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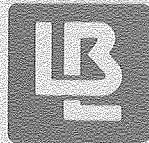
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# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## Materials & Molecular Research Division

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Thomas Stafford Briggs  
(Ph.D. thesis)

September 1980

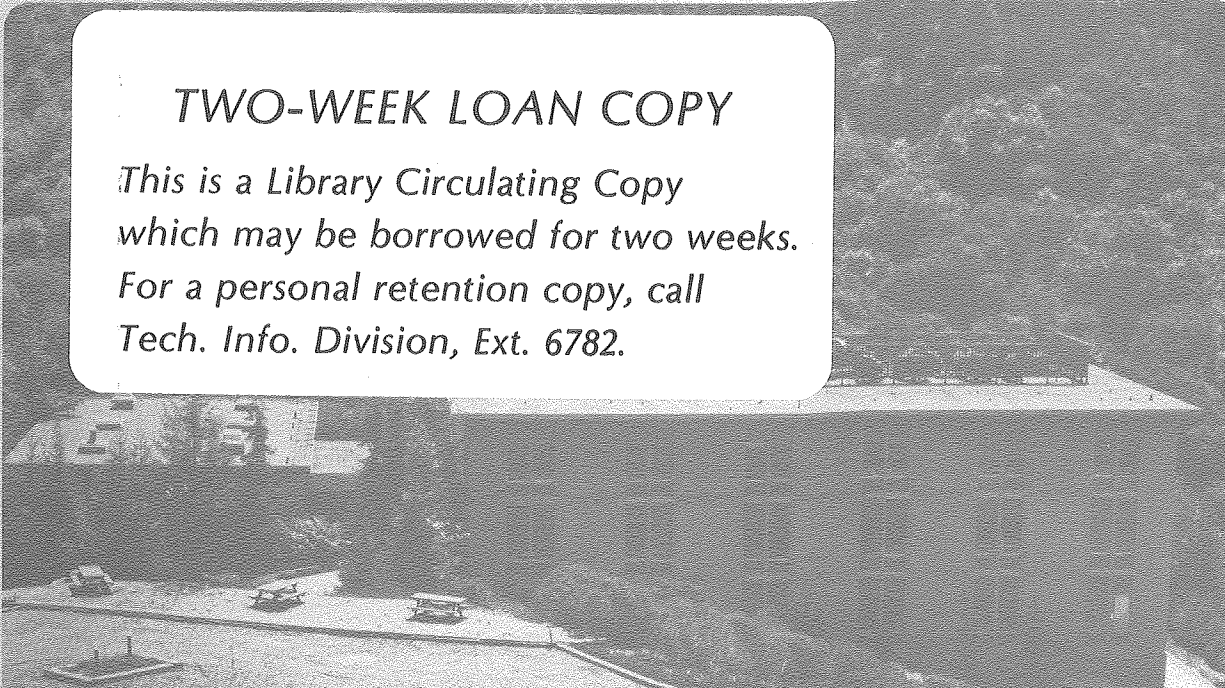
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KINETIC AND SYNTHETIC STUDIES ON BORON-NITROGEN  
HYDRIDES

Thomas Stafford Briggs  
(Ph.D. Thesis)

September 1980

Prepared for the Division of Chemical Sciences  
Office of Basic Energy Sciences  
U. S. Department of Energy  
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KINETIC AND SYNTHETIC STUDIES ON BORON-NITROGEN  
HYDRIDES

Thomas Stafford Briggs

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## ABSTRACT

The acid-catalysed ammonolysis of hydroborate ion has been studied in warm liquid ammonia solution, in the ammonium ion concentration range 0.001-0.8 M. The reaction of  $\text{BH}_4^-$  with  $\text{NH}_4^+$  to yield  $\text{NH}_3\text{BH}_3$  was found to be first order in both ions. The second order rate constant in a solution of ionic strength 0.2 at 30° is  $1.94 \times 10^{-4} \text{M}^{-1} \text{sec}^{-1}$ . Varying the ionic strength at 30° gave rate constants that followed the Bronsted-Bjerrum relationship below an ionic strength of 0.9. The rate was studied in the range 25-45°, and the activation energy was determined to be 38.5 kcal/mol.

The preparation of  $\text{NH}_3\text{BH}_3$  by the above reaction in warm, dilute liquid ammonia solution (in a pressure vessel) was found to yield a very pure product. Pure  $\text{NH}_3\text{BH}_3$  was also prepared by a new synthesis in which ammonium sulfamate reacts with sodium hydroborate in a concentrated ammonia solution at room pressure.

