Results of Other Preparations. Dimethylmethoxyboron was identified using vacuum and spectral techniques. A gas density molecular weight determination yielded a value of 70.8 gms/mole (theoretical, 71.34). The vapor pressure at -22.4°C was 90.8 mm (Literature (42,43), 89.0 mm at -22.4°C; 94.4 mm at -22.4°C). The ambient temperature nmr spectrum consisted of two resonances at 3.65 and 0.34 ppm downfield from TMS which integrated in a 1:2 ratio and are assigned to OCH_3 and $B(CH_3)_2$ respectively. Mass spectral data were consistent with that expected for dimethylmethoxyboron, as shown in Table V.

Dimethylpentafluorophenoxyboron was identified by microanalysis, mass spectrum and nmr.

TABLE IV

Vibrational Frequencies and Suggested Assignments for Dimethylboric Anhydride[a]

cm^{-1}	suggested assignments
2990 m ca 2920 sh	C-H sym. and asym.
1405 vsb[b]	CH_3 def. asym. B-O asym. B-O sym.
1320 vs	CH_3 def. sym.
1165 sh	CH_3 rock
1135 s	B-C asym.
940 m	CH_3 rock
730 w	B-C sym.

[a] Abbreviations:
w = weak, m = medium,
s = strong, v = very,
b = broad, sh = shoulder

Spectra taken in the gas phase at 4 mm and 16 mm pressure in a 5 cm cell.

[b] Approximate half-width at 16 mm is 200 cm^{-1}.

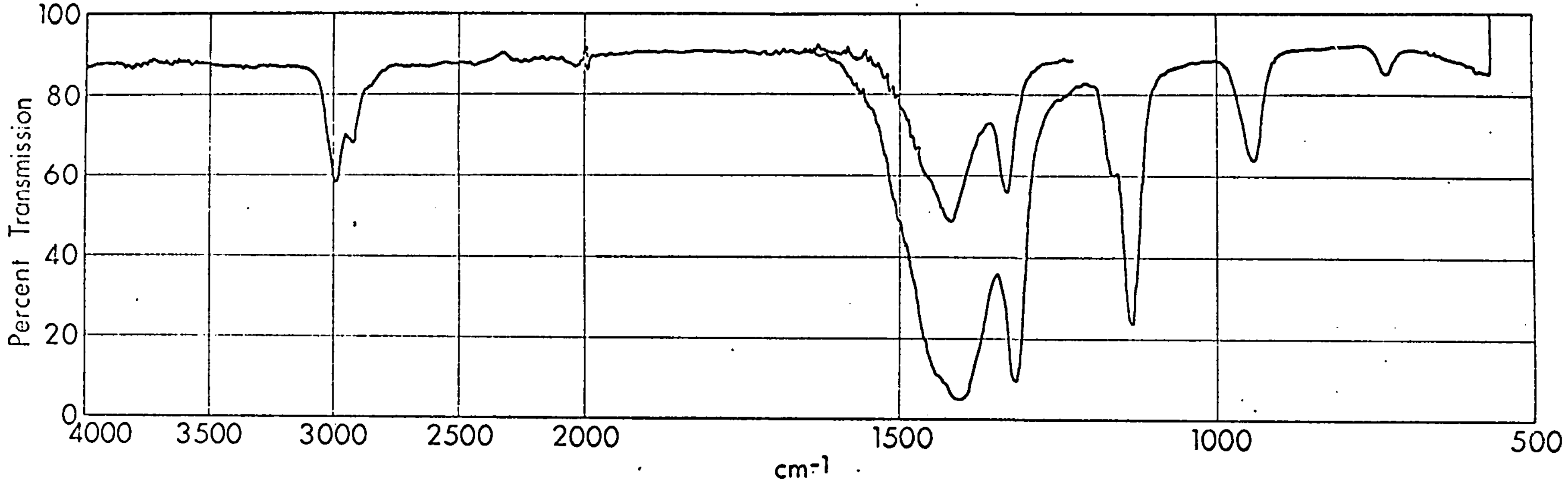


FIGURE 2. Gas phase infrared spectrum of dimethylboric anhydride. Full trace obtained from 16 mm sample pressure; inset from 4 mm sample pressure; cell length 5 cm.

TABLE V

Abbreviated Mass Spectral Data for Dimethylmethoxyboron

m/e	Ion [a]	I, % [b]
15	CH_3	53.3
28	$B^{11}OH$	5.6
29	C_2H_5	13.3
31	OCH_3	4.3
40	$C_2H_6B^{10}$	2.9
41	$C_2H_6B^{11}$	6.0
42	$CH_4B^{10}O$	5.3
43 [c]	$CH_4B^{11}O$	14.0
56	$C_2H_6B^{10}O$	25.5
57 [d]	$C_2H_6B^{11}O$	100
71	$C_3H_9B^{10}O$	≈0
72	$C_3H_9B^{11}O, C_2H_6B^{10}O_2$	<1.0
73 [e]	$C_2H_6B^{11}O_2$	3.0

[a] Suggested assignments.

[b] Intensity relative to the base peak.

[c] Exact mass calcd, 43.0355; found, 43.0351.

[d] Exact mass calcd, 57.0512; found, 57.0516.

[e] Exact mass calcd, 73.0459; found, 73.0460.

Anal. Calcd for $C_8H_6BOF_5$: C, 42.91; H, 2.70

Found: C, 42.08; H, 3.10.

The mass spectrum exhibited fragments appropriate to $(CH_3)_2BOC_6F_5$ as shown in Table VI, while the ambient temperature nmr spectrum exhibited a single proton resonance 0.55 ppm downfield from TMS.

Dimethyl-t-butoxyboron was characterized by mass spectral results which are listed in Table VII and are consistent with the compound. The nmr spectrum consisted of two resonances at 1.36 and 0.37 ppm downfield from TMS which integrated in a 3:2 ratio and which are assigned to $C(CH_3)_3$ and $B(CH_3)_2$ respectively.

3. Complex Formation with Diemthylboric Anhydride

Dimethylboric Anhydride-trimethylamine. A 9.7 cc[1] sample of dimethylboric anhydride, when treated with a carefully matched volume of trimethylamine, resulted in the formation of liquid, presumably the result of complex formation by the equilibrium

$$(CH_3)_2BOB(CH_3)_2\cdot N(CH_3)_3 \rightleftarrows (CH_3)_2BOB(CH_3)_2 + N(CH_3)_3.$$

---

[1] The abbreviation cc in this section refers to gas volumes at S.T.P. Pressures were measured using a cathetometer reading to 0.01 mm and errors in the calculated volumes are considered to be about 1%.

TABLE VI

Abbreviated Mass Spectral Data for Dimethylpentafluorophenoxyboron

m/e	Ion[a]	I, %[b]	m/e	Ion[a]	I, %[b]
15	CH_3	15.5	93	C_3F_3	14.2
31	CF,OCH_3	25.2	113	$C_5F_2CH_3$	28.5
38	COB^{10}	5.7	117	C_5F_3	39.2
39	$C_2H_6B^{11}$	18.8	136	C_5F_4	18.4
40	$C_2H_6B^{10}$	33.1	145	C_6F_3O	11.0
41	$C_2H_6B^{11}$	100	163	$C_6F_4CH_3$	44.3
42	$CH_4B^{10}O$	22.7	184	C_6F_5HO	12.7
43	$CH_4B^{11}O$	70.5	208	$CH_3B^{10}OC_6F_5$	3.6
44	$CH_3B^{10}F$	25.6	209	$CH_3B^{11}OC_6F_5$	14.5
45	$CH_3B^{11}F$	84.1	223	$(CH_3)_2B^{10}OC_6F_5$	6.5
63	C_2F_2H	18.1	224	$(CH_3)_2B^{11}OC_6F_5$	27.3
69	CF_3	10.1			

[a] Suggested assignments.

[b] Intensity relative to base peak.

TABLE VII

Abbreviated[a] Mass Spectrum of Dimethyl-t-butoxyboron

m/e	Ion[b]	I, %[c]
15	CH_3	9.3
27	$B^{11}O, CH_4B^{11}$	7.4
28	C_2H_4	8.7
29	C_2H_5	19.5
38	$B^{10}OC$	3.2
39	$B^{11}OC$	12.8
40	$C_2H_6B^{10}$	14.9
41	$C_2H_6B^{11}, C_3H_5$	85.9
42	$C_3H_6, CH_4B^{10}O$	15.4
43	$C_3H_7, CH_4B^{11}O$	10.7
57	C_4H_9	100
59	C_3H_7O	37.1
98	$C_5H_{12}B^{10}O$	5.1
99	$C_5H_{12}B^{11}O$	20.5
113	molecular ions	≃0
114		≃0

[a] Peaks of greater than 5% of the base peak.

[b] Suggested assignments.

[c] Intensity relative to the base peak.

TABLE VIII

Saturation Pressures of Dimethylboric Anhydride-Trimethylamine

Temp. °C	24.6	28.3	34.6	36.3	42.5	44.8	54.3	58.3
P_{mm} (obsd.)	9.6	12.4	19.2	21.4	32.0	37.7	69.3	87.4
P_{mm}[a] (calcd)	9.5	12.5	19.4	21.7	32.8	38.0	68.9	87.4

a. Calculated from $\log P_{mm} = 10.43 - 2816/T$

The saturation pressures in Table VIII correspond to the equation log P_{mm} = 10.43 - 2816/T, implying a "boiling point" of 99.5°C and a Trouton constant of 34.6.

The 1:1 adduct (4.5 cc) was treated with an additional 4.5 cc of trimethylamine. After standing fifteen hours at -78.5°C, 4.5 cc of trimethylamine were recovered by distillation into a -196° trap, while the sample was kept at -78.5°C; this indicates that a 2:1 complex, if it does exist at this temperature, is very weak.

The above equilibrium was studied in the gas phase using a sample prepared by treating 2.7 cc of dimethylboric anhydride with a matched volume of trimethylamine. In the temperature range 47 to 72°C, dissociation ranged from 72 to 85%. The variation of pressure with temperature, and derived data are recorded in Table IX and illustrated in Figure 3. A check of the dissociation pressures as the sample was cooled showed that no decomposition had taken place. Variation of the equilibrium constant with temperature is represented by the equation log K_p(atm) = 5.007 - 2073/T; values for the standard error of estimate, $S_{y,x}$, and r^2, are 0.0121 and 0.994 respectively. Therefore, for the above reaction, the enthalpy and entropy of dissociation are calculated to be: $\Delta H° = 9.5 \pm 0.6$ kcals and $\Delta S° = +22.9$ e.u.

TABLE IX

Gas Phase Dissociation Dimethylboric Anhydride-Trimethylamine

temp °C	P_{mm} (obsd.)	P_{mm} (calcd.)^{a}	α	K_p (atm) ^{b}	K_p(atm) (calcd.)^{c}
47.0	25.10	14.62	0.717	0.0330	0.0341
50.0	25.57	14.75	0.733	0.0390	0.0392
53.0	26.08	14.89	0.751	0.0444	0.0449
55.0	26.38	14.98	0.761	0.0478	0.0491
57.0	26.84	15.07	0.781	0.0551	0.0536
60.0	27.22	15.21	0.789	0.0592	0.0611
63.0	27.67	15.35	0.803	0.0659	0.0693
65.0	28.08	15.44	0.819	0.0750	0.0755
67.0	28.47	15.53	0.833	0.0849	0.0820
70.0	28.88	15.67	0.843	0.0934	0.0927
72.0	29.17	15.76	0.851	0.101	0.100

[a] Calculated pressure for no dissociation.

[b] Calculated from observed data.

[c] Calculated from $\log K_p = 5.007 - 2073/T$

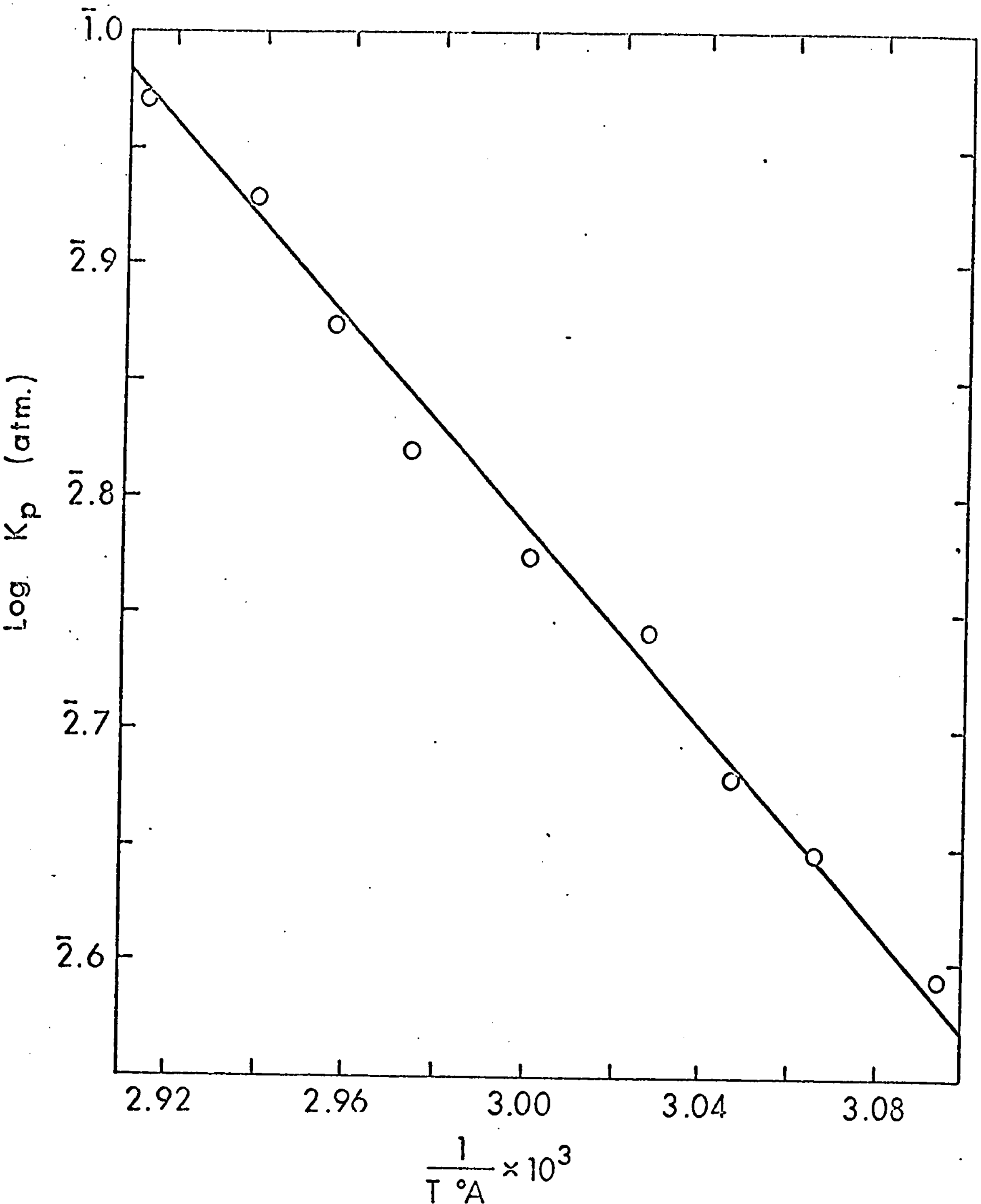


FIGURE 3. The variation of the equilibrium constant with temperature for the gas phase dissociation of the dimethylboric anhydride-trimethylamine adduct.

Trimethylphosphine-dimethylboric anhydride. The addition compound was formed in the tensimeter by bringing together 18.8 cc of dimethylboric anhydride and a matched volume of trimethylphosphine. In the gas phase at room temperature, the complex was found to be 98% dissociated. The saturation pressures of the liquid reported in Table X determine the equation log $P_{mm} = 9.077 - 2019/T$, from which one calculates a "boiling point" of 52.6°C and the Trouton constant as 28.4.

Dimethyl ether-dimethylboric anhydride. Dimethyl ether was treated with a matched volume of dimethylboric anhydride. The volumes in the gas phase at room temperature were found to be additive. Furthermore when the mixture was cooled to -78.5°C the pressure above the liquid was slightly greater (6%) than that calculated using Raoult's law. It may be concluded that an adduct does not form down to -78.5°C. It should be noted that pure dimethylboric anhydride has a negligible vapor pressure at -78.5°.

Dimethyl sulfide-dimethylboric anhydride. Dimethyl sulfide was treated with a matched volume of dimethylboric anhydride. The volumes in the gas phase at room temperature were found to be additive. At temperatures below

TABLE X

Saturation Pressures of Dimethylboric Anhydride-Trimethyl Phosphine

Temp. °C	-15.0	-10.0	- 6.0	- 4.0	0.0	4.0	5.0	7.4	10.0	15.0	20.0
P_{mm} (obsd.)	18.1	25.7	33.2	36.4	48.6	61.1	65.8	75.4	89.6	119.9	156.5
$P_{mm}{}^{a}$ (calcd.)	18.1	25.5	33.2	37.8	48.6	62.2	66.0	76.1	88.7	118.9	155.2

[a] Calculated from $\text{Log } P_{mm} = 9.077 - 2019/T$.

-45.2°C, the pressures observed were only 10% below those expected for pure dimethyl sulfide. This presumably indicates some degree of insolubility of dimethylboric anhydride in dimethyl sulfide at these temperatures and it may be concluded that a complex does not form.

Trimethylboron-dimethylboric anhydride. A 49.6 cc sample of trimethylboron was treated with an equivalent amount of dimethylboric anhydride in the tensimeter. Below -78.5°C, the observed pressures were within 5% of those expected for pure trimethylboron. These data would suggest that dimethylboric anhydride is quite insoluble in trimethylboron at these temperatures and it may be concluded that a complex does not form.

Dimethylboron chloride-dimethylboric anhydride. A 24.1 cc sample of dimethylboron chloride was treated with a matching volume of dimethylboric anhydride in the tensimeter. After standing six hours at -78.5°C, the observed pressure was 7.7 mm, essentially the same as that of pure dimethylboron chloride at -78.5°C. We conclude that no complex is formed and that dimethylboric anhydride is insoluble in dimethylboron chloride in this temperature region.

4. Ambient Temperature NMR Analyses of the Complexes.

The complexes of dimethylboric anhydride were also examined by nmr. The results are listed in Table XI. Chemical shifts of the protons on dimethylboric anhydride show shifts to high field when complexed to a Lewis base, while the Lewis base protons are shifted to lower field. Comparing these data to the tensimetric data shows that the magnitude of the chemical shift increases as the strength of the complex increases, in agreement with the results of other workers (57,58,59). The single resonance observed for the dimethylboron chloride-dimethylboric anhydride system will be discussed in a later section.

5. Variable Temperature NMR Studies of Some Dimethylboric Anhydride Systems.

Dimethylboric anhydride. The room temperature proton nmr spectrum of dimethylboric anhydride (5 mole % in $CFCl_3$) comprised a single broad (ca 3.5 cps) resonance at 0.52 ppm upfield from $(CH_3)_4C$.[2] As the temperature was decreased, the resonance broadened and eventually separated into two equal resonances (coalescence temperature -69°C) at 0.389 and 0.775 ppm upfield from $(CH_3)_4C$ (see Figure 4, A and B). This phenomenon has been interpreted as due to the stabil-

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[2] The chemical shift of $(CH_3)_4C$ is reported to be at 9.06 τ, or 0.94 ppm downfield from tetramethylsilane (TMS): G.V.D. Tiers, Characteristic Nuclear Magnetic Resonance (NMR) "Shielding Values" (Spectral Positions) for Hydrogen in Organic Structures, Central Research Dept., Minnesota Mining and Manufacturing Co., St. Paul, Minn., Project 737602.

TABLE XI

60 Mc. N.M.R. Chemical Shifts of Some Acid-Base Systems

	Proton Chemical Shifts (ppm relative to TMS)[a]	
System	Me_4B_2O	Other
Me_4B_2O	0.43	
Me_3N		2.23
$Me_4B_2O:NMe_3$	0.03	2.45
Me_3P		1.02[b]
$Me_4B_2O:Me_3P$	0.38	1.13[c]
Me_2O		3.30
$Me_4B_2O:Me_2O$	0.43	3.30
Me_2S		2.12
$Me_4B_2O:Me_2S$	0.43	2.12
Me_3B		0.77
$Me_4B_2O:Me_3B$	0.43	0.77
Me_2BCl		0.97
$Me_4B_2O:Me_2BCl$	0.62[d]	0.62[d]

a. All samples 10% in chloroform.

b. Doublet J_{P-C-H} = 8.0 cps

c. Doublet J_{P-C-H} = 6.7 cps.

d. Single peak indicating rapid exchange

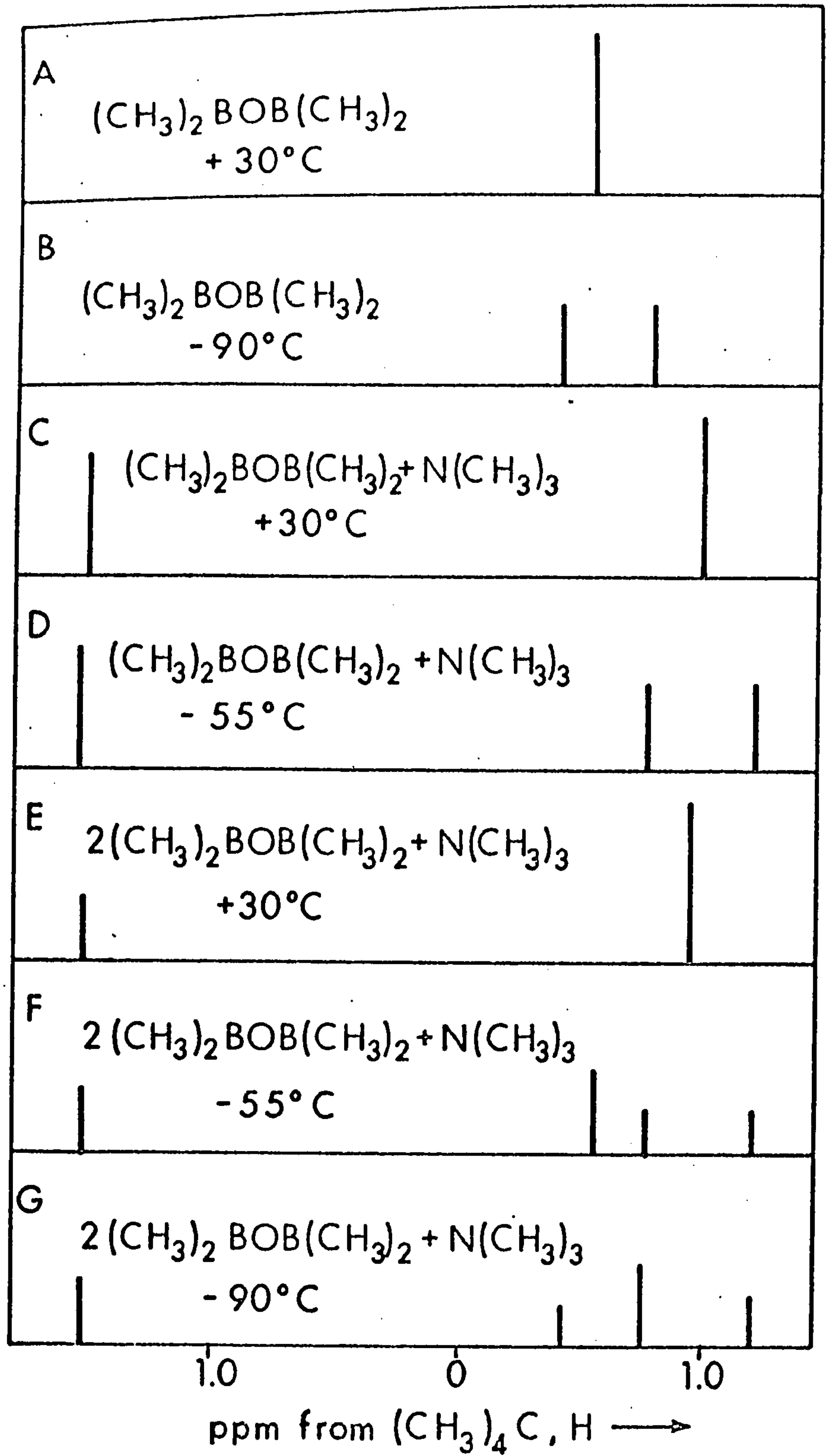

FIGURE 4. Schematic representations of nmr spectra of dimethylboric anhydride and dimethylboric anhydride-trimethylamine systems at various temperatures.

ization of a particular conformation (see Figure 5) by boron-oxygen π-bonding. Applying the Eyring equation, in the form $\log 1/2\pi(\nu_a-\nu_b)\tau T = 10.318/\pi(\overset{\circ}{\nu}_A-\overset{\circ}{\nu}_B) + \Delta S^{\ddagger}/2.3R - \Delta H^{\ddagger}/2.3RT$ (the transmission coefficient is assumed to be unity), to the data listed in Table XII and illustrated in Figure 6, results in the relation $\log k/T = 7.472 - 2014/T$, where $r^2 = 0.993$ and $s_{y,x} = 0.0216$. From this relation, the enthalpy and entropy of activation are calculated to be 9.2 ± 0.7 kcals. and -3.5 e.u. respectively.

Di-*iso*propyl ether, the most sterically similar carbon analogue of dimethylboric anhydride, was examined under similar conditions. The nmr spectrum of a 5% solution in $CFCl_3$ remained unchanged between +30 and -90°C. Since π-interaction is not a factor in this compound, any change in the spectrum would be attributed to steric factors. Since these factors give rise to no observable effect, it is concluded that the non-equivalence observed in dimethylboric anhydride is caused by boron-oxygen π-bonding.

Dimethylboric anhydride-Trimethylamine, 1:1. At room temperature, the nmr spectrum consisted of two resonances 1.49 ppm downfield and 0.93 ppm upfield from $(CH_3)_4C$, which integrated in a 3:4 ratio. These were assigned to $(CH_3)_3N$ and $(CH_3)_2BOB(CH_3)_2$ respectively. Upon lowering the sample temperature, the B-methyl resonance was observed to broaden and then separate into two resonances. This occurred at a

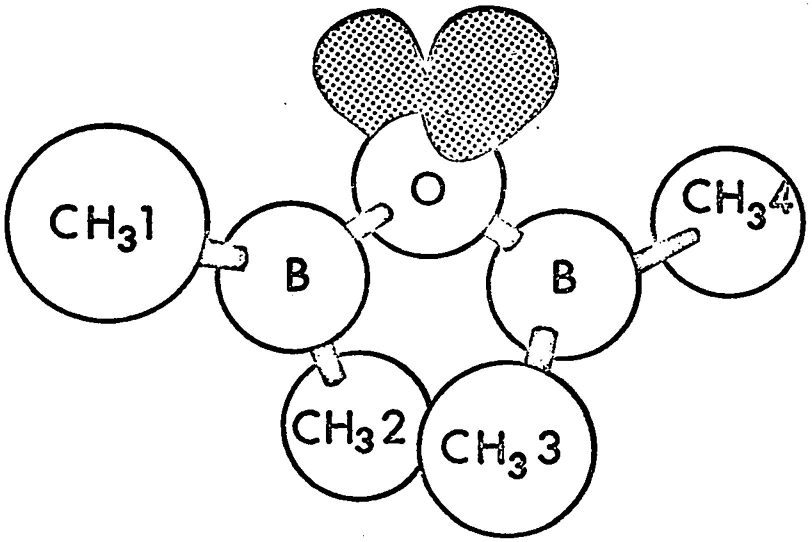

FIGURE 5. Conformation of dimethylboric anhydride permitting maximum overlap of oxygen lone pairs (shaded) with vacant boron orbitals.

TABLE XII

Results of the Variable Temperature Study on Dimethylboric Anhydride

Temp. °C	$(\nu_A-\nu_B)$ cps.[a]
-68	collapsed
-70.5	22.6
-72	27.8
-75	33.1
-77	34.7
-78	35.1
-79	36.4
-80	37.0
-84	38.0
-86	38.6
-89	38.6
-92	38.6

[a] $(\nu_A-\nu_B)$ represents the separation between the maxima of the two resonances which are due to the non-equivalent $B(CH_3)_2$ groups. Recorded at 100 Mc/s.

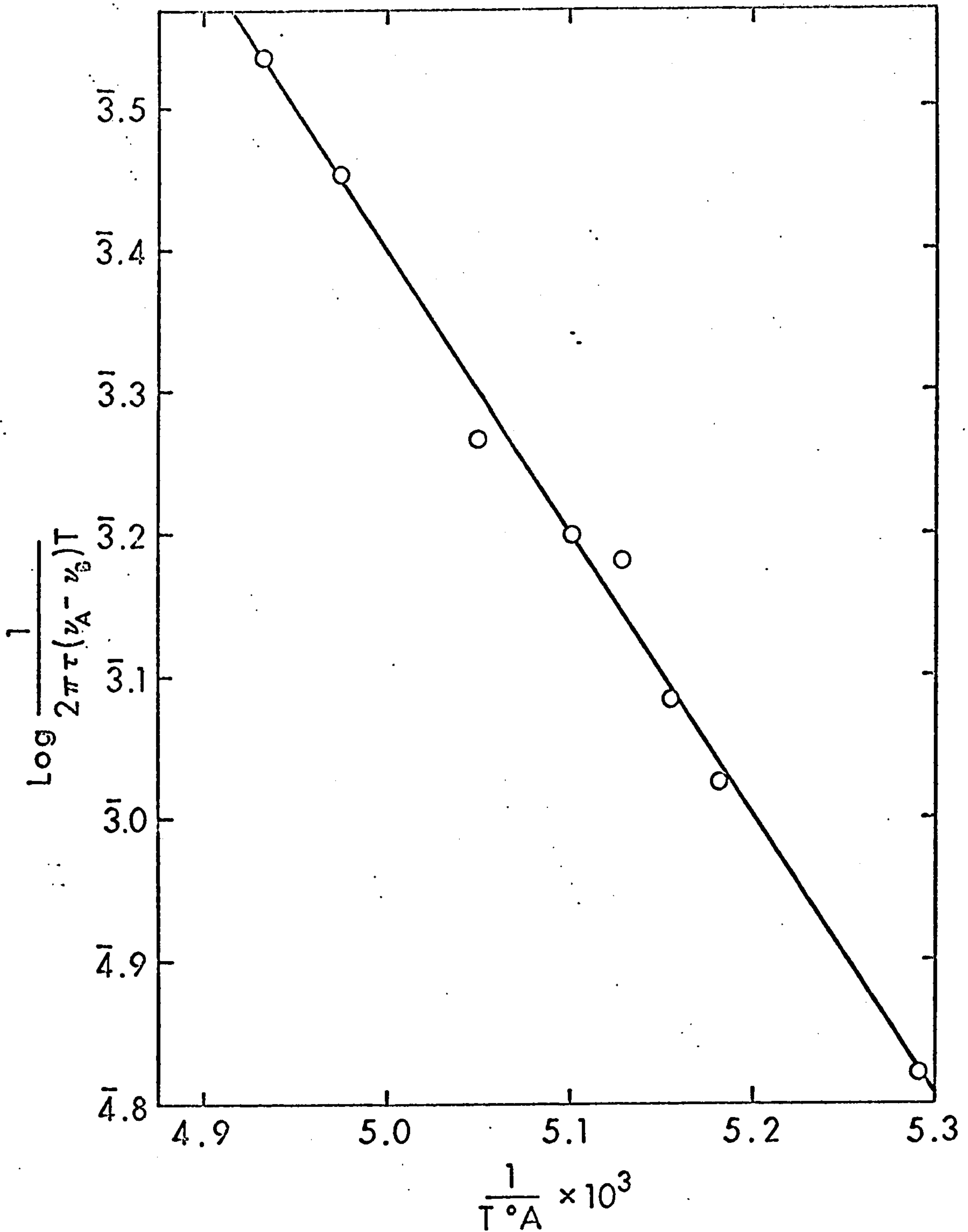

FIGURE 6. Temperature dependence of the reorientation rate constant (1/2τ) for dimethylboric anhydride.

much higher temperature than previously observed with only dimethylboric anhydride present. In this case the coalescence temperature was found to be -41°C, while in the latter case it was -69°C. The resonances were found at 0.766 and 1.198 ppm upfield from $(CH_3)_4C$ (see Figure 4, D). The N-methyl resonance was essentially unchanged except for a slight downfield shift of 4 to 5 cps. This phenomenon is interpreted as due to the slowing down of the exchange reaction:

$$(CH_3)_2BOB(CH_3)_2 \cdot N(CH_3)_3 \rightleftarrows (CH_3)_2BOB(CH_3)_2 + N(CH_3)_3$$

The two resonances observed for the B-methyls are attributed to the adducted $B(CH_3)_2$ group and the non-adducted $B(CH_3)_2$ group <u>of the same molecule.</u> Using the Eyring equation, the data listed in Table XIII and illustrated in Figure 7, give rise to the relation $\log k/T = 8.340 - 2513/T$, where $r^2 = 0.982$ and $s_{y,x} = 0.0320$. From this relation the enthalpy and entropy of activation are calculated to be 11.5 ± 1.1 kcals. and 0.7 e.u. respectively.

<u>Dimethylboric anhydride-trimethylamine, 2:1.</u> Studies on this system yielded results which are consistent with the previous interpretations. The room temperature spectrum (see Figure 4E), consisted of two resonances at 1.51 ppm downfield and 0.725 ppm upfield from $(CH_3)_4C$, which integrated in a 3:8 ratio. The low field resonance was assigned to $(CH_3)_3N$ and the upfield to $(CH_3)_2BOB(CH_3)_2$. The position

TABLE XIII

Results of Variable Temperature Study on the Dimethylboric Anhydride - Trimethylamine System 1:1 ratio.

Temp. °C	$(\nu_A-\nu_B)$ cps.[a]
-42	collapsed
-43	17.9
-44	27.2
-45	30.8
-46	35.0
-47	37.0
-48	38.2
-50	40.0
-52	41.1
-53	41.4
-57	42.0
-60	43.0
-70	43.2
-80	43.2

[a] $(\nu_A-\nu_B)$ represents the separation between the maxima of the two resonances which are due to the adducted $B(CH_3)_2$ group and the non-adducted $B(CH_3)_2$ group. Recorded at 100 Mc/s.