A new compound, diaminoborane,  $\text{HB}(\text{NH}_2)_2$ , was discovered in the products from the pyrolysis of  $\text{HN}_3\text{BH}_3$  in

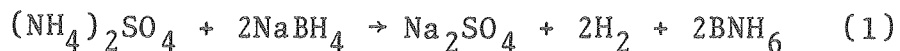


an atmosphere of ammonia. This molecule was characterized by chemical analysis, mass spectra, boron-11 nmr, infrared spectra, and microwave spectra. In liquid ammonia solutions of ammonium iodide (0.1-1.0 M  $\text{NH}_4^+$ ) diaminoborane reacts to produce two new species in labile equilibrium. Boron-11 nmr data allow identification of one of these species as the triaminehydroboron ion,  $\text{HB}(\text{NH}_3)_3^{2+}$ , and suggest that the other is diaminoborane ammine,  $\text{HB}(\text{NH}_2)_2\text{NH}_3$ .

Part I. Kinetics of the Reaction of Ammonium Ion  
with Hydroborate Ion in Liquid Ammonia\*

Introduction

The acid-catalyzed hydrolysis of hydroborate has been thoroughly studied,<sup>1</sup> but little has been reported on the analogous ammonolysis in liquid ammonia. Armstrong<sup>2</sup> studied the reaction



in ammonia from 40 to 70°. The  $\text{BNH}_6$  product was not completely identified. We have investigated the kinetics of this reaction from 25 to 45° using  $\text{NH}_4\text{Br}$  instead of  $(\text{NH}_4)_2\text{SO}_4$ . In addition to obtaining rate constants and the heat of activation, we have determined the effect of ionic strength from  $\mu = 0.01 \text{ M}$  to  $\mu = 1.92 \text{ M}$  and have identified the product as  $\text{BH}_3\text{NH}_3$ .

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\*This work by T. S. Briggs and W. L. Jolly was published in *Inorg. Chem.*, 14, 2267 (1975).

### Experimental Section

Reagent grade ammonium and sodium bromide (dried at 85°) and analytical reagent sodium hydroborate (Ventron) were used. Ammonia was distilled from a sodium solution.

The reactions were carried out in a magnetically-stirred, glass-lined 128-ml Parr general-purpose bomb. This was connected by high pressure fittings to one side of a mercury-containing U-tube manometer. The other side of the manometer was connected to a reference bomb containing pure liquid ammonia. The bombs were held in a thermostated water bath, and the entire apparatus was enclosed in an air bath thermostated at a temperature slightly above that of the water bath. The reaction rates were measured by reading the manometer with the aid of a cathetometer as a function of time.

The ammonia was first distilled into a separate bomb and weighed. The amounts of  $\text{NaBH}_4$ ,  $\text{NH}_4\text{Br}$ , and  $\text{NaBr}$  required to make a solution of predetermined ionic strength were then weighed out into the reaction bomb, and the ammonia was finally distilled into the bomb. Either the  $\text{NaBH}_4$  or the  $\text{NH}_4\text{Br}$  was always in at least a nine-fold excess. After each run, the evolved hydrogen was Toepler-pumped into a gas buret and measured. The pressures measured with the manometer corresponded to the partial pressures of hydrogen gas in the reaction bomb side.

Rate constants were determined from plots of  $\log [(P_\infty - P_t)/P_\infty]$  vs time.

The  $\text{BNH}_6$  product was isolated by removal of ammonia on a vacuum line and extraction of the residue with ethyl ether. Evaporation of the ether left a white, crystalline solid which melted at  $110-113^\circ$ . This melting temperature corresponds to that of  $\text{NH}_3\text{BH}_3$ .<sup>3</sup> Anal. Calcd for  $\text{BNH}_6$ : B, 35.03; N, 45.48. Found: B, 35.24; N, 46.16.

### Results and Conclusions

From  $\log[P_\infty - P]/P_\infty$ -vs-time plots such as that shown in Fig. 1, the reaction of  $\text{NH}_4^+$  with  $\text{BH}_4^-$  was found to be first order in both  $\text{NH}_4^+$  and  $\text{BH}_4^-$ . The second order rate constants calculated from the slopes of such plots for various temperatures are given in Table I. A  $\log k$ -vs- $1/T$  plot of the data, shown in Fig. 2, gives a least-squares heat of activation of  $38.5 \pm 0.6$  kcal/mol. Our data may be compared with those of Gardiner and Collat,<sup>4</sup> who studied the aqueous reaction of  $\text{NH}_4^+$  with  $\text{BH}_4^-$ . They obtained a rate constant of  $2.4 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$  at  $\mu = 1$  and  $25^\circ$  and a heat of activation of  $23 \pm 2$  kcal/mol at  $\mu = 0.5$ . The higher rate constant and lower activation energy of the aqueous reaction may be due to the participation, in the aqueous reaction, of water molecules hydrogen bonded to the ammonium ion. A Grotthuss-type proton transfer such as the following may be involved:

Table I

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Rate Constants in Liquid Ammonia at  $\mu = 0.9$

Temperature, °C	$k$ ( $M^{-1} \text{ sec}^{-1}$ )
25	$5.88 \times 10^{-6}$
30	$1.79 \times 10^{-5}$
35	$5.04 \times 10^{-5}$
40	$1.43 \times 10^{-4a}$
42	$2.17 \times 10^{-4}$
45	$3.40 \times 10^{-4b}$

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<sup>a</sup>Average of  $1.49 \times 10^{-4}$  and  $1.37 \times 10^{-4}$ , from separate experiments.