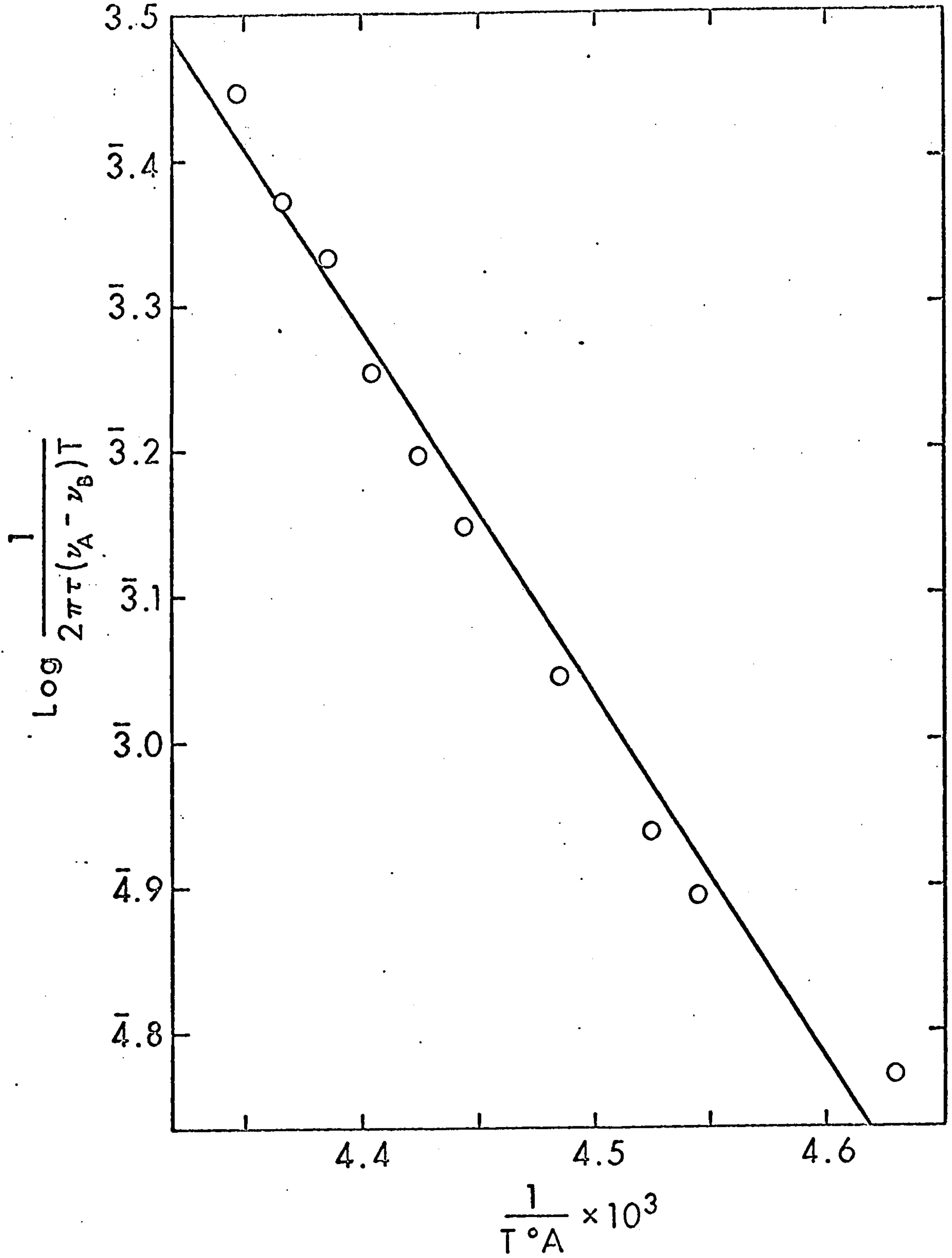

FIGURE 7. Temperature dependence of the rate constant (1/2τ) for the exchange reaction between dimethylboric anhydride and trimethylamine.

of the B-methyl resonance is half-way between the position observed for free dimethylboric anhydride (Figure 4 A) and that observed for dimethylboric anhydride-trimethylamine, 1:1 (Figure 4 C). Lowering the temperature of the sample causes the B-methyl resonance to broaden, and initially, to separate into three resonances. Integration showed the peak areas to be in a 2:1:1 ratio, numbering from low to high field. The coalescence temperature for this process is -41°C, while the chemical shifts are 0.52, 0.71 and 1.15 ppm upfield from $(CH_3)_4C$. The reader is reminded that the chemical shifts are the same as those observed for the resonance of unadducted dimethylboric anhydride (Figure 4 A), and the two resonances observed for dimethylboric anhydride adduct at low temperature (Figure 4 D). Furthermore, the coalescence temperature is the same as that observed for the 1:1 sample described in the previous section.

As the temperature is decreased further, the low field resonance attributed to unadducted dimethylboric anhydride begins to broaden and eventually separates into two resonances. The coalescence temperature for this process is -69°C. However, the spectrum observed at temperatures where this process is slow does not exhibit four resonances of equal area, because the high field resonance of the latter process coincides with the low field resonance of the former process giving rise to three resonances which were shown by integration to be in a 1:2:1 ratio. The maximum separations of the resonances for these phenomena are 44 cps for the higher temperature process and 39 cps for the lower temperature process. These are the same values as observed in the previous two sections.

Dimethylboric anhydride-trimethylamine, 1:2. This system exhibited single resonances for both the N-methyl and the B-methyl signals throughout the temperature range, +50 to -90°C. (Table XIV). While these results could be interpreted in terms of rapid exchange throughout the entire temperature range studied, the formation of a di-adduct of dimethylboric anhydride with trimethylamine would be expected to give a similar spectrum. The fact that the chemical shift of the trimethylamine resonance is very close to the expected average value of the free trimethylamine and adducted trimethylamine chemical shifts, favors the former interpretation.

Dimethylboric anhydride-trimethylamine, 1:4. In order to clarify the above system, a study was carried out on a sample containing four equivalents of trimethylamine and one equivalent of dimethylboric anhydride. The spectrum exhibited two resonances throughout the temperature region +50 to -90°C. Integration showed the low field resonance, attributed to trimethylamine, to contain twice the area of the upfield

TABLE XIV

Table of Chemical Shifts for Dimethylboric Anhydride-Trimethylamine Systems[a]

Sample	B-Methyl Resonance[b] (cps)		N-methyl Resonance[c] (cps)	
	Warm	Cold	Warm	Cold
$(CH_3)_2BOB(CH_3)_2$	52	39 , 78	-----	-----
$(CH_3)_2BOB(CH_3)_2 + (CH_3)_3N$	98	77 , 120	151	154
$(CH_3)_2BOB(CH_3)_2 + 2(CH_3)_3N$	92	92	132	132
$(CH_3)_2BOB(CH_3)_2 + 4(CH_3)_3N$	95	95	124	124
$(CH_3)_3N$	----	----	118	118

[a] Recorded at 100 Mc/s.

[b] Measured upfield from $(CH_3)_4C$.

[c] Measured downfield from $(CH_3)_4C$.

resonance, attributed to dimethylboric anhydride. The chemical shift of the N-methyl resonance is the same value as that expected for the average of three non-adducted and one adducted species.

Dimethylboric anhydride-dimethylboron chloride. As mentioned earlier, this system exhibited a single resonance at ambient temperature. A low temperature study was carried out on a sample composed of 5 mole % dimethylboron chloride and 2.5 mole % dimethylboric anhydride in $CFCl_3$.

As the temperature was lowered, the single resonance broadened and separated into two broad peaks (-59°C) which were shown to be of equal area by integration. The low field resonance was assigned to dimethylboron chloride and the high field resonance to dimethylboric anhydride. As the sample cooled further, the high field resonance was observed to broaden and separate (-69°C) into two resonances, which were shown to be of equal area. As shown previously this latter process is expected for free dimethylboric anhydride. At -91°C, the spectrum consisted of three resonances; the two equal resonances at high field separated by ca 39 cps, as in the case of pure dimethylboric anhydride, and the low field resonance of free dimethylboron chloride, located ca 51 cps downfield from the lower of the two dimethylboric anhydride resonances.

In order to analyse this system and determine the activation energies involved in the exchange process,

$$(CH_3)_2BOB^*(CH_3)_2 + (CH_3)_2BCl \rightleftarrows (CH_3)_2BOB(CH_3)_2 + (CH_3)_2B^*Cl$$

the following method was used. In the region where two resonances existed for the dimethylboric anhydride ($< -69°C$), the separation, measured in cps between the <u>mid-point</u> of these resonances, and the resonance due to dimethylboron chloride, was used to calculate $(\nu_a-\nu_b)$. In the region where a single resonance existed for dimethylboric anhydride, the separation, measured in cps, between this resonance and the resonance due to dimethylboron chloride, was used for $(\nu_a-\nu_b)$. The data are listed in Table XV, and illustrated in Figure 8. From these data the equation $\log k/T - 3.144 - 1220/T$ was calculated, where $r^2 = 0.993$ and $s_{y,x} = 0.0247$. The enthalpy and entropy of activation are 5.6 ± 0.4 kcals and -24.4 e.u. respectively.

6. Studies of Dimethylmethoxyboron.

Tensimetric Study. Dimethylmethoxyboron was treated with matched volume of trimethylamine in the tensimeter. In the gas phase at room temperature, the complex was found be completely dissociated. The saturation pressures of the liquid reported in Table XVI determine the equation $\log P_{mm} = 12.92 - 2860/T$ from which one calculates a "boilint point" of 12°C and the Trouton constant of 46 e.u. The very high value of the Trouton constant is indicative that

TABLE XV

Results of the Variable Temperature Study on the Dimethylboric Anhydride-Dimethylboron Chloride System

Temp. °C	$(\nu_A - \nu_B)$ cps [a]	$(\nu_A - \nu_B)$ cps [b]
-57	collapsed	collapsed
-59	collapsed	39.0
-61	collapsed	50.0
-66	collapsed	60.0
-68.5	27.4	63.2 [c]
-71.5	32.4	65.7 [c]
-74	34.8	67.3 [c]
-76	37.4	68.4 [c]
-81	38.5	69.8 [c]
-86	38.7	70.2 [c]
-91	38.9	70.6 [c]
-95	38.9	70.6 [c]

[a] $(\nu_A - \nu_B)$ represents the separation between the maxima of the two resonances which are due to the non-equivalent $B(CH_3)_2$ groups of dimethylboric anhydride. Recorded at 100 Mc/s.

[b] $(\nu_A - \nu_B)$ represents the separation between the maxima of the two resonances which are due to the collapsed resonance of dimethylboric anhydride and that due to dimethylboron chloride.

[c] These separations are measured between the mid-point of the two dimethylboric anhydride resonances and the dimethylboron chloride resonance.

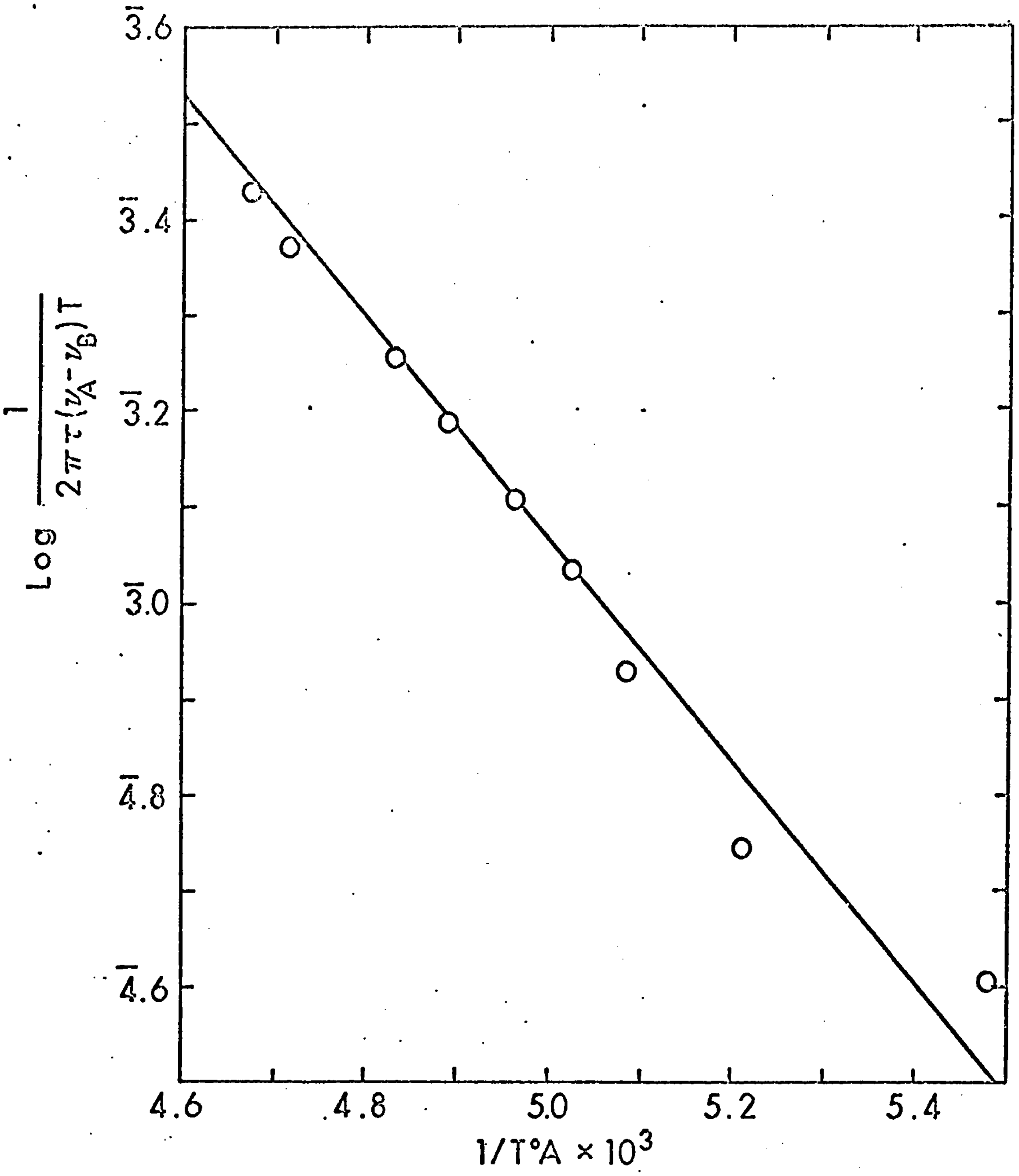

FIGURE 8. Temperature dependence of the rate constant (1/2τ) for the exchange reaction between dimethylboric anhydride and dimethylboron chloride.

TABLE XVI

Saturation Pressures of Dimethylmethoxyboron-Trimethylamine

Temp. °C	-45.2	-35.0	-22.9	-14.2
P_{mm} (obsd.)	2.4	8.2	34.0	75.8
P_{mm}[a] (calcd.)	2.4	8.1	33.1	75.9

[a] Calculated from $\log P_{mm} = 12.92 - 2860/T$

vaporization of the addition compound is accompanied by an increase in dissociation (60).

Variable temperature nmr studies. The nmr spectrum of pure *dimethylmethoxyboron* exhibited temperature dependent phenomena. As the temperature was decreased, the B-methyl resonance was observed to broaden and then separate into two resonances while the O-methyl resonance remained unaffected.

Two studies of the system were undertaken; a 15% solution in $CFCl_3$, and a 30% solution in C_7D_{14}. Table XVII lists the data obtained from measurements of peak separation versus temperature. From these data, values of τ, the lifetime of the species, were calculated. These results were then used in the Eyring equation.

For the 15% solution in $CFCl_3$, the data lead to the equation $\log k/T - 5.076 - 1739/T$ where $r^2 = 0.987$ and $s_{y,x} = 0.0241$. From this relation, the enthalpy and entropy of activation are calculated as 8.0 ± 0.8 kcals. and -17.4 e.u. respectively. The coalescence temperature was -44°C.

The study of the 30% solution in C_7D_{14} was complicated by the small maximum separation of the B-methyl signals under conditions of slow exchange. Correction for overlap, using a relation described by Gutowsky and Holm (61), was necessary for calculating the true (rather than observed) maximum separation. The data then lead to the equation $\log k/T =$

TABLE XVII

Effect of Temperature upon the B-Methyl Resonance of Dimethylmethoxyboron

15% in $CFCl_3$		30% in C_7D_{14}	
Temp. °C	$(\nu_A-\nu_B)$ cps [a]	Temp. °C.	$(\nu_A-\nu_B)$ cps [a]
-43	collapsed	-43	collapsed
-44	<2	-44	1.4
-45	3.6	-45	2.1
-46	5.5	-46	2.8
-47	5.7	-47	3.1
-48	6.4	-48	3.5
-50	7.0	-50	4.1
-52	7.5	-53	4.1
-53	7.8	-54	4.3
-55	8.2	-58	4.4
-61	8.7	-60	4.5[3]
-66	8.8[6]	-70	4.5[3]
-76	8.8[6]		
-89	8.8[7]		

[a] $(\nu_A-\nu_B)$ represents the separation between the maxima of the two resonances which are due to the non-equivalent CH_3 groups on the boron atom. Recorded at 100 Mc/s.

5.671 - 1880/T where $r^2 = 0.985$ and $s_{y,x} = 0.0255$. In this case, the enthalpy and entropy of activation are calculated to be 8.6 ± 1.1 kcals and -16.0 e.u. respectively, while the coalescence temperature is again -44°C.

The combined results are illustrated in Figure 9. The least mean square treatment of the combined data leads to the equation log k/T - 5.180 - 1766/T where $r^2 = 0.977$ and $s_{y,x} = 0.0302$.

From this relation, the enthalpy and entropy of activation are calculated to be 8.1 ± 0.7 kcals and -17.4 e.u. respectively.

The data indicate little or no effects due to solvent and concentration, as may be seen in Figure 9, and, this fact appears to justify combining the two sets of data.