<sup>b</sup>This value obtained in two experiments.

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Because hydrogen bonding is relatively unimportant in liquid ammonia, the analogous mechanism in ammonia is unlikely.

The Bronsted-Bjerrum theory of ionic reaction leads to the expression

$$\log_{10}(k/k_0) = \frac{2\alpha Z_A Z_B}{1 + \beta \frac{\alpha}{\sqrt{\mu}}}$$

which was applied to rate constants measured at various ionic strengths at 30° (Table II). Using the dielectric constant<sup>5</sup> of 16.5 for ammonia at 30°, we calculated<sup>6</sup>  $\alpha = 5.16$  and  $\beta = 0.711$ . A value for  $\alpha$  of 4.7 Å was used in constructing the Bronsted-Bjerrum plot of the data, shown in Fig. 3. The experimental points at relatively low ionic strengths have a slope close to that predicted by equation 2, whereas the points at higher ionic strengths are low, probably because of the pairing of reactant ions with inert ions. Dewald and Browall<sup>7</sup> correlated rate data for the reaction of the electron with the tri-n-butyl-n-propylammonium ion with the Bronsted-Bjerrum equation using a value for  $\alpha$  of 6 Å.

Table II  
Rate Constants in Liquid Ammonia at 30°

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Ionic Strength	BH <sub>4</sub> <sup>-</sup> , conc., <u>M</u>	NH <sub>4</sub> <sup>+</sup> , conc., <u>M</u>	k ( <u>M</u> <sup>-1</sup> sec <sup>-1</sup> )
0.0098	0.00888	0.00094	2.07x10 <sup>-3</sup>
0.049	0.0446	0.0045	6.23x10 <sup>-4</sup>
0.20	0.1954	0.0046	1.94x10 <sup>-4</sup>
0.90	0.818	0.0818	1.79x10 <sup>-5</sup>
1.92 <sup>a</sup>	0.818	0.0818	4.95x10 <sup>-6</sup>

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<sup>a</sup>NaBr was added to increase the ionic strength.

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Acknowledgement

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## FIGURE CAPTIONS

- Fig. 1. Plot of  $\log [(P_\infty - P)/P_\infty]$  vs time for reactions at  $45^\circ$  and  $\mu = 0.9$ : O from  $0.08 \text{ M } \text{BH}_4^-$  with  $0.82 \text{ M } \text{NH}_4^+$ ;  $\Delta$  from  $0.08 \text{ M } \text{NH}_4^+$  with  $0.82 \text{ M } \text{BH}_4^-$ .
- Fig. 2. Temperature dependence of  $k$  at  $\mu = 0.9$ .
- Fig. 3. Ionic strength dependence of  $k$  at  $30^\circ$ . The line is drawn with the slope given by Eq. 2.

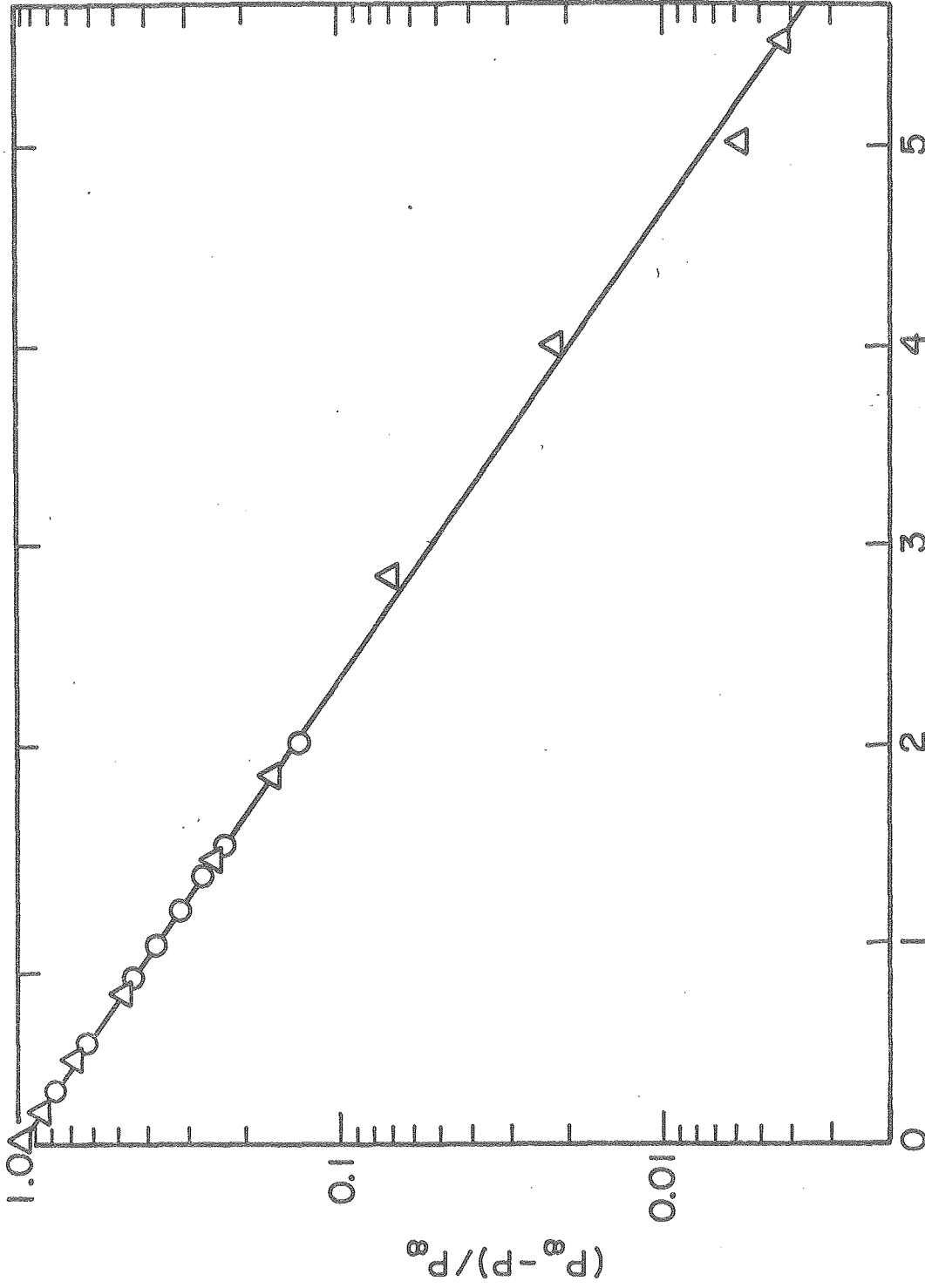


Fig. 1

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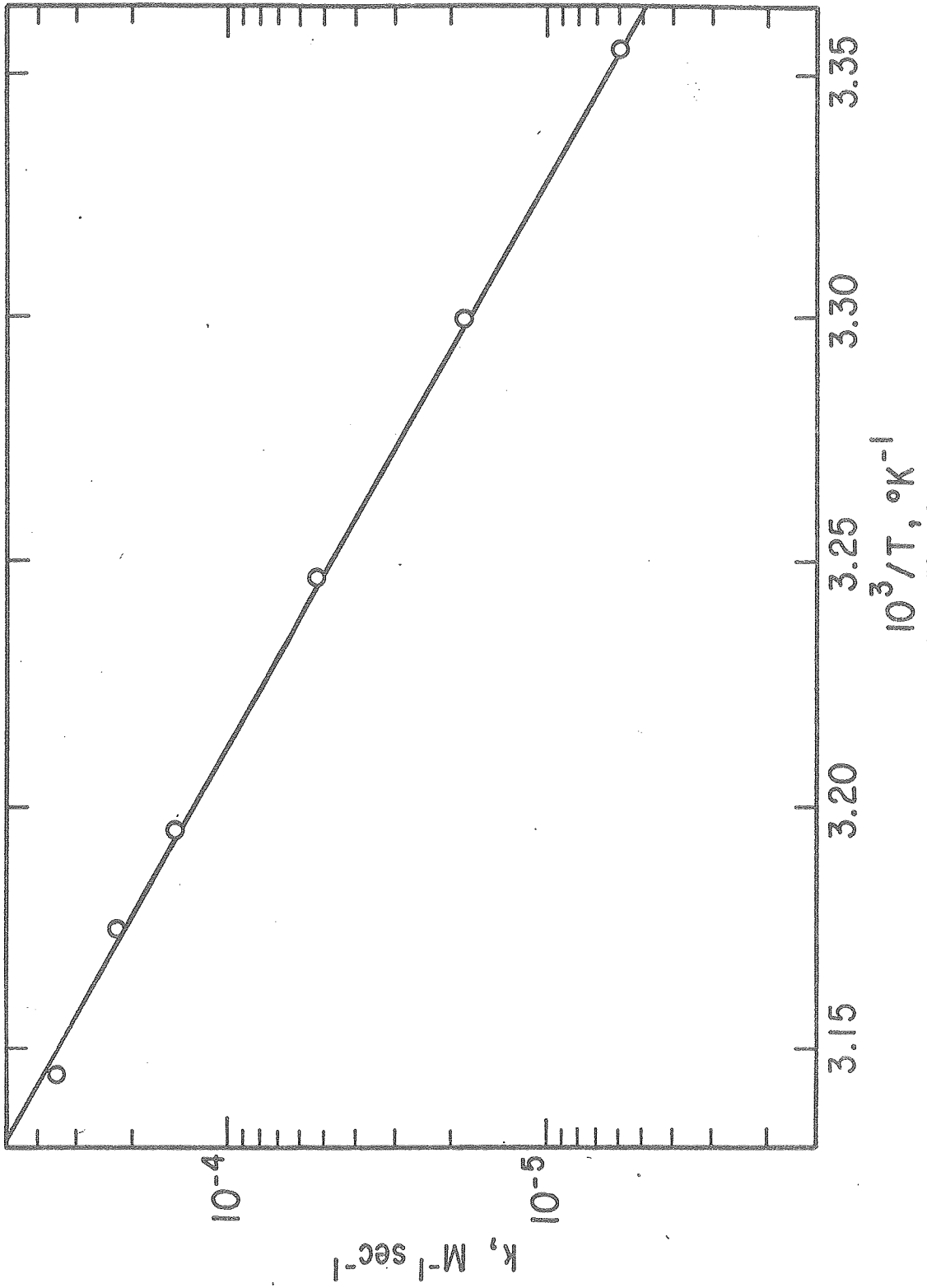