Effect of amine. In the course of this study, it was found that the presence of small quantities of trimethylamine lowered the activation energy and the coalescence temperature of the process described above. When 0.1 equivalent of trimethylamine was present in the sample, the spectrum no longer showed two B-methyl resonances, even as low as -100°C.

Equilibrium study. It was observed that the chemical shifts of each proton resonance of 1:1 trimethylamine-dimethylmethoxyboron samples, at room temperature, were

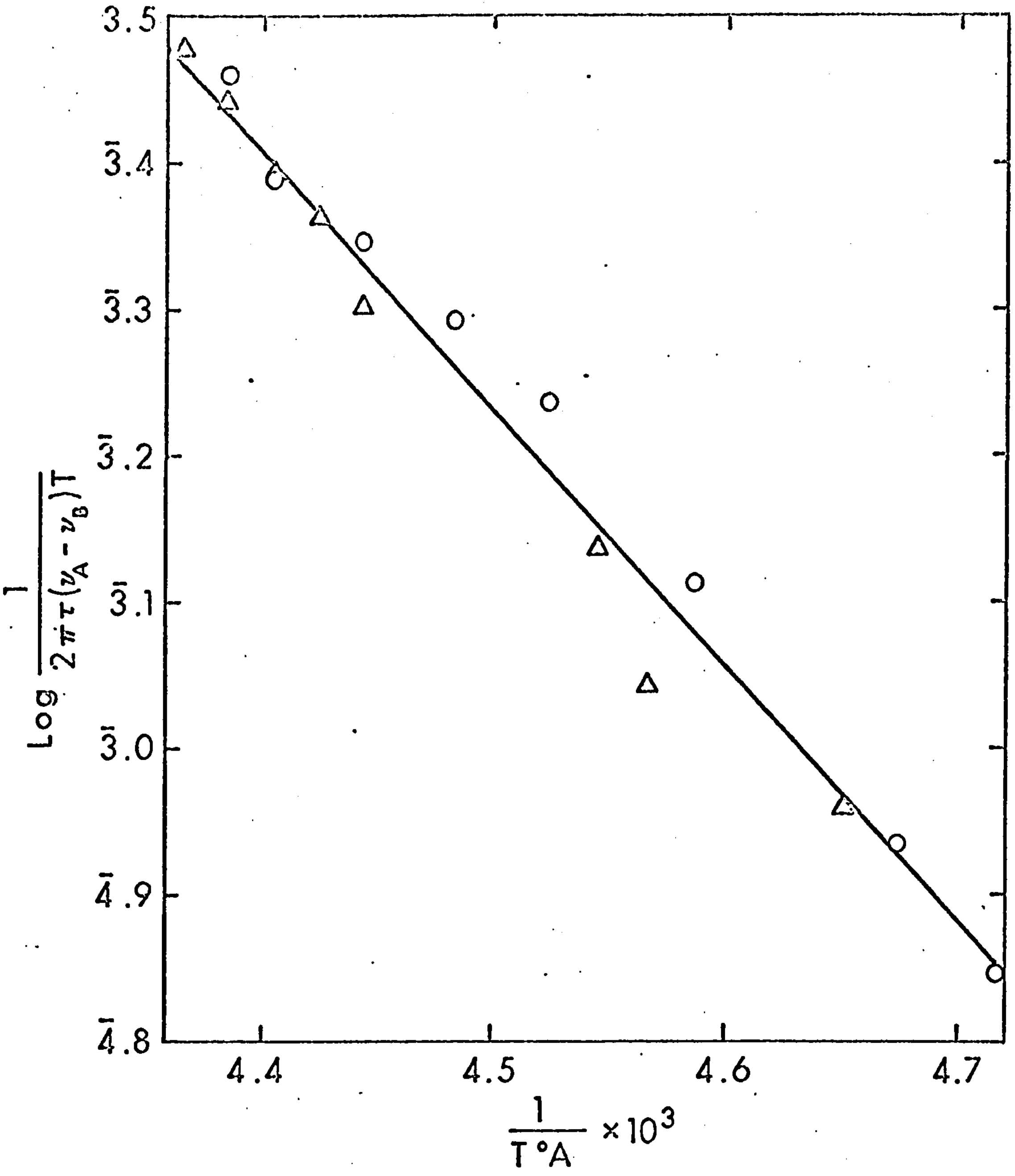

FIGURE 9. Temperature dependence of the reorientation rate constant ($1/2\tau$) for dimethylmethoxyboron showing combined results of two studies. Circles describe data obtained from a 15% solution in $CFCl_3$ and triangles in 30% solution in $CD_3C_6D_{11}$.

very close (1-2 cps) to the chemical shifts for the free compounds, indicating almost complete dissociation. As the temperature was lowered, the B-methyl and O-methyl resonances shifted upfield, while the N-methyl resonance shifted downfield. Furthermore, below -80°C, the changes in chemical shift per unit change in temperature decreased, approaching zero near -100°C, the lowest accessable temperature in these studies. This indicates an observable range of the equilibrium for the reaction $(CH_3)_2BOCH_3 \cdot (CH_3)_3N \rightleftarrows (CH_3)_2BOCH_3 + (CH_3)_3N$, from essentially complete dissociation to essentially complete association.

A sample containing 0.61 millimoles of $(CH_3)_2BOCH_3$, 0.61 millimoles of $(CH_3)_3N$, 0.31 millimoles of $(CH_3)_4C$ as reference, and 2.30 millimoles of $CFCl_3$ as solvent was studied from +60 to -98°C. The variation of the chemical shifts with temperature is illustrated in Figure 10. Since the B-methyl resonance exhibits the greatest change in chemical shift with temperature, these values were used for calculations. The maximum upfield shift (low temperature) was obtained by fitting the six low temperature points to a three constant equation in temperature:

$$\nu = 41.99 - (6.696 \times 10^{-1})T - (2.827 \times 10^{-3})T^2.$$

Differentiation showed the maximum shift to be at -118°C. Substitution yielded a value of 44.6 cps for ν at -118°C. The maximum downfield shift (high temperatures) is the

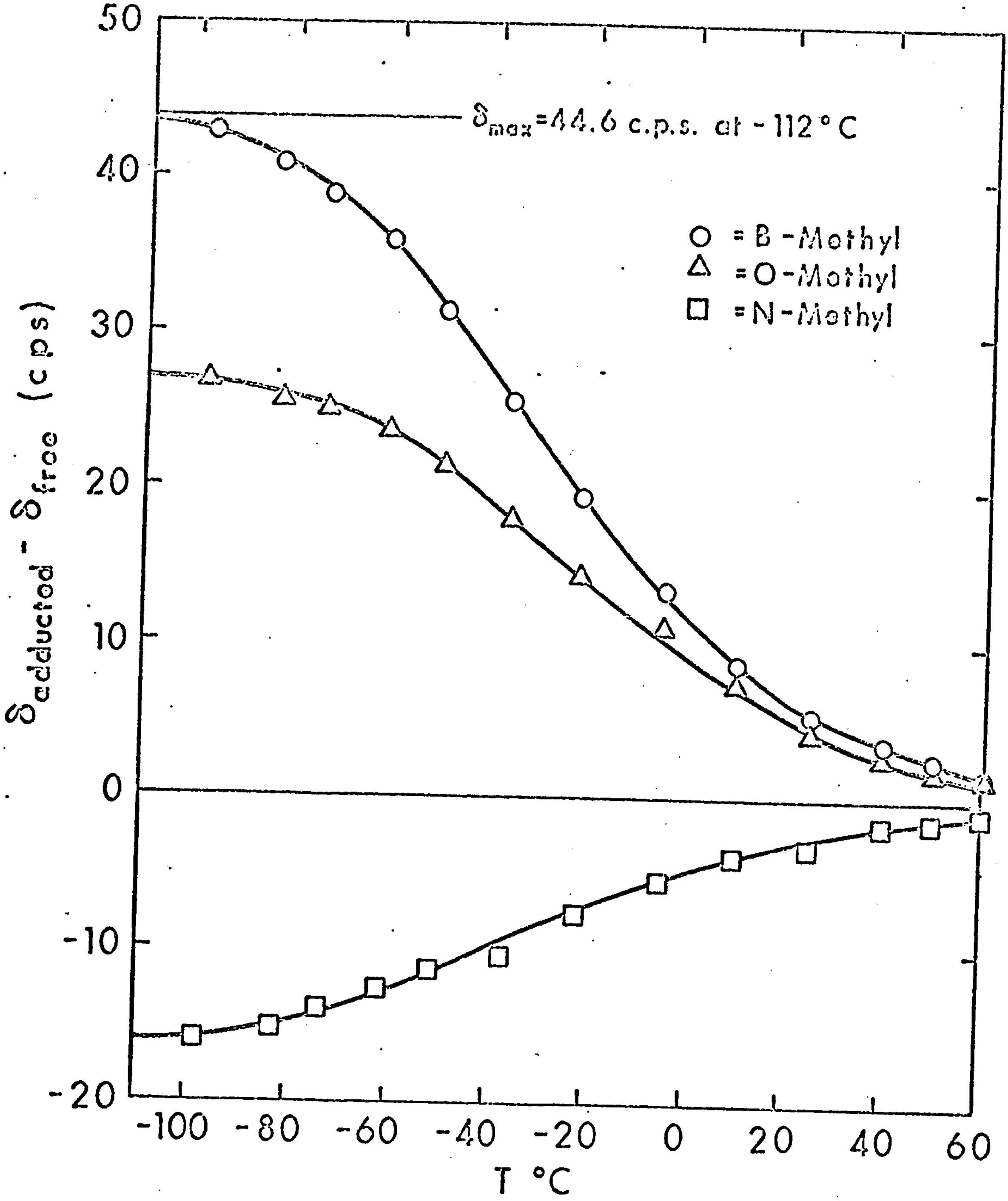

FIGURE 10. Temperature dependence of the chemical shifts for the proton resonances in the dimethylmethoxyboron-trimethylamine system in $CFCl_3$ solution.

value observed for the free dimethylmethoxyboron. To calculate the equilibrium constant for the above dissociation reaction, the data was used in the following manner.

If, initially, there are c moles of complex and s moles of solvent (including reference), at any temperature, x moles of acid and x moles of base will be formed by dissociation,

$$(CH_3)_2BOCH_3 \cdot N(CH_3)_3 \rightleftarrows (CH_3)_2BOCH_3 + N(CH_3)_3$$

At equilibrium, we have the following:

	Moles	Mole fraction
Complex	c-x	$c-x/c+x+s = n_c$
Acid=Base	x	$x/c+x+s = n_a = n_b$
Solvent	s	$s/c+x+s = n_s$

After substitution and simplification, K_{eq} in mole fraction units becomes:

$$K_{eq} = \frac{\text{Acid Base}}{\text{Complex}} = \frac{x^2}{(c-x)(c+x+s)} .$$

If α is the degree of dissociation of the complex, then $x = \alpha c$ millimoles; or, using the numerical values of c and s in the previous equation,

$$K_{eq} = \frac{\alpha^2}{5.28 - 4.28\alpha - \alpha^2}$$

As the system is rapidly exchanging, only a single averaged resonance is observed which is related to the relative quantities of free and adducted compound present, $\nu_{obs.} = \alpha\nu_a + (1-\alpha)\nu_c$ where $\nu_{obs.}$ is the observed frequency, ν_a is the frequency of the free acid and ν_c is the frequency of the complexed acid. It follows, then, that

$$\alpha = \frac{\nu_{obs.} - \nu_c}{\nu_a - \nu_c}$$

Employing these relations, the equation $\log K_{eq} = 4.960 - 1481/T$ was obtained from the data listed in Table XVIII, and illustrated in Figure 11, where $r^2 = 0.999$ and $s_{y,x} = 0.0358$. The following thermodynamic constants were calculated for the equilibrium reaction:

$$\Delta H° = 6.80 \pm 0.20 \text{ kcals.}, \quad \Delta S° = +22.7 \text{ e.u. and}$$
$$\Delta F°_{25°} = 0.014 \text{ kcals.}$$

7. Other Systems.

Dimethylpentafluorophenoxyboron. Variable temperature nmr studies of this system proved interesting, because unlike dimethylmethoxyboron, the B-methyl resonance remained unchanged from +40 to -90°C. The chemical shift remained constant throughout the temperature range studied, while the peak width at half height was similarly unaffected. The fluorine nmr spectra showed the chemical shift of the ortho fluorine atoms to be -4.2 ppm relative to C_6F_6, while the

TABLE XVIII

Dissociation Data for Dimethylmethoxyboron-Trimethylamine in Solution [a]

Temp. °C	$\delta_F - \delta_A$ (cps)[b]	α	K(mole fraction units)[c]	K(mole fraction units)[d] (calcd).
60	1.5	0.951	2.95	3.26
50	2.3	0.937	2.24	2.37
41	3.3	0.922	1.74	1.75
25	5.5	0.877	1.02	1.02
10	8.6	0.809	5.62×10^{-1}	5.28×10^{-1}
- 5	13.2	0.697	2.68×10^{-1}	2.72×10^{-1}
-22	19.3	0.563	1.24×10^{-1}	1.15×10^{-1}
-36	25.5	0.428	5.60×10^{-2}	5.22×10^{-2}
-51	31.3	0.294	2.20×10^{-2}	1.95×10^{-2}
-61	35.8	0.193	8.42×10^{-3}	9.42×10^{-3}
-74	38.5	0.126	3.36×10^{-3}	3.30×10^{-3}
-83	40.8	0.081	1.33×10^{-3}	1.46×10^{-4}
-98	42.8	0.025	1.21×10^{-4}	3.70×10^{-4}

[a] 19 mole % of adduct in $CFCl_3$ solution.

[b] Chemical shift of $(\underline{CH}_3)_2B$ resonance relative to free $(\underline{CH}_3)_2BOCH_3$ as recorded at 60 Mc/s.

[c] Calculated from observed data.

[d] Calculated from log K = 4.960 - 1481/T

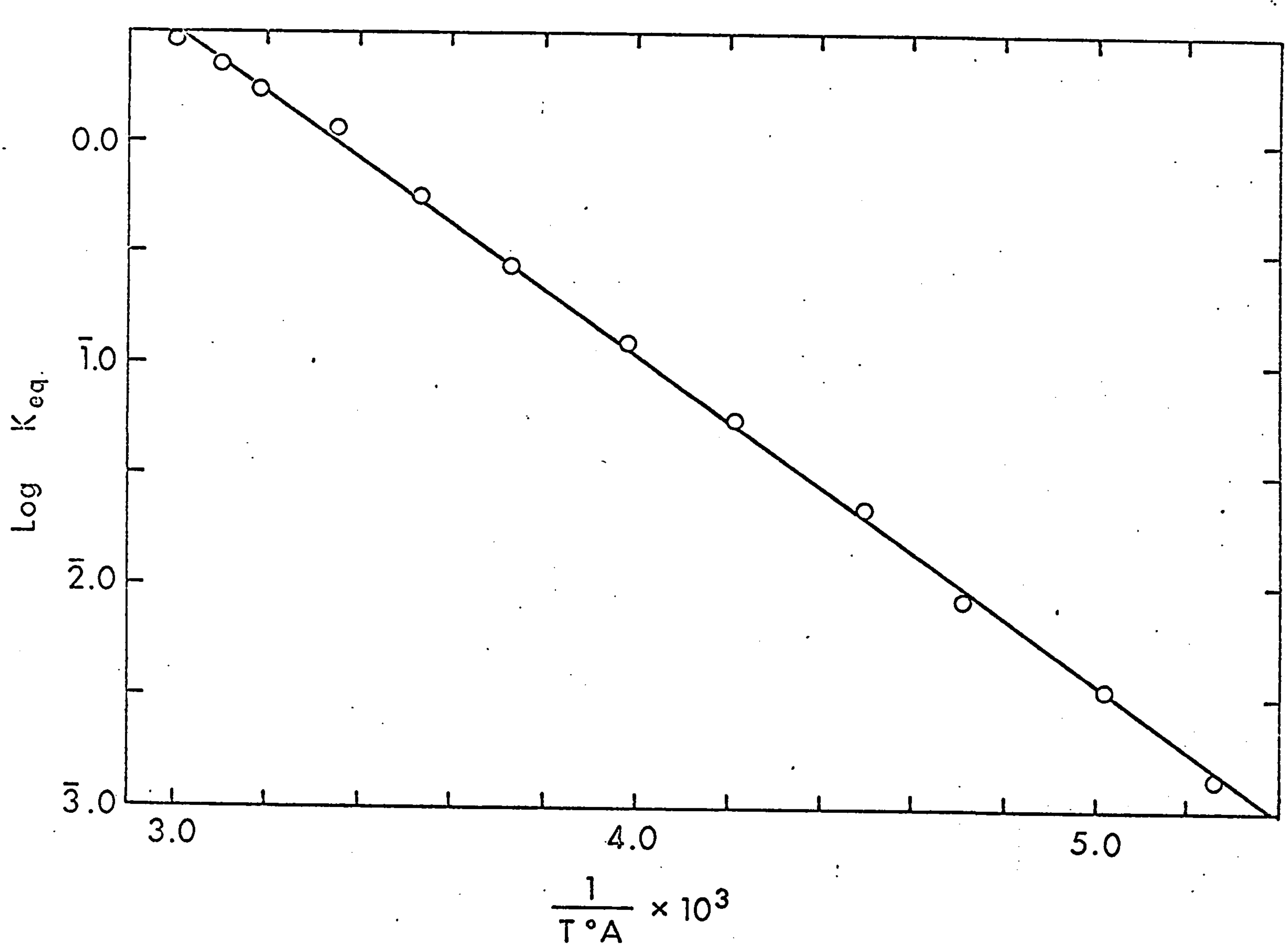

FIGURE 11. Temperature dependence of the equilibrium constant for the dissociation of the dimethylmethoxyboron-trimethylamine adduct in a $CFCl_3$ solution.

chemical shifts of the meta and para fluorine atoms were both +1.3 ppm. No change in the F^{19} spectrum was observed throughout the temperature range studied.