Fig. 2

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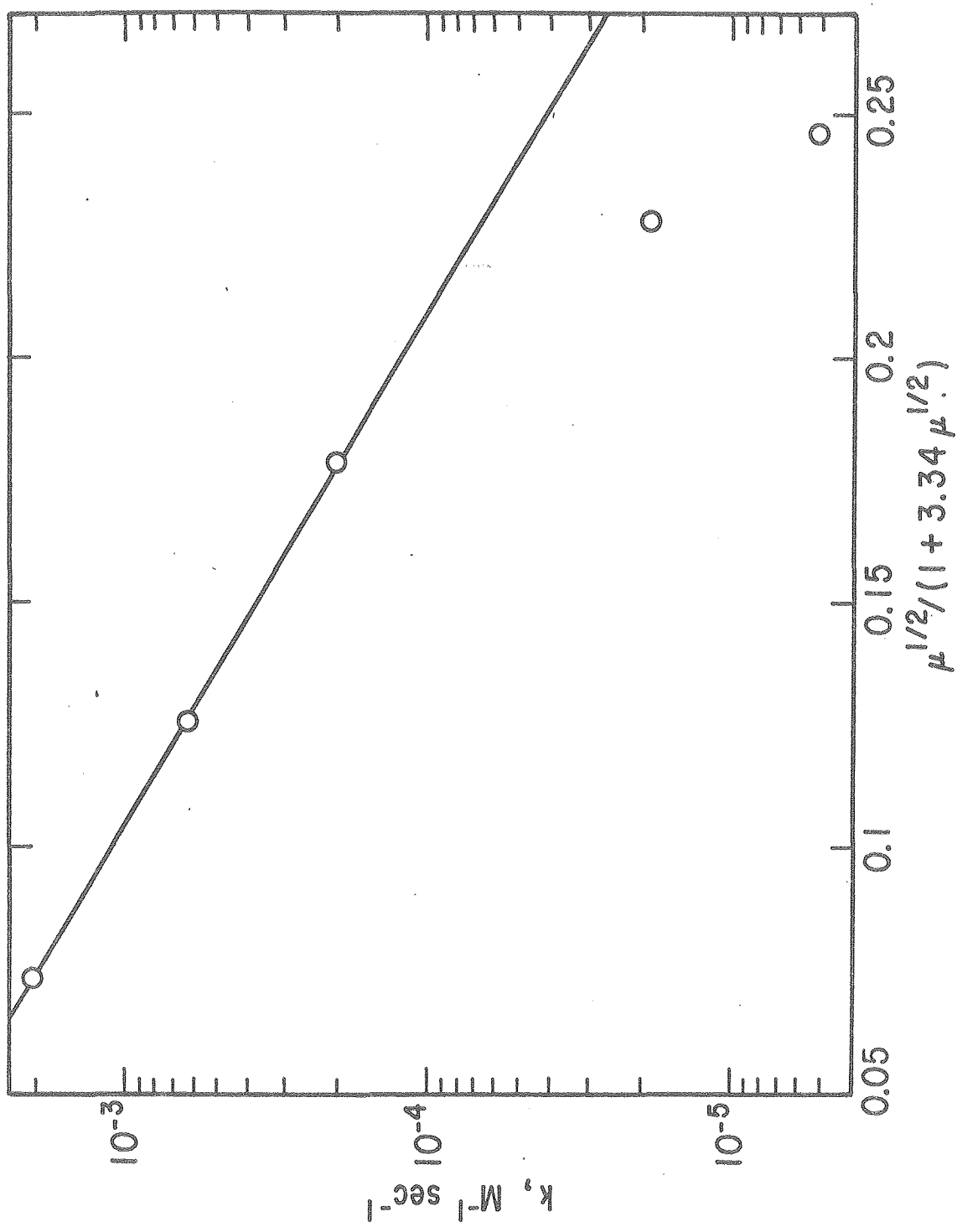