Dimethyl-t-butoxyboron. As in the case of dimethylmethoxyboron, the B-methyl resonance of dimethyl-t-butoxyboron was observed to broaden and separate into two resonances at low temperature. However, the coalescence temperature, in this case, was in the region of -90°C. No kinetic studies were carried out on this compound since the limit of the variable temperature probe did not allow the maximum separation ($\nu_A°-\nu_B°$) to be measured.

Trimethylboron-Trimethylamine. In order to test the validity of the techniques used in obtaining the results reported in this study, the well-characterized (62) trimethylboron-trimethylamine system was studied using identical techniques. The sample comprised 2.5 mole % trimethylboron, 1.25 mole % trimethylamine, the solvent being $CFCl_3$.

The ambient temperature spectrum was composed of two resonances which integrated in a 1:2 ratio. (As the "lock" was the CH_3 resonance of the CH_3OH capillary, no meaningful line positions are available.) As the sample was cooled, the B-methyl resonance was observed to broaden and separate into two resonances, which, in the region of slow exchange, were found to be separated by 119 cps. Integration showed the peaks to be of equal area.

The data from this study are listed in Table XIX and illustrated in Figure 12. Treatment of this data yielded the equation log k/T = 12.06 - 3745/T where $r^2 = 0.974$ and $s_{y,x} = 0.0417$. From this equation, the enthalpy and entropy of activation are calculated to be 17.1 ± 1.8 kcals and +8.0 e.u. respectively. The coalescence temperature was -16°C. As discussed later the similarity of these results with those of Brown et al (62), imply that the techniques and analysis are reasonably accurate.

8. Chloroform Dilution Shift Study.

The purpose of this study was to measure the relative base strength (63) of the oxygen atom(s) in various boron-oxygen containing compounds. The method relies upon the fact that the chloroform proton can form hydrogen bonds with appropriate 'electron donating' atoms. The degree of hydrogen bonding is reflected in the chemical shift of the chloroform resonance, when chloroform is dissolved in the appropriate "solvents". Since chloroform itself is hydrogen bonded, it is necessary to use solutions of chloroform in cyclohexane, extrapolated to infinite dilution, as a reference; cyclohexane is assumed to exhibit no basicity towards chloroform. The extrapolated infinite

TABLE XIX

Results of the Variable Temperature Study of the Trimethylboron-Trimethylamine System

Temp. °C	$(\nu_A-\nu_B)$ cps [a]
-16	collapsed
-17	35
-18	54
-19	79
-20	90
-21	96
-22	103
-24	110
-25	112
-27	117
-33	118
-41	119
-44	120
-48	120

[a] $(\nu_A-\nu_B)$ represents the separation between the maxima of the two resonances which are due to the free trimethylboron and the adducted trimethylboron. Recorded at 100 Mc/s.

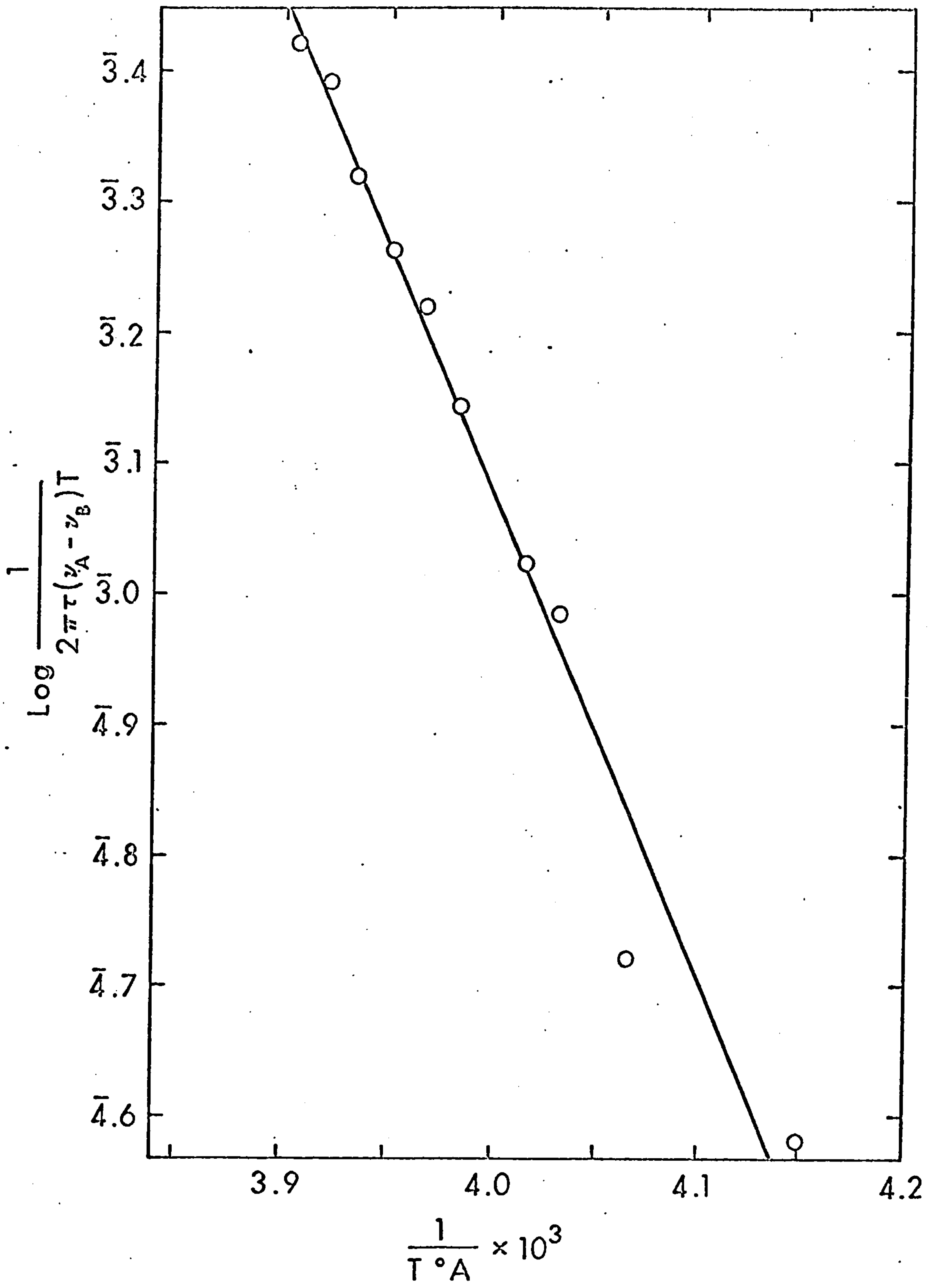

FIGURE 12. Temperature dependence of the rate constant $(1/2\tau)$ for the exchange reaction between trimethylboron and trimethylamine.

dilution chemical shifts of chloroform when dissolved in the compounds to be studied, are then compared to this value. Since the chemical shift of the chloroform is measured relative to pure chloroform contained in a capillary, it is necessary to correct the infinite dilution shifts for bulk susceptibility differences. The final corrected values are a measure of the relative base strength of the compounds under study.

The chemical shifts of the chloroform proton, at six different concentrations in the "solvents" $(CH_3)_2BOB(CH_3)_2$, $(CH_3)_2BOCH_3$, $CH_3B(OCH_3)_2$, $B(OCH_3)_3$ and C_6H_{12}, were measured relative to the chemical shift of pure chloroform contained in a capillary in the nmr sample tube. The results are shown in Figure 13. Corrections for the bulk susceptibility errors were made only for the extrapolated infinite dilution values, using the relation $\delta_T = \delta_O + (2/3)(\kappa_{CHCl_3} - \kappa_{base})$ (reference 21, p.81). The bulk susceptibility values for the compounds were determined using the method described by Li _et_ _al_ (64). In this method, concentric sample tubes are used with benzene in the annular space, with the material under study in the central tube. When the tubes are stationary, the benzene resonance is observed as two broad maxima; the separation of these maxima is determined (with geometry held constant) by the magnetic susceptibility of the substance in the inner tube. The

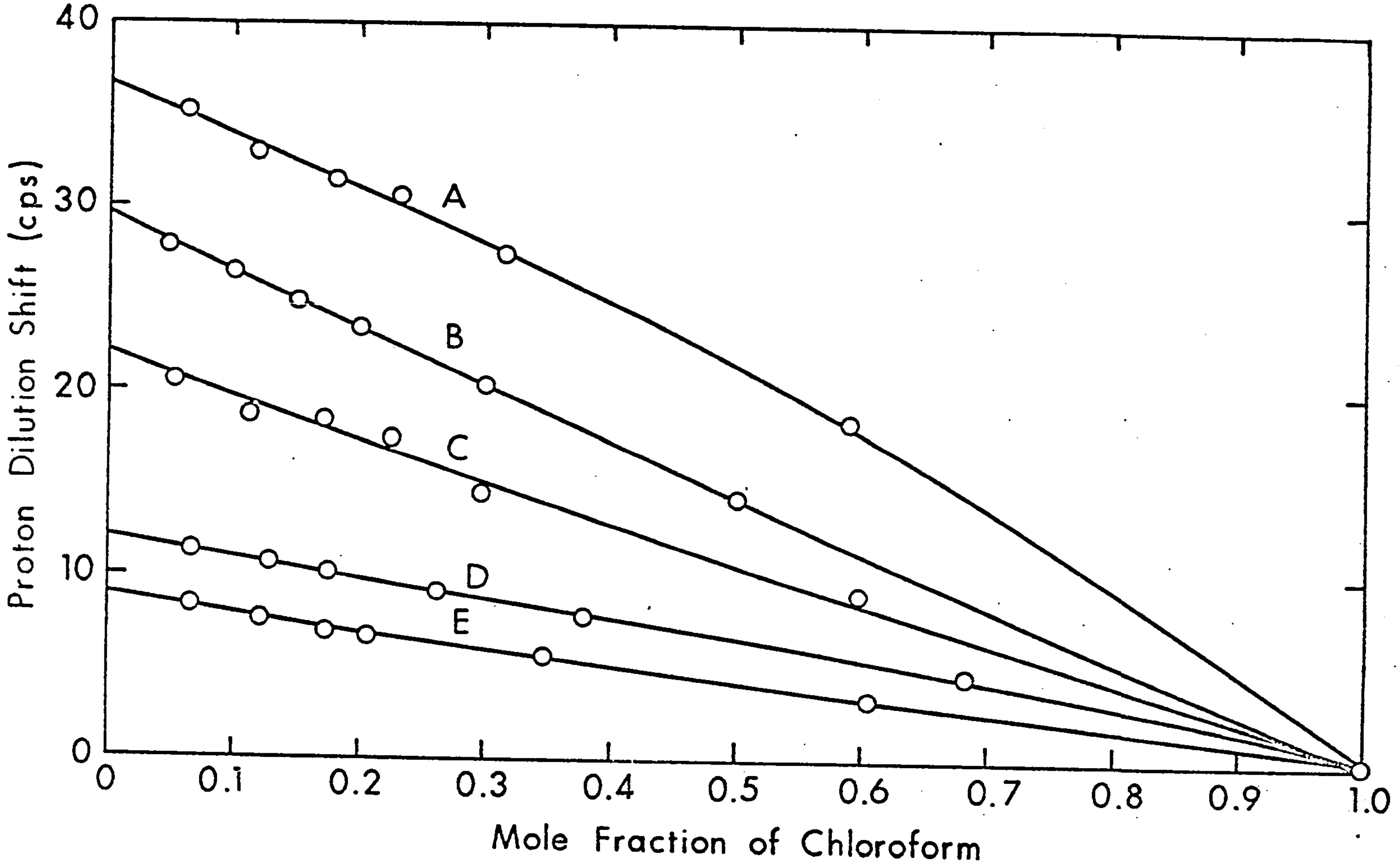

FIGURE 13. Uncorrected dilution curves for chloroform in (A) $(CH_3)_2BOB(CH_3)_2$ (B) C_6H_{12} (C) $(CH_3)_2BOCH_3$ (D) $CH_3B(OCH_3)_2$ (E) $B(OCH_3)_3$.

apparatus is calibrated using solvents of known susceptibility. The following are results of these measurements: $(CH_3)_2BOB(CH_3)_2$, 0.483 x 10^{-6}; $(CH_3)_2BOCH_3$, 0.491 x 10^{-6}; $CH_3B(OCH_3)_2$, 0.496 x 10^{-6}; $(CH_3O)_3B$, 0.501 x 10^{-6}.

The bulk susceptibility corrected shifts, as measured relative to the corrected shift for the chloroform proton in cyclohexane, are listed in Table XX.

9. Study of Dimethylboric Acid.

Association of dimethylboric acid. The vapor pressure lowering in *n*-butane solutions of dimethylboric acid was investigated over a range of temperature and concentration. The results summarized in Table XXI establish that the system is complex, with an average degree of association higher than two or three. While the calculated values are subject to some uncertainty, particularly at low concentrations where the vapor pressure lowering is small, they permit a simple dimeric or trimeric system to be ruled out. As expected, the degree of association becomes smaller as the temperature increases.

Nmr studies. The proton nmr spectrum of dimethylboric acid shows the expected two peaks. At 36°C, we find the OH and CH_3 peaks at 1.28 τ and 9.64 τ, respectively, for the neat liquid containing 1 mole % cyclohexane as internal standard. The shift of the CH_3 protons is

TABLE XX

List of Bulk Susceptibility Corrected Shifts for the Chloroform Proton Relative to the Corrected Shift of this Proton in Cyclohexane

Base	Shift (cps)[a]
Cyclohexane	0[b] (standard)
$(CH_3)_2BOB(CH_3)_2$	8.3[b]
$(CH_3)_2BOCH_3$	22.0[b]
$CH_3B(OCH_3)_2$	34.4[b]
$B(OCH_3)_3$	29.9[b]
$(CH_3)_2HCOCH(CH_3)_2$	46.3[c]
$(CH_3)_3COCH_2CH_3$	44.5[c]

[a] Recorded at 60 Mc/s.

[b] Probe operating at 41°C.

[c] E. W. Abel, D. A. Armitage and S. P. Tyfield, J. Chem. Soc. (A), 554 (1967). Probe operating at 37°C.

TABLE XXI

Association of Dimethylboric Acid in n-butane[a]

Temp. °C	$(CH_3)_2BOH$,[b] cc	n-C_4H_{10},[c] cc	$P^d_{solution}$	Degree of Association
-63.5	2.6	63.2	28.62	7.1
	7.0	63.2	28.38	7.8
	12.9	63.4	27.90	6.5
	23.8	63.6	27.23	6.6
-45.3	2.5	48.0	92.02	3.4
	7.1	48.4	90.66	4.7
	11.8	48.8	88.91	4.7
	24.0	50.0	84.08	4.3
-36.0	2.5	33.3	155.49	4.0
	7.1	34.7	149.80	3.6
	11.8	35.8	145.40	3.7
	24.0	38.4	134.98	3.6

[a] The abbreviation "cc" in this Table refers to gas volume at standard conditions.

[b] Refers to monomeric species measured in the gas phase.

[c] Refers to quantity in the solution, after correction for gaseous n-C_4H_{10} in the tensimeter over the solution.

[d] Vapor pressures of pure n-butane at -63.5°, -45.3°, and -36.0° are 28.78 mm, 93.45 mm, and 158.38 mm, respectively.

essentially independent of concentration and temperature, in contrast to the OH shift, as discussed below. An earlier report (65) on the nmr spectrum of neat liquid dimethylboric acid gave values of 6.65 τ and 9.97 τ, using a substitution method for calibration. The latter value is in reasonable agreement with our measurements when the difference in standardization is considered, but the 6.65 τ value for the OH proton is incompatible with the present work.

The concentration dependence of the chemical shift of the hydroxyl proton was studied over the range 1-99 mole % in cyclohexane solution. The shift varied markedly from 3.48 - 7.28 ppm downfield from cyclohexane, as shown graphically in Figure 14.

The temperature dependence of the hydroxyl proton resonance was studied between -100° and 60°, using a 1 mole % solution of dimethylboric acid in methylcyclohexane, with results as shown in Figure 15. The limiting shift at high temperature was approached but not achieved, since further heating caused the sample to reflux, even under nitrogen, and the signal was lost; however, a value near 4.1 ppm downfield from tetramethylsilane would be a close estimate of the shift of pure monomer.