Fig. 3

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## Part II. Improvements in the Synthesis of Borane Ammine

Introduction

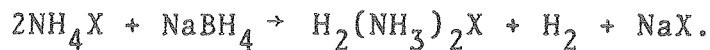
Borane ammine was first characterized by Parry and Shore<sup>1,2</sup> who synthesized this compound by refluxing a solution of  $\text{LiBH}_4$  in ethyl ether with an ammonium salt. A number of additional ways of preparing  $\text{NH}_3\text{BH}_3$  are now known, including reaction of diborane with ammonia,<sup>3</sup> base displacement by ammonia on reactive Lewis salts of  $\text{BH}_3$ ,<sup>4</sup> the decomposition of  $\text{H}_2\text{B}(\text{NH}_3)_2\text{BH}_4$  in ethers<sup>5</sup> and the reaction of  $\text{NaBH}_4$  with  $(\text{NH}_4)_2\text{CO}_3$  in THF.<sup>6</sup> The most convenient bench scale synthesis is the latter because it avoids the use of diborane or exotic reactants and attains a relatively high yield of 80%. Because the reactants in this synthesis are only slightly soluble in THF, a day of stirring with heating is required to complete the reaction.

Attempts to use most ammonium salts in liquid ammonia, ethers, or other inert solvents, give low yields of  $\text{NH}_3\text{BH}_3$  when reacted with hydroborate ion. The synthetic reaction sought after is the symmetric elimination of hydrogen from  $\text{NH}_4\text{BH}_4$ :



While this is the principal reaction in warm, dilute liquid

ammonia solutions,<sup>7</sup> a side reaction to give diamminedi-hydroboron ion<sup>8</sup> occurs in the concentrated solutions or slurries needed to effect a reasonable reaction rate:



We have found that ammonium sulfamate in addition to ammonium carbonate<sup>7</sup> gives high yields of  $\text{NH}_3\text{BH}_3$  at a useful rate. Since  $\text{HN}_4\text{SO}_3\text{NH}_2$  and  $\text{NaBH}_4$  are both soluble in liquid ammonia, this synthesis can be completed in a few hours because homogeneous mixing of the reactants is possible. Also, to readily obtain reasonable yields from a common ammonium salt such as ammonium chloride, we have conducted the  $\text{NH}_3\text{BH}_3$  synthesis in an autoclave in which the ammonia solutions could be relatively warm and dilute.

### Experimental Section

Material-Metal hydrides sodium hydroborate (98%) was used without further purification. All reactants were reagent grade and the ammonia was distilled from sodium.

Procedures - A) An Autoclave Synthesis of Borane Ammine: Working in a nitrogen filled bag, 13.4 grams of ammonium chloride (.25 m) and 9.5 grams of sodium borohydride (.25 m) were placed in a 300 ml pressure bomb and the bomb head screwed on. The bomb was then removed from the bag and the head, fitted with a high pressure valve, torqued tightly in place. Then the bomb was attached to a vacuum line and evacuated to a pressure

of approximately 20 microns. Following evacuation, the bomb, while still attached to the vacuum line, was cooled in a dry ice-acetone bath and 50-60 ml of ammonia dried over sodium metal were distilled into it. The bomb was then sealed and placed in a heating jacket with rocking for 12 hours at 40°.

Upon completion of the reaction, the bomb was vented of accumulated hydrogen and most of the ammonia, and the head was removed in a hood. The product, still moist with ammonia, was then scraped into a cold 500 ml side arm flask and dried of residual ammonia to a vacuum of approximately 100 microns. The product was extracted from the dried powder with successive 200 ml portions of cold, anhydrous diethyl ether and subsequently isolated through the evaporation of the collected ether extract on a rotary evaporator. Extraction was repeated until no significant amount of product was obtained, which, based on the above amounts of starting material, usually consisted of 6-8 extractions. The  $\text{NH}_3\text{BH}_3$  product was in the form of short needle shaped crystals which melted with decomposition in the range of 112 - 118°C. The yield based upon the starting materials as given in this procedure was approximately 4.2 grams - 4.3 grams, or about 55%.