Infrared spectra. The gas phase infrared spectrum of dimethylboric acid has been reported by Ulmschneider

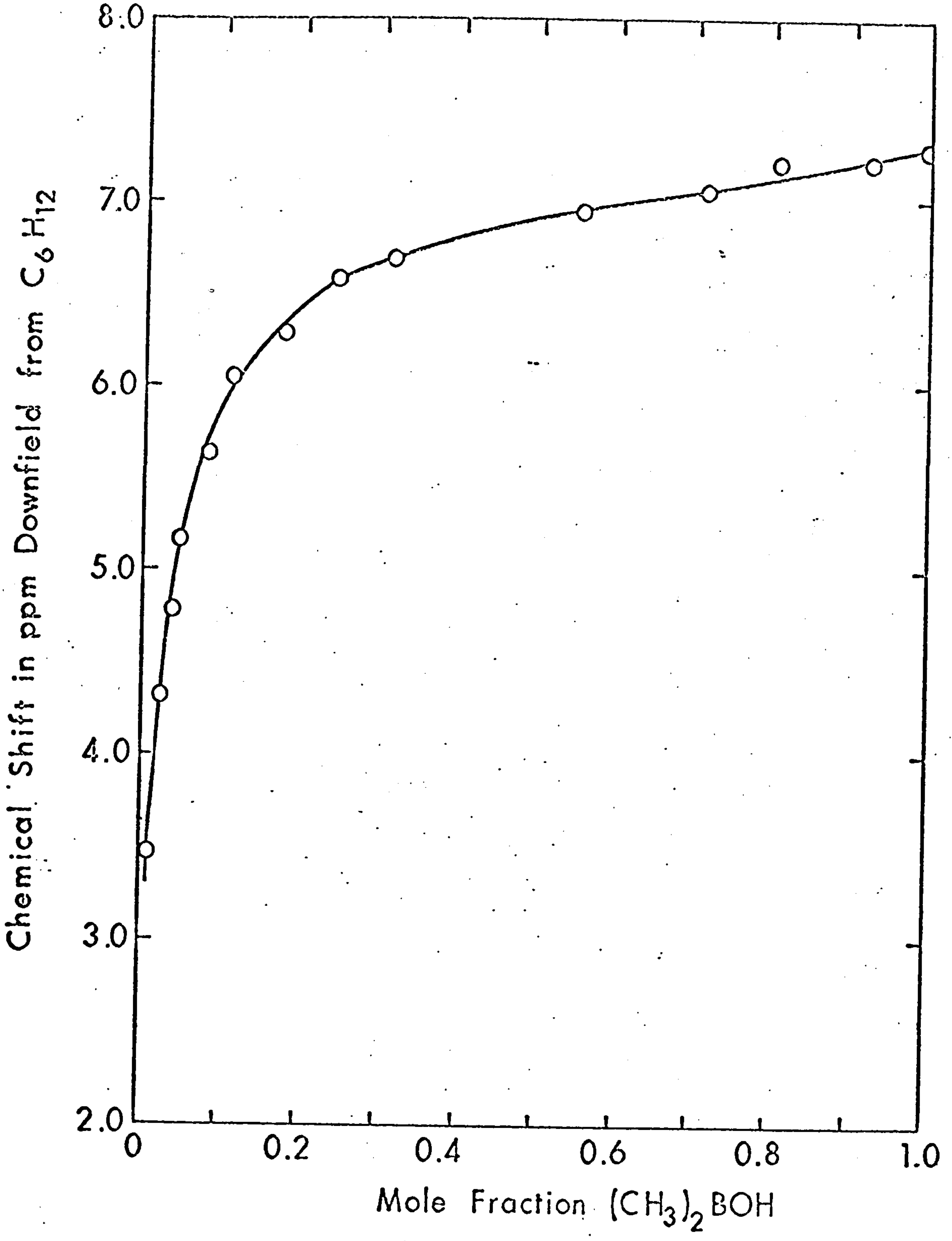

FIGURE 14. Chemical shift of the OH proton resonance *versus* mole fraction of dimethylboric acid in cyclohexane at 36°C.

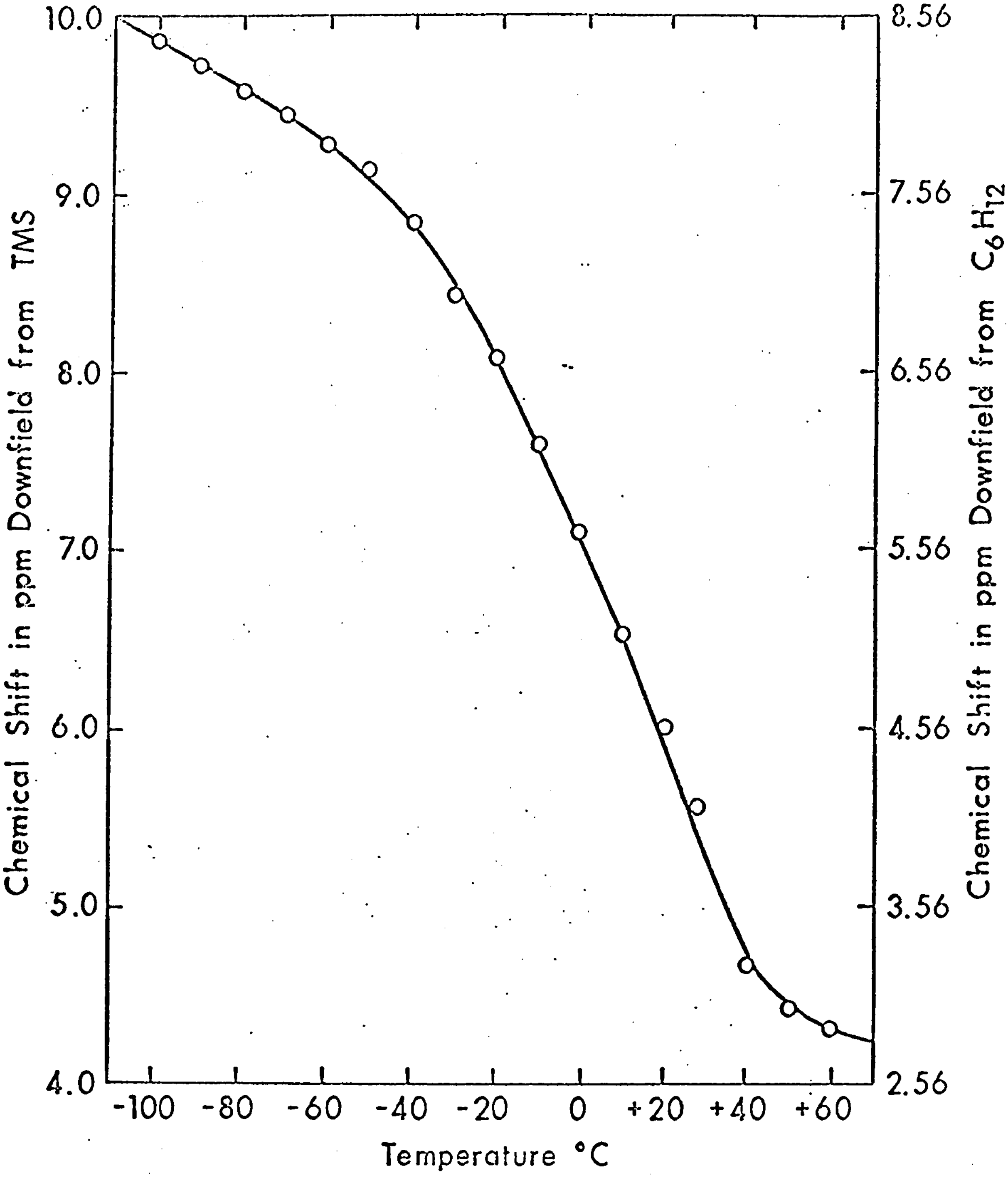

FIGURE 15. Chemical shift of the OH proton resonance *versus* temperature for a 1 mole % solution of dimethylboric acid in methylcyclohexane. Shifts relative to cyclohexane are calculated by subtracting 1.44 ppm from the chemical shift relative to tetramethylsilane (TMS).

and Goubeau (66) and by De Moor and Vander Kelen (67). The OH stretch previously reported at 3675 resolves into a triplet at 3682, 3672 and 3662 when run on an expanded scale with the higher resolution our grating instrument affords (Figure 16). The overall half-width of this triplet absorption is ca. 25 cm^{-1}. The shape of the multiplet strongly resembles incompletely resolved P, Q and R bonds. This absorption is attributed to the monomeric species.

A 5 - 10% solution of the acid in carbon tetrachloride exhibited characteristic hydrogen bond effects. Two absorptions occur for the OH stretch; a sharp high frequency absorption at 3635 cm^{-1} (half-width 27 cm^{-1}) and a broad absorption centered at 3375 cm^{-1} (half-width ca. 250 cm^{-1}, see Figure 16). The latter, a smooth curve exhibiting no fine structure, is attributed to the hydrogen bonded species.

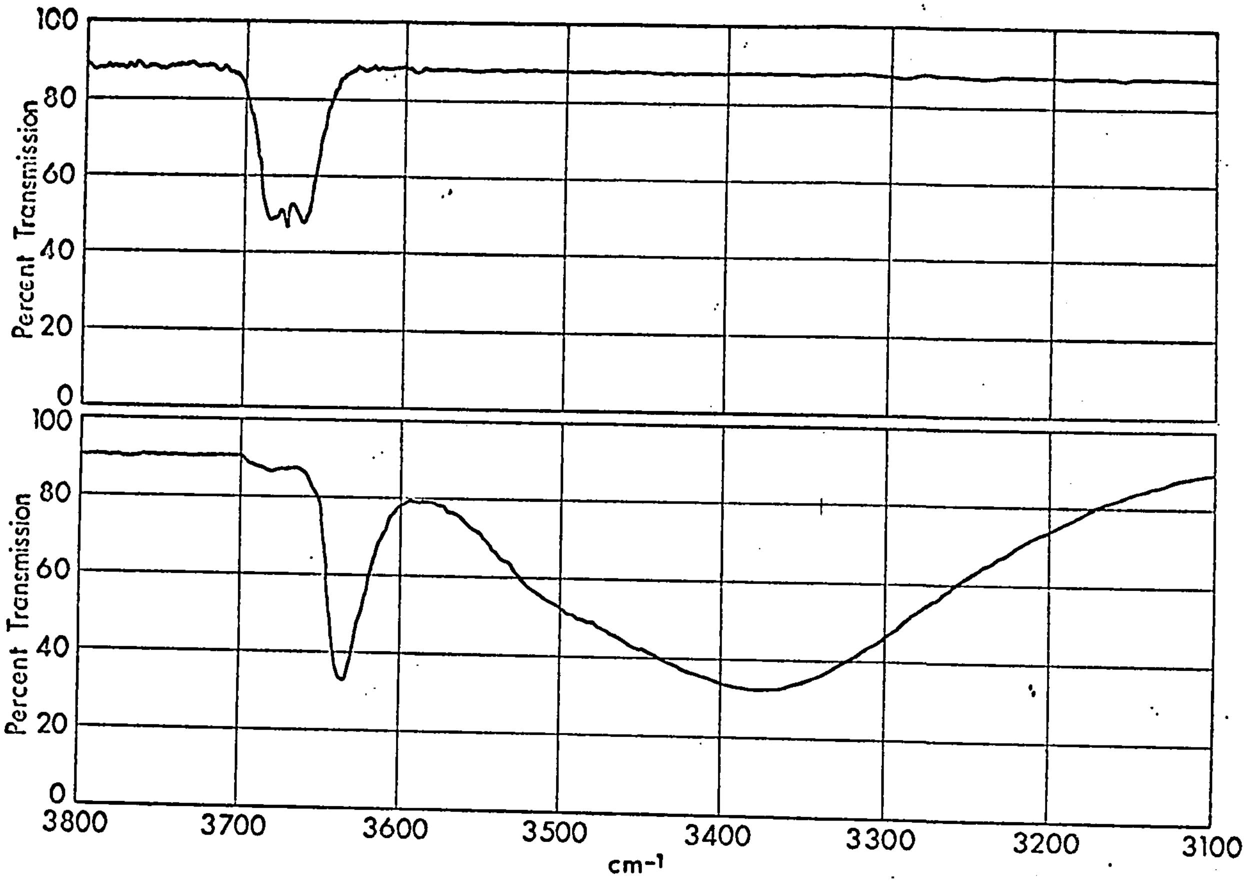

FIGURE 16. Expanded infrared spectra of the OH stretching frequencies in dimethylboric acid. The upper spectrum was obtained from the gas phase; the lower from a 5-10% solution in CCl_4.

DISCUSSION

Chapter IV

This chapter will interpret and discuss the results described in Chapter III. The discussion will center around the interaction of the sp^3-hybridized lone pair electrons of oxygen with the vacant p_z orbital of boron in the B-O bond.

1. The Characterization of Dimethylboric Anhydride.

The original synthesis of dimethylboric anhydride involved dehydration of dimethylboric acid using phosphorus pentoxide (24):

$$2(CH_3)_2BOH + P_2O_5 \rightarrow 2HPO_3 + (CH_3)_2BOB(CH_3)_2.$$

This method proved to be quite unsatisfactory. The products obtained were highly variable, and a pure compound exhibiting the reported vapor pressure of 118 mm at 0°C (24), could not be isolated. An alternative route was deemed necessary, and a convenient, reproducible method involving partial hydrolysis of dimethylboron chloride,which gives rise to easily separable products is reported here:

$$2(CH_3)_2BCl + H_2O \rightarrow (CH_3)_2BOB(CH_3)_2 + 2HCl$$

A similar reaction has been used to prepare diphenylboric anhydride (38) and di-n-butylboric anhydride (39).

Although an elemental analysis of dimethylboric anhydride was not carried out, the preparative method, the gas density molecular weight, and the accumulated spectroscopic data establish the identity of the compound beyond all reasonable doubt.

Mass Spectrum (Table III). While mass spectral data concerning alkylalkoxyboron compounds is rather limited, it has been reported (68), that the parent ions are of markedly lower abundance than in the case of borates. Furthermore, it is stated that most of the prominent peaks are characteristic of alkoxyboron compounds and one finds peaks due to $(p\text{-}R)^+$, $(p\text{-}OR)^+$, OR^+ and R^+. Rearrangement ions $ROBOH^+$ (and presumably $RBOH^+$) are also notable.

Although dimethylboric anhydride is not an alkylalkoxyboron compound, similar features were evident (Table III). For example, the very low abundance of the parent ion, the prominent $(p\text{-}CH_3)^+$ and CH_3^+ peaks and the rearrangement ion CH_3BOH^+ are the most obvious features of the spectrum.

It is evident from the spectrum that rearrangements are taking place. For example, the base peak at 43 m/e was shown by its exact mass to be $CH_4B^{11}O$. Only one metastable peak at 20.3 m/e was observed, corresponding to $(CH_3)_2B^{11}OB^{11}(CH_3)^+ \rightarrow (CH_3)_2B^{11+} + (CH_3)B^{11}O$. Suggested assignments of other peaks are listed in Table III. The presence of only one observable metastable peak, coupled with occurrence of rearrangement, allows little interpretation of the fragmentation pattern. The isotopes of boron simplify identification of boron containing ions.

The region of 33, 33.5 and 34 m/e is of some interest. The peak at 33.5 must be due to a double charged ion, and $(CH_3)B^{10}OB^{11}(CH_3)^{++}$ is the assignment. The peak at 34 has a C^{13} isotope peak at 34.5, indicating it is also a doubly charged ion, assigned to be $(CH_3)B^{11}OB^{11}(CH_3)^{++}$. Any C^{13} isotope peak of the peak at 33 is masked by the 33.5 peak mentioned. The removal of two electrons from a molecule is facilitated by the presence of π-electron density (69). The presence of these peaks, and also a small peak at 26.5 attributed to $CH_3B^{11}B^{11}O^{++}$, lend supporting evidence for B-O π interaction.

<u>Infrared Spectrum</u> (Table IV and Figure 2). The C-H stretching frequencies require no comment. In accord with Lehmann <u>et</u> <u>al</u>., (70), who place all B-C asymmetric stretching frequencies in the range from 1116 to 1138 cm^{-1}, we assign the 1135 cm^{-1} absorption to the B-C asymmetric stretch. The B-C symmetric stretch is assigned to the weak absorption at 730 cm^{-1}, following Ulmschneider and Goubeau (66), who have similarly assigned absorptions at 718 and 738 cm^{-1} in dimethylboric acid. From the work of Lehmann <u>et</u> <u>al</u>. on trimethylboron (70) and tetramethyldiborane (71), it is clear that the absorptions at 1165 and

940 cm^{-1} may be assigned to CH_3 rocking modes.

There is general agreement that in methylboron compounds the asymmetric methyl deformation occurs in the region of 1450 cm^{-1}, while the symmetric mode occurs in the region 1350 - 1300 cm^{-1} (reference (2) p.226). On this basis, the absorption at 1320 cm^{-1} is assigned to the symmetrical methyl deformation, while the band due to asymmetric methyl deformation presumably lies within the very broad absorption centered at 1405 cm^{-1}.

The B-O stretching frequencies are somewhat difficult to assign. Ulmschneider and Goubeau (65) assign a weak shoulder at 1276 cm^{-1} in the spectrum of dimethylboric acid to the B-O stretch. No equivalent exists in the spectrum of the anhydride. Abel _et_ _al_. (72) report two B-O stretching frequencies [3] for diphenylboric anhydride at 1262 and 1378 cm^{-1}. It is conceivable that both symmetric and asymmetric modes of the B-O-B group, as well as the symmetric CH_3 deformation mentioned previously, are contained in the broad band at 1405 cm^{-1}.

2. Other Compounds Prepared. Dimethylmethoxyboron has been prepared and characterized previously (25,26) and pre-

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[3] Diphenylboric anhydride, as synthesized in this laboratory, exhibited a strong absorption at 1262 cm^{-1}, although there was no appreciable absorption at 1378 cm^{-1}.

sents no special interest except for the new preparation which has been described in Chapter II, and the mass spectrum (Table V), which has apparently not been previously reported. As expected for alkylalkoxyboron compounds (68), the parent ion is weak; in this case it is covered by an impurity, of which more will be said later. It was also found that the $(p\text{-}CH_3)^+$, $(p\text{-}OCH_3)^+$, OCH_3^+ and CH_3^+ peaks were quite prominent. Furthermore, the rearrangement ion, CH_3BOH^+, was strong.