Procedures - B) A Rapid, Ambient Pressure Synthesis of Borane Ammine: Borane ammine was synthesized in a 500 ml round-bottom, three-neck flask, one neck of which was fitted with a paddle stirrer. Another neck was connected through a stopcock to a source of dry ammonia gas and, if desired, nitrogen. In a typical synthesis, the flask was flushed with dry ammonia or nitrogen, and the reactants, 6.5 g  $\text{NH}_4\text{SO}_3\text{NH}_2$  and 1.9 g  $\text{NaBH}_4$ , were added quickly to avoid their absorbing water from the air. The flask was then cooled in a dry ice bath. While stirring the mixture quickly, enough ammonia (about 50 ml) was condensed to dissolve the solids completely. Any undissolved lumps were crushed by a glass rod inserted through one of the necks while the flask was under a positive pressure of ammonia or nitrogen. Next, the dry ice bath was removed, and the flask was allowed to warm. When the ammonia began to boil 300 ml of dry diethyl ether, cooled to  $-30^\circ\text{C}$ , was added. As the vessel warmed, the reaction began at about  $0^\circ\text{C}$  as evidenced by the evolution of hydrogen gas. After two hours, a white, fluffy precipitate of  $\text{NaSO}_3\text{NH}_2$  was filtered off and discarded, and the ether was removed in vacuo with a rotary evaporator to isolate the borane ammine. The yield was typically 70%. The product purity was indicated by its melting point in the range of  $113 - 115^\circ$ .

## Results and Discussion

This investigation resulted in two new methods of preparing borane ammine. They both give a very pure product which melts above 112°C and yields clear, stable solutions in ethyl ether. We note that the literature synthesis using ammonium carbonate gave a product that melted at 108 - 110°C and slowly precipitated a white solid in THF solution.<sup>6</sup> Since this synthesis required 24 hours of stirring above room temperature, it is likely that some decomposition of the product might occur. Moisture from decomposing ammonium carbonate might also lower the purity of this  $\text{NH}_3\text{BH}_3$ .<sup>2</sup> We believe there is a definite advantage in choosing a synthesis that gives a pure product because  $\text{NH}_3\text{BH}_3$  is very difficult to purify. Even sublimation does not raise the melting point of an impure sample above 112°C.<sup>6,9</sup>

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PART III. SYNTHESIS, CHARACTERIZATION,  
AND STRUCTURE OF DIAMINOBORANE

The percentage involvement in the following reprint is 90% for the synthesis of compounds, 55% for the analytic experiments, and 55% for the drafting of the article.

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Synthesis, Characterization, and Structure  
of Diaminoborane

Sir:

Apparently none of the aminoboranes  $BH_x(NH_2)_{3-x}$  has been previously isolated as a stable molecular species at ordinary temperatures. Aminoborane,  $BH_2NH_2$ , is well known in the form of polymers and oligomers, but is unstable as a monomer under ordinary conditions.<sup>1-3</sup> A material having a composition corresponding to triaminoborane,  $B(NH_2)_3$ , can be prepared at low temperatures, but when isolated at ordinary temperatures it loses ammonia to form  $B_2(NH_2)_3$ .<sup>4,5</sup> The only previous claims for the preparation of diaminoborane,  $BH(NH_2)_2$ , were mere postulates to account for the evolution of excess hydrogen in the reaction of alkali metals with the diammoniate of diborane in liquid ammonia.<sup>6-8</sup> However, in these liquid ammonia studies, no attempts were made to isolate or to analyze directly the postulated diaminoborane.

We report here the first preparation and preliminary chemical and structural characterization of  $BH(NH_2)_2$ . Diaminoborane was synthesized by passing a stream of ammonia through molten borane ammine at 125 °C in a coiled-tube reaction vessel designed to minimize foam:

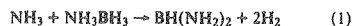


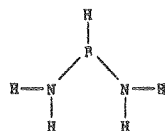
Table I. Rotational Constants for Four Isotopic Species of Diaminoborane

	$^{10}\text{B}(\text{NH}_2)_2$	$^{11}\text{B}(\text{NH}_2)_2$	$^{10}\text{B}(\text{ND}_2)_2$	$^{11}\text{B}(\text{ND}_2)_2$
A, MHz	53752.6 $\pm$ 0.42 <sup>a</sup>	52382.9 $\pm$ 0.47	33035.1 $\pm$ 1.2	32507.6 $\pm$ 2.7
B, MHz	9092.31 $\pm$ 0.074	9093.23 $\pm$ 0.085	7424.7 $\pm$ 0.37	7424.8 $\pm$ 0.87
C, MHz	7777.42 $\pm$ 0.052	7748.59 $\pm$ 0.060	6064.4 $\pm$ 0.37	6045.9 $\pm$ 1.2
$\alpha$	-0.942800	-0.939749	-0.89913	-0.89578
$\Delta$ , amu $\text{Å}^2$	-0.0047 $\pm$ 0.001	-0.0032 $\pm$ 0.001		

<sup>a</sup> Error limits are one standard deviation.

The product and excess ammonia were collected in a  $-196^\circ\text{C}$  trap. The product was then separated from ammonia by fractional condensation in a  $-104^\circ\text{C}$  trap. Yields were 10–17%. Anal. Calcd for  $\text{BN}_2\text{H}_4$ : B, 24.65; N, 63.86; H, 11.49. Found: B, 24.15; N, 60.66; H, 11.60. In the liquid state, diaminoborane decomposes to form a glassy solid with the evolution of ammonia. Hence properties such as the melting point and the vapor pressure of the liquid have not been determined. However, as a vapor the compound can be kept for several days at room temperature with negligible formation of ammonia, and solutions in liquid ammonia appear to be indefinitely stable even at room temperature. No significant mass spectral peaks with  $m/e > 44$  (corresponding to  $^{11}\text{B}(\text{NH}_2)_2$ ) were observed for  $\text{BH}(\text{NH}_2)_2$  or mixtures of  $\text{BH}(\text{NH}_2)_2$  and  $\text{NH}_3$ .

The  $^{11}\text{B}$  NMR spectrum of  $\text{BH}(\text{NH}_2)_2$  in either liquid ammonia or tetrahydrofuran is a 126-Hz doublet, consistent with the structure shown. When either borazine or the glassy



solid from the decomposition of  $\text{BH}(\text{NH}_2)_2$  is dissolved in liquid ammonia, the ultimate products are  $\text{BH}(\text{NH}_2)_2$  and a small amount of  $\text{NH}_3\text{BH}_3$  and  $\text{B}(\text{NH}_2)_3$ .  $^{11}\text{B}$  NMR spectra show that several intermediates are involved in these reactions. The chemical shifts in liquid ammonia of  $\text{BH}(\text{NH}_2)_2$  and  $\text{B}(\text{NH}_2)_3$  are 28.0 and 26.7 ppm downfield of  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ , respectively.

The infrared spectrum of gaseous diaminoborane has not been completely assigned, but several features are clearly evident. There are four strong N–H stretching bands (two at  $3556\text{ cm}^{-1}$  and two at  $3464\text{ cm}^{-1}$ ) and a strong BH stretch at  $2517\text{ cm}^{-1}$ . A preliminary normal coordinate analysis shows the B–N stretching to be highly mixed with the motions of other internal coordinates. Consequently, it is not obvious which of the strong bands at  $1605$  or  $1393\text{ cm}^{-1}$  corresponds to the often cited<sup>9</sup> asymmetric B–N stretch.

A total of 33 rotational transitions in the 8–42-GHz region have been assigned for four different isotopic species of diaminoborane. The spectra are consistent with a slightly asymmetric top having a permanent dipole parallel to the B principal axis. Determination of the line centers is complicated by the splitting due to the nuclear electric quadrupole coupling of the boron and the two nitrogens.

Table I lists the rotational constants based on a least-squares

fit of the transition frequencies. Because of a limited supply of the two perdeuterio species, their rotational constants have not yet been as well determined as those of the normal species. The small negative inertial defect  $\Delta$  strongly suggests a planar  $C_{2v}$  structure for diaminoborane. Using the 12 rotational constants, and assuming a planar structure, a least-squares procedure was used to determine the following bond lengths and angles:<sup>10</sup>  $r_{\text{BN}} = 1.190 \pm 0.02$ ,  $r_{\text{BN}} = 1.419 \pm 0.002$ ,  $r_{\text{NH cis}} = 1.028 \pm 0.01$ ,  $r_{\text{NH trans}} = 0.983 \pm 0.01$   $\text{Å}$ ;  $\angle\text{NBN} = 121.95 \pm 0.1$ ,  $\angle\text{BNH (cis)} = 117.5 \pm 2.0$ , and  $\angle\text{BNH (trans)} = 125.0 \pm 2.0^\circ$ . There are large error limits for the two BNH angles because they are highly correlated. The rotational constants of unsymmetrically deuterated species are being determined since they substantially reduce this correlation and the other error limits. The 1.42- $\text{Å}$  BN bond length is between the single-bond length of 1.54  $\text{Å}$  and double-bond length of 1.36  $\text{Å}$ . This indicates substantial  $\pi$  bond character in the NBN framework. The other bond lengths are typical.

From Stark splitting data, the dipole moment is found to be  $1.25 \pm 0.01$  D (OCS taken as 0.71521) and is coaxial with the B–H bond. The sign of the dipole moment has not been determined.

**Acknowledgments.** This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (T.S.B. and W.L.J.), and the National Science Foundation (W.D.G. and L.R.T.)

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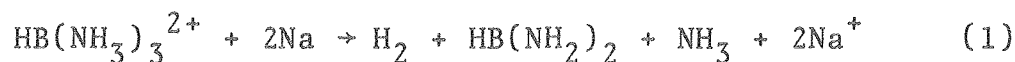
PART IV. BORON-11 STUDIES OF THE REACTION OF  
DIAMINOBORANE WITH AMMONIUM ION IN LIQUID AMMONIA

## ABSTRACT

In liquid ammonia solutions of ammonium iodide (0.1-1.0 M  $\text{NH}_4^+$ ) diaminoborane reacts to produce two new species in labile equilibrium. Boron-11 nmr data allow identification of one of these species as the triamminehydroboron ion,  $\text{HB}(\text{NH}_3)_3^{2+}$ , and suggest that the other is diaminoborane ammine