The presence of a single metastable peak at 14.7 m/e corresponds to the transition $CH_3BOCH_3^+ \rightarrow CH_3CH_2^+ + BOH$. The assumption that the ion at 57 m/e is $CH_3BOCH_3^+$ rather than $(CH_3)_2BO^+$ is based upon bond energy data (73), which shows the B-C bond to be somewhat weaker than the O-C bond. As in the case of dimethylboric anhydride, the presence of rearrangement, coupled with only a single metastable peak, allows little interpretation of the fragmentation pattern.

An accurate mass determination identified the peak at 73 m/e as being $(CH_3O)_2B^{11}$. As recombination is unlikely, it would appear that the compound $CH_3B(OCH_3)_2$ was present as an impurity. Since this $(p\text{-}CH_3)^+$ peak at 73 m/e is only 3% of the $(p\text{-}CH_3)^+$ peak of $(CH_3)_2BOCH_3$, it may be concluded that the amount of impurity is small. Gerrard (74) reports that in the preparation of alkylalkoxyboron compounds, there has been little success in obtaining pure specimens because of exchange reactions. Therefore, the $CH_3B(OCH_3)_2$ may have originated from the exchange reaction

$$2(CH_3)_2BOCH_3 \rightleftarrows (CH_3)_3B + CH_3B(OCH_3)_2.$$

A peak at 55 m/e, attributable to $(CH_3)_3B^{10}$ or $CB^{11}O_2$, of similar abundance (3%) supports this suggestion.

Dimethylpentafluorophenoxyboron is a new compound, the preparation of which presented no problems. The results of the microanalysis, nmr, and mass spectrum (Table VI) leave no doubt concerning the identity of the compound.

The parent ions at 223 and 224 m/e are strong in contrast to the methoxy derivative, and exhibit the ratio of intensities of $B^{10}:B^{11}$ in natural abundance. The $(p\text{-}CH_3)^+$ ions are also strong, and again exhibit the same ratio of intensities. The base peak at 41 m/e is attributed to $(CH_3)_2B^{11+}$. A good deal of fragmentation is evident, as well as some rearrangement. No fragmentation pattern is suggested because of the lack of metastable peaks.

Dimethyl-t-butoxyboron, a compound not previously reported, was prepared but not without some difficulty. Abel *et al.* (75) reported poor yields in the reaction

$$(C_6H_5)_2BCl + \underline{t}\text{-BuOH} \xrightarrow{\text{solvent}} (C_6H_5)_2BO\text{-}\underline{t}\text{-Bu} + HCl$$

presumably caused by dealkylation of the ester by hydrogen chloride and secondly, by the reaction of hydrogen chloride with t-BuOH.

$$(C_6H_5)_2BO\text{-}\underline{t}\text{-}Bu + HCl \rightarrow (C_6H_5)_2BOH + \underline{t}\text{-}BuCl$$

$$\underline{t}\text{-}BuOH + HCl \rightarrow \underline{t}\text{-}BuCl + H_2O$$

The first attempt to produce dimethyl-t-butoxyboron involved the reaction of t-butanol with dimethylboron chloride in a closed Pyrex vessel. The exclusive products were t-butyl chloride and dimethylboric acid, no doubt due to the side reactions involving hydrogen chloride which is formed *in situ*. When the reaction was repeated, using an appropriate quantity of trimethylamine to remove free hydrogen chloride, a fair yield of dimethyl-t-butoxyboron was obtained, lending strong support to Abel's hypothesis.

While the mass spectrum (Table VII) fails to show peaks for the molecular ions at 113 and 114 m/e, strong peaks corresponding to the $(p\text{-}CH_3)^+$, $(p\text{-}OC(CH_3)_3)^+$, and $C(CH_3)_3^+$ ions are present. The $(p\text{-}CH_3)^+$ ions at 98 and 99 m/e exhibited the ratio of intensities expected for boron containing compounds. However, the $(p\text{-}OC(CH_3)_3)^+$ ions at 40 and 41 m/e do not. The presence of a single metastable peak at 29.5 corresponds to the transition $(CH_3)_3C^+ \rightarrow CH_3C^+CH_2 + CH_4$. The presence of $CH_3C^+CH_2$ may account for the unexpectedly high intensity of the peak at 41 m/e. The strong peak at 59 m/e is attributed to $(CH_3)_2C^+OH$.

These data, coupled with the nmr spectrum, which shows two resonances in the regions expected for $(CH_3)_2BO$ and $(CH_3)_3C$ in the correct intensity ratio, leave no doubt concerning the identity of the compound.

3. Studies on Dimethylboric Anhydride.

Complex formation. The results of the tensimetric studies (Chapter III, Section 3), provide interesting information about the donor strength of the oxygen atom towards acceptor molecules, and the acceptor strength of the boron atoms toward strong Lewis bases, such as trimethylamine. This information, when examined with reference to other acceptor-donor systems, provides some insight into the B-O bond, and the effects of π-bonding in this bond.

Examining first the data on oxygen base strength, it is evident that dimethylboric anhydride does not behave as a Lewis base towards trimethylboron; this is not unexpected, since no complex is formed between dimethyl ether and trimethylboron under equivalent conditions (76). Unfortunately, the boron trihalides, which are stronger Lewis acids, cannot be used since the following cleavage reaction occurs (77):

$$3(CH_3)_2BOB(CH_3)_2 + 2BX_3 \rightarrow 6(CH_3)_2BX + B_2O_3$$

However, if a dimethylboron halide were used as the reference Lewis acid, the products would be identical to the reactants:

$$(CH_3)_2BOB(CH_3)_2 + (CH_3)_2B^*Cl \rightleftarrows (CH_3)_2B^*OB(CH_3)_2 + (CH_3)_2BCl$$

In fact, the single resonance observed in the room temperature spectrum of this system (Table XI) is consistent with a rapidly exchanging system of this nature. Dimethylboron chloride, a stronger acceptor than trimethylboron, shows no indication of complex formation, and it may be concluded that the basicity of oxygen in dimethylboric anhydride is rather low.

The results of the study of the Lewis acid characteristics of dimethylboric anhydride show that it is considerably weaker than trimethylboron. The enthalpies of dissociation of $(CH_3)_2BOB(CH_3)_2 \cdot N(CH_3)_3$ and $(CH_3)_3B \cdot N(CH_3)_3$ are 9.5 kcals. and 17.62 kcals. (62), respectively. The trimethylphosphine adduct of dimethylboric anhydride is completely dissociated in the gas phase, while $(CH_3)_3B \cdot P(CH_3)_3$ is not (78). Finally, dimethyl sulfide forms a recognizable adduct at -78.5°C with trimethylboron (76) but not with dimethylboric anhydride.

<u>Constant temperature nmr</u>. (Chapter III, Section 4). The nmr data support the tensimetric results fully. Tensimetric studies show that only trimethylamine, of the bases

studied, was strong enough to form a measurable complex in the gas phase. The large upfield shift of the B-methyl resonance in the 1:1 $(CH_3)_4B_2O{\cdot}N(CH_3)_3$ sample, as compared to the B-methyl resonance in the free $(CH_3)_4B_2O$, is consistent with formation of a strong complex (57). The large downfield shift of the N-methyl resonance in the 1:1 $(CH_3)_4B_2O{\cdot}N(CH_3)_3$, as compared to the N-methyl resonance of free $N(CH_3)_3$ is also to be expected (58,59). The lack of any change of chemical shift for all resonances in the samples involving dimethyl ether, dimethyl sulfide and trimethylboron indicate little or no complex formation, in accord with the results of the tensimetric studies. In the case of trimethylphosphine the small shifts of the P-methyl and B-methyl resonance are in accord with the weak complexing found in tensimetric work.

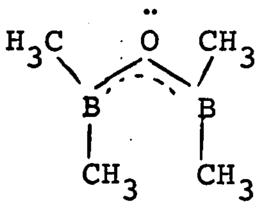
It is feasible to discuss these results in terms of the boron-oxygen bond, presuming that two competitive effects are involved. Purely inductive effects would be expected to increase the acceptor strength of the boron atoms relative to trimethylboron, oxygen being more electronegative than CH_3; this effect would also increase the donor strength of the oxygen atom relative to dimethyl ether, since $B(CH_3)_2$ is more electropositive than CH_3. On the other hand, the effect of π-bonding involving oxygen lone pairs and the vacant boron 2p orbitals would be to weaken both the Lewis acidity of boron and the Lewis basicity of oxygen.

It is therefore reasonable to attribute the lower Lewis acidity of dimethylboric anhydride to this effect. The lack of evidence for a 2:1 complex between trimethylamine and dimethylboric anhydride is not inconsistent with this interpretation. When one of the two boron atoms is "electronically saturated" due to complexing with trimethylamine, the vacant p orbital is no longer available to an oxygen lone pair. Therefore the decreased delocalization of oxygen lone-pair electrons should increase the double bond character between oxygen and the remaining uncomplexed boron atom, thereby lowering the Lewis acidity towards excess trimethylamine.

Variable temperature nmr studies. (Chapter III, Section 5). To account for the unexpected splitting of the resonance for dimethylboric anhydride into two 1:1 resonances at low temperature, it is suggested that the dimethylboron groups are so aligned as to maximize their individual overlaps with the two sp^3-hybridized lone pairs of oxygen. In such a conformation, shown schematically in Figure 5, there are two distinct environments which might be termed "inner" ($CH_3$2 and $CH_3$3) and "outer" ($CH_3$1 and $CH_3$4).

A molecular model indicates that rotations of the B-methyl groups about the B-O bond are sterically hindered and this phenomenon, rather than π-interaction, could conceivably give rise to the aforementioned effect. To clarify the situation, a similar study was done on di*iso*propylether, the most sterically similar carbon analogue of dimethylboric anhydride. As the nmr spectrum was unchanged from +30° to -90°, it appears likely that π-interaction, rather than steric factors, is responsible for the non-equivalence of the B-methyl groups.

Although the above interpretation and Figure 5 assume sp^3 hybridization of oxygen, it should be pointed out that the low-temperature non-equivalence could also be explained on the assumption that oxygen is sp^2 hybridized, with one lone pair in a hybrid orbital and the other in the p_z orbital. Thus, a single oxygen lone pair would be involved in a delocalized π-bond including both boron atoms. The resulting planar structure, shown in V, could equally well account for the observed non-equivalence. The



V

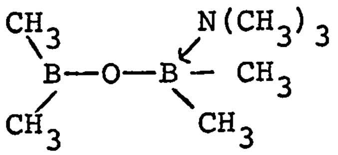
results of the chloroform dilution shift study, to be discussed later, favor the sp^3 model.

The possibility that the B-O-B bond is linear, with sp hybridization for oxygen, was also considered. In this case, one would expect two boron-oxygen π bonds at 90° to one another, in an allene-like structure, which does not allow for non-equivalence of methyl groups.

Dimethylboric anhydride-trimethylamine systems. As reported in Chapter III, (especially Figure 4), the introduction of one equivalent of trimethylamine had a marked effect upon the behavior of the B-methyl resonance(s). The upfield shift of the B-methyl resonance (0.46 ppm) at room temperature is typical complex formation. The separation of the B-methyl resonance into two 1:1 resonances at -41°C (separation in the pure anhydride occurred at -69°C) indicates that the process is different from that in the pure anhydride. This new splitting is considered to be due to the slowing down of the exchange rate in the reaction

$$(CH_3)_2BOB(CH_3)_2 \cdot N(CH_3)_3 \rightleftarrows (CH_3)_2BOB(CH_3)_2 + N(CH_3)_3.$$

The two B-methyl resonances observed below -41°C are then due to the non-equivalence of the B-methyl groups *at each end of the molecule.* The unadducted boron atom is



VII

still sp^2-hybridized, presumably with some degree of B-O π-interaction existing; the adducted boron atom is now sp^3-hybridized with no B-O π-interaction possible.

Evidence for the correctness of this interpretation comes from the study involving only one half equivalent of trimethylamine. Upon cooling the sample, the single B-methyl resonance broadened, and at -41°C separated into three resonances (cf. Figure 4). The low field resonance, which contained the same area as the other two resonances combined, had the same chemical shift as that observed for free dimethylboric anhydride. The two 1:1 high field resonances exhibited the same chemical shifts and maximum separations as the resonances observed for the sample containing one equivalent of trimethylamine. Therefore, it appears that the exchange rate of trimethylamine-dimethylboric anhydride has slowed sufficiently such that the individual species are observable.

The individual species in this study must then be one equivalent of uncomplexed dimethylboric anhydride (the low-field resonance) and one equivalent of complexed dimethylboric anhydride (the two 1:1 high-field resonances).

If the low field resonance is due to uncomplexed dimethylboric anhydride, it would be expected to exhibit two non-equivalent resonances below the coalescence temperature for this phenomena, -69°C. In fact, this was observed. However, due to coincidental overlap of the high field resonance of this latter process, with the low field resonance of the previous process, a 1:2:1 spectrum was observed.

The enthalpy of activation of the dimethylboric anhydride-trimethylamine exchange reaction was calculated to be 11.5 ± 1.1 kcals. The tensimeter studies yielded a value of 9.5 ± 0.6 kcals. for the enthalpy of dissociation. These results are quite similar, bearing in mind that the first figure was obtained from solution studies and the second from gas phase studies. The similarity of ΔH°_{diss} and $\Delta H^{\ddagger}_{diss}$ warrants further comment.

The activation energy requirements for a number of boron trifluoride complexes are small or perhaps negligible (79) although boron trifluoride is an example of a Lewis acid for which the reorganization energy term must be considerable (80). It appears that this statement can be carried over to the compound in question, since the observed enthalpy of activation is only slightly larger than the observed enthalpy of dissociation. This leads to the conclusion, that the activated complex is very similar to the dissociated species. Furthermore, the similar values of the two energies suggests an exchange mechanism such as the following:

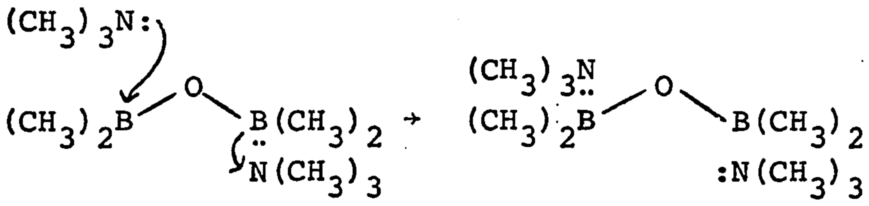
$$(CH_3)_2BOB(CH_3)_2\cdot Base(1) \xrightarrow{slow} (CH_3)_2BOB(CH_3)_2 + Base(1) \quad (I)$$

$$\left.\begin{array}{l}(CH_3)_2BOB(CH_3)_2 + Base(1) \xrightarrow{fast} (CH_3)_2BOB(CH_3)_2\cdot Base(1) \\ (CH_3)_2BOB(CH_3)_2\cdot Base(2) + Base(1) \xrightarrow{fast} (CH_3)_2BOB(CH_3)_2\cdot Base \\ \qquad\qquad\qquad\qquad\qquad\qquad (1) + Base(2)\end{array}\right\} (II)$$

A similar mechanism has been suggested for the $Ga(CH_3)_3$ - $N(CH_3)_3$ system (81). Furthermore, the small entropy is consistent with the postulated mechanism (82).

As reported in Chapter III, when two equivalents of trimethylamine were present in the sample, the spectrum remained unchanged throughout the temperature range +30 to -90°C. Two interpretations are possible. The first is the formation of a di-adduct, which would be expected to give rise to equivalent B-methyl groups and a single resonance. Against this interpretation lies the fact that the chemical shift of the N-methyl resonance is that expected for the average signal of rapidly exchanging free and adducted $N(CH_3)_3$ groups.

The second interpretation is that the exchange reaction

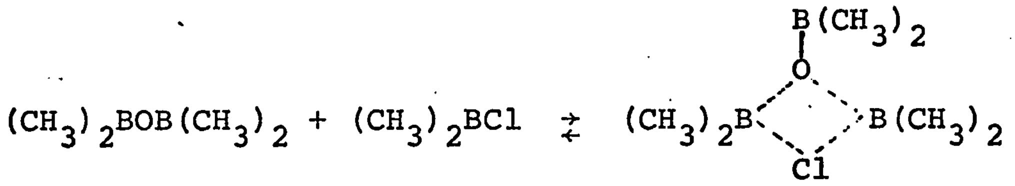


is taking place at a rapid pace. This mechanism, where free base attacks the unadducted end of the molecule, provides a low energy pathway to exchange. Supporting the above view is the fact that a 10% excess of one equivalent of base caused the B-methyl spectrum to collapse to a single resonance which was observed to broaden only in the region of -95°C, rather than separate into two signals at -41°C. Other systems susceptible to excess base have been described in the literature (81,83,84).

In order to provide further information concerning the possibility of a di-adduct of dimethylboric anhydride with trimethylamine, a system containing four equivalents of trimethylamine was studied. If a di-adduct existed, and if the rate of exchange were slow, two N-methyl resonances would be expected; one resonance at higher field due to free $N(CH_3)_3$ and an equal resonance at lower field due to adducted $N(CH_3)_3$. In fact, only a single resonance was observed, indicating exchange with either the di-adduct or with the mono-adduct. However, the chemical shift observed for the N-methyl resonance is approximately at the position expected for the averaged resonance for three equivalents of free trimethylamine and one equivalent of complexed trimethylamine. Furthermore, the chemical shift of the B-methyl resonance is essentially the averaged shift of the two resonances in the 1:1 sample. These data indicate that if a di-adduct does exist, it is quite weak (cf. Chapter III, Section 3).

Dimethylboric anhydride - Dimethylboron chloride. The room temperature spectrum of this system, containing two moles of the chloride to one mole of the anhydride, exhibited a single resonance. The position was that of a weighted average for $(CH_3)_2BCl$ and $(CH_3)_2BOB(CH_3)_2$. As described in Chapter III Section 5, at temperatures where exchange was slow, the spectrum contained three resonances, integrating 2:1:1, and attributed to $(CH_3)_2BCl$ and $(CH_3)_2BOB(CH_3)_2$ respectively.

Several conclusions may be drawn from these results. Firstly, exchange does occur and the enthalpy of activation for this exchange is calculated to be 5.6 ± 0.4 kcals. This somewhat low energy may indicate a four-center mechanism



where the dotted lines represent bond breaking and forming. The high negative entropy of activation -22.4 e.u., suggests a four-center mechanism where two bond-making and two bond-breaking steps are synchronous, or an intermediate complex containing both reagents in a donor-acceptor relation (82).

Secondly, it is apparent that a complex does not exist at low temperature. If this were the case, two resonances would be expected for $(CH_3)_2BCl$, one for free

$(CH_3)_2BCl$, and one for complexed $(CH_3)_2BCl$. Only a single resonance with a chemical shift identical to that observed for free $(CH_3)_2BCl$ is observed, while the chemical shifts for the resonances of $(CH_3)_2BOB(CH_3)_2$ are identical to those exhibited by the pure compound.

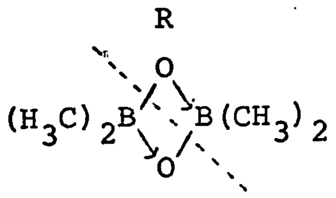
4. Dimethylmethoxyboron and Related Compounds.

Tensimetric Studies. The data reported in Chapter III section 6, show the adduct between dimethylmethoxyboron and trimethylamine to be completely dissociated in the gas phase, although the high value of the Trouton constant indicates association in the liquid phase. Coates (25) reports similar behavior for the dimethylamine adduct. It is, therefore, a weaker Lewis acid than dimethylboric anhydride. In the series, trimethylboron, dimethylboric anhydride and dimethylmethoxyboron, the Lewis acidity of the boron atom(s) decreases as the ratio of oxygen to boron increases, as expected for the occurrence of π-bonding. Further studies on this system, using nmr techniques, will be discussed shortly.

Variable temperature nmr studies. (Chapter III, Section 6). The separation of the B-methyl resonances at temperatures below -41°C has been attributed in this work to the barrier to rotation about the B-O bond due to overlap of an oxygen lone pair with the vacant p orbital of boron. This is similar to the interpretation of the results for dimethylboric anhydride. Similar phenomena have been observed for many other systems involving partial π bond formation (9,10,11,12,61,85). The enthalpy of activation, calculated from the averaged data, is 8.1 ± 0.7 kcals., a substantially smaller value than the values found for the B-N bond (9,10,11,12), which range from 14 to 21 kcals. This is in agreement with the results obtained by other workers (8,14), where nitrogen was found to "back donate" to boron more powerfully than oxygen.

It is well to draw the attention of the reader to the fact that the observed coalescence of the B-methyl resonances of dimethylmethoxyboron could conceivably be due to a process other than that of rotation about the B-O bond.

It is well established that alkoxy-group exchange occurs among esters of boric acid and its alkyl and aryl derivatives (86,87,88). Heyes and Lockhart (87) postulate a four-center intermediate (VIII) for this exchange



VIII

It is evident that in this intermediate, the non-equivalence of the B-methyl groups has been lost; the coalescence of B-methyl nmr signals at higher temperatures could thus arise through the formation and dissociation of this species.

However, from the work of Heyes and Lockhart (87) one calculates that the lifetimes with respect to alkoxy-group exchange at -44°C are of the order of one second. The lifetimes of the B-methyl groups at a particular site, as observed in the present work, are in the range 0.025 - 0.051 seconds [4] at -44°C. The alkoxy group exchange mechanism can therefore be excluded as the process by which B-methyl groups become equivalent in this work. One is left with rotation about the boron oxygen bond as the operative process.

<u>Dimethylmethoxyboron-trimethylamine.</u> The presence of a small quantity of amine, 0.10 equivalents, caused the B-methyl doublet observed for pure dimethylmethoxyboron at low temperatures to collapse. This is attributed to the rapid exchange reaction:

$$(CH_3)_2BOCH_3 + N(CH_3)_3 \rightleftarrows (CH_3)_2BOCH_3 \cdot N(CH_3)_3$$

Apparently, this reaction is rapid enough to shorten the lifetime of the free $(CH_3)_2BOCH_3$ to such an extent, that the B-methyls in non-equivalent sites (due to hindered

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[4] The first value refers to a 30% methylcyclohexane solution, the second to a 15% $CFCl_3$ solution of dimethylmethoxyboron. The variation is due to the fact that maximum separations ($\nu_A°-\nu_B°$) differ in the two solvents, and as mentioned in Chapter II, the critical lifetime for coalescence depends on this separation.

rotation about the B-O bond) are no longer observable using nmr techniques. When adducted to trimethylamine, the boron atom becomes sp^3-hybridized, causing the B-methyls to become equivalent. Therefore the observed B-methyl resonance is a weighted average of the free and adducted resonances.

Studies on the system containing two equivalents of trimethylamine also showed signs of rapid exchange rate. Throughout the temperature range +30 to -90°C, the N-methyl groups exhibited a single resonance, rather than a doublet due to free and complexed trimethylamine. It was observed that the chemical shift of all resonances were temperature dependent; the B-methyl and O-methyl resonances moving upfield with decreasing temperature, while the N-methyl resonance shifted downfield. This would indicate a shift in the equilibrium constant to the right for the above reaction.

Studies on the system containing one equivalent of trimethylamine are described in Chapter III Section 6. The enthalpy of dissociation, $\Delta H° = 6.8 \pm 0.2$ kcals., can be compared to that for dimethylboric anhydride-trimethylamine (9.5 ± 0.5 kcals.) and trimethylboron-trimethylamine (17.62 kcals.) (62). As the ratio of oxygen to boron in the compound increases, the enthalpy of dissociation, $\Delta H°$, decreases. This is consistent with the expected decreasing availability of the vacant p_z orbital on boron towards the amine, due to interaction of the oxygen lone pair electrons with this p_z orbital of boron.

Dimethylpentafluorophenoxyboron. (Chapter III, Section 7). The failure of this compound to exhibit broadening and separation of the B-methyl resonance as low as -90°C is attributed to the electron-withdrawing power of the pentafluorophenyl groups (89). This would tend to lower the amount of electron delocalization towards the boron atom, thereby decreasing the barrier to internal rotation about the B-O bond. This can be interpreted as an indication of the susceptibility of B-O π-bonding to the nature of the substituent on the oxygen atom.

Dimethyl-t-butoxyboron. (Chapter III, Section 7). The interest in this compound lies in the steric requirements of the t-butyl group, and the effect upon the barrier to rotation about the boron-oxygen bond. As results in Chapter III show, the barrier is observable, although the coalescence temperature is in the region of -90°C rather than -40°C observed for the methyl analogue. However, it is well to point out that the coalescence temperature is not directly related to the activation energy of the process. It is concluded that in spite of the bulky t-butyl group, the molecule can still align itself in the conformation which permits maximum overlap.

5. The Relative Base Strength of Oxygen, (Chapter III, Section 8).

If interaction of the lone pair electrons on oxygen is the cause of the lowered Lewis acidity of the boron compounds discussed, it is evident that the Lewis basicity of the oxygen atoms must be decreased as the ratio of boron to oxygen in the compounds increases. Since the usual Lewis acids (trimethylboron, boron trifluoride) are either too weak or too reactive, an alternative method was needed, the obvious choice being the chloroform dilution shift method, which has been fully described by Abel *et al*. (63).

The results of this study (Table XIX) fully support the previous interpretations. Of particular interest is the low value obtained for dimethylboric anhydride. This indicates a marked lowering of the availability of the oxygen lone pairs relative to the carbon analogue, di-*iso*propyl ether. As is made clear in reference (63), "steric effects are extremely important". The similarity of the steric requirements in the above case minimize this effect. The view that both lone pairs in dimethylboric anhydride are involved in π-bonding is upheld by the intermediate value of the shift in dimethylmethoxyboron, where only one lone pair is available for complexing to chloroform.

6. Dimethylboric acid. This work, while not directly related to boron-oxygen π-bonding, may be considered an auxiliary study, rounding out the study of acid, anhydride and ester.

The Trouton constant for dimethylboric acid is reported to be 29.7 (27). The results of the study involving the vapor pressure lowering of butane containing various mole fractions of dimethylboric acid (Table XXI) show that the association is complex, with higher polymers present.

The gas phase infrared spectrum of dimethylboric acid has been reported by Ulmschneider and Goubeau (66), The OH stretch previously reported at 3675 cm^{-1} resolves into a triplet at 3682, 3672 and 3662 cm^{-1} when run on an expanded scale with the higher resolution our grating instrument affords. The overall half-width of this triplet absorption is *ca.* 25 cm^{-1}. The shape of the multiplet strongly resembles incompletely resolved P, Q and R bands. This absorption is attributed to the monomeric species.

A 5 - 10% solution of the acid in carbon tetrachloride exhibited characteristic hydrogen bonding effects. Two absorptions occur for the O-H stretch; a sharp high frequency absorption at 3635 cm^{-1} (half-width 27 cm^{-1}) and a broad absorption centered at 3375 cm^{-1} (half-width ca. 250 cm^{-1}). The latter, a smooth curve exhibiting no fine structure, is attributed to the hydrogen bonded species.

The broad OH stretching band in carbon tetrachloride, and the concentration and temperature dependence of the hydroxyl proton chemical shift, (Figures 14,15) are typical for hydrogen bonded protons. No attempt has been made to calculate the bond energy from the temperature dependence of the nmr spectrum since the system involves several species in unknown concentrations. Further, extrapolation to obtain the maximum downfield shift of the hydrogen bonded proton is somewhat uncertain (see Figure 15).

It is of interest to examine the present results in terms of a correlation proposed by Ferraro and Peppard (90); these authors found a linear relation between the chemical shift of the hydroxyl proton in the region of "minor bond breaking" (i.e., the relatively flat portion of Figure 14 at higher concentration) and the hydrogen bond energy. A similar relation was noted between the bond energy and the difference in the infrared stretching frequencies of free and hydrogen bonded OH groups (90). Using this correlation, our value of ca. 7.3 ppm downfield from cyclohexane (8.7 ppm from tetramethylsilane) for the chemical shift of the hydroxyl proton in the region of minor bond breaking corresponds to a hydrogen bond energy of 4.6 kcals. Furthermore, the value of 260 cm^{-1} obtained by subtracting the frequency of the bonded OH from the frequency of the free OH corresponds to an energy of 4.8 kcals. The good agreement between those two values leads us to place some confidence in the values obtained.

It is of interest to note that the shift of the hydroxyl proton of the monomer, _ca_. 4.1 ppm downfield from tetramethylsilane occurs at a much lower field than that of the monomeric proton in ethanol, 0.76 ppm downfield.[5] This would indicate decreased shielding of the hydroxyl proton in dimethylboric acid, which is in keeping with the expected lowering of the electron density on the oxygen atom caused by the acceptor capability of the boron atom. A similar proposal has been put forward by Stone (91) for other systems involving the OH resonance.

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[5] This value is derived from the work of E. D. Becker, U. Liddel, and J. N. Shoolery, J. Mol. Spectr., 2, 1 (1958), on the assumption that the central peak of the CH_3 triplet is 8.83 ppm downfield from tetramethylsilane.

CONCLUSIONS

Chapter 5.

Strong supporting evidence for the existence and importance of π-bonding in the boron-oxygen bond has been presented. While this phenomenon has been generally accepted in recent years, only qualitative evidence was available. Some effects of π-bonding, particularly the existence of a barrier to internal rotation about the boron-oxygen bond, have been measured quantitatively, thereby allowing comparisons to other systems such as the well characterized boron-nitrogen system.

A variety of experimental techniques has been used in this study, in particular, tensimetric, ambient and variable temperature nmr, and infrared spectroscopy. Lewis acid and base measurements have provided a great deal of information concerning the effects of boron-oxygen π-bonding.

The results of tensimetric studies showed that, in the series $(CH_3)_3B$, $(CH_3)_2BOB(CH_3)_2$, $(CH_3)_2BOCH_3$, the Lewis acidity of the boron atoms, with respect to the reference base $N(CH_3)_3$, decreases as the ratio of oxygen to boron increases. From this information, it would appear that $p_\pi - p_\pi$ interaction, rather than an inductive effect, is of predominant importance in determining the Lewis acid character of these compounds.

Using ambient temperature nmr techniques, the chemical shift of chloroform when diluted in these compounds, was measured. Results showed that the availability of the oxygen lone pair electrons for hydrogen bonding with chloroform decreases as the ratio of boron to oxygen increases. These data, a measure of the relative Lewis basicity of oxygen in these compounds, support the π-bonding interpretation.

Variable temperature nmr studies established a barrier to rotation about the B-O bond which, in the case of $(CH_3)_2BOCH_3$, is ca. 8.0 kcals. This barrier to rotation is considered to result from the interaction of the lone pair electrons on oxygen with the vacant p_z orbital on boron. While this has long been postulated, this is the strongest evidence yet reported and the only quantitative study. Furthermore, in the anhydride, $(CH_3)_2BOB(CH_3)_2$, nmr studies suggested that each of the sp^3-hybridized lone pairs of electrons on the oxygen atom overlaps separately with the vacant p_z orbitals of the boron atoms. This novel phenomenon gives rise to a favored conformation, for which the enthalpy of activation is measured as 9.5 kcals.

The average degree of association of dimethylboric acid in solution was found to range from three to seven in the temperature region -36° to -63°C. Nmr and ir techniques established that hydrogen bonding is the source of the observed association. A correlation of the data obtained in this work with that for other systems leads to an estimate of 4.7 kcals. for the enthalpy of dissociation for the hydrogen bond in this compound.

A convenient preparation for dimethylboric anhydride, as well as some dimethylboric esters is reported and described. A full characterization of the little-known anhydride is described.

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APPENDIX A

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SRHOW

      SIMPLE REGRESSION
      T←X SR Y
      ENTERED:10/08/67

   X AND Y ARE VECTORS GIVING THE (SAME NUMBER OF) OBSERVATIONS
ON AN INDEPENDENT VARIABLE X AND A DEPENDENT VARIABLE Y. T IS
A MATRIX WITH 5 ROWS AND 3 COLUMNS CONTAINING THE RESULTS OF
FITTING THE STRAIGHT LINE Y=A+B×X BY THE METHOD OF LEAST SQUARES
IN THE FOLLOWING FORMAT:
   ROW1: MEAN OF X, ST DEV OF X, 0
   ROW2: MEAN OF Y, ST DEV OF Y, 0
   ROW3: A, 0, 0
   ROW4: B, ST ERROR OF B, T-VALUE
   ROW5: ST ERROR OF ESTIMATE, R=SIMPLE CORR COEFF, R*2 .


    ∇ T←X SR Y;N;MX;SX;MY;SY;B1;B0;R;RSQ;TV;SE;A;B
[1]    SX←((A←+/(X-MX←(+/X)÷N)*2)÷(N←(ρX))-1)*0.5
[2]    SY←((B←+/(Y-MY←(+/Y)÷N)*2)÷N-1)*0.5
[3]    B0←MY-MX×B1←(+/(X-MX)×(Y-MY))÷A
[4]    SE←((B×1-RSQ←(R←B1×SX÷SY)*2)÷N-2)*0.5
[5]    TV←B1÷SB1←(SY÷SX)÷((N-2)÷(1-RSQ))*0.5
[6]    T←(5 3)ρMX,SX,0,MY,SY,0,B0, 0 0 ,B1,SB1,TV,SE,R,RSQ
    ∇
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APPENDIX B

Table[a] giving values of the correlation coefficient, (r_{xy}), which have certain probabilities of being exceeded for observations of variables whose parent distributions are independent. To illustrate: for a sample of 10 pairs of unrelated variables, the probability is 0.10 that it will have (r_{xy}) $\geq$ 0.549.

	Probability			
N	0.10	0.05	0.01	0.001
3	0.988	0.997	1.000	1.000
5	0.805	0.878	0.959	0.992
7	0.669	0.754	0.874	0.951
10	0.549	0.632	0.765	0.760
15	0.441	0.514	0.641	0.760
30	0.307	0.362	0.464	0.572
60	0.219	0.259	0.337	0.422
100	0.168	0.199	0.259	0.327

[a] Adapted from Table V, Reference (53).

APPENDIX C

Table[a] giving values of t for use in calculating confidence limits with the equation on page . To illustrate: to calculate the 95% confidence level for 10 observations, the value of t will be 2.23.

	Confidence Level		
No. observations	0.90	0.95	0.99
2	6.31	12.71	63.66
3	2.92	4.30	9.93
4	2.35	3.18	5.84
5	2.13	2.78	4.60
6	2.02	2.57	4.03
7	1.94	2.45	3.71
8	1.90	2.37	3.50
9	1.86	2.31	3.36
10	1.83	2.26	3.25
11	1.81	2.23	3.17
12	1.80	2.20	3.11
13	1.78	2.18	3.06
14	1.77	2.16	3.01
15	1.76	2.15	2.98
16	1.75	2.13	2.95

[a] Adapted from Table 9.2, Reference (52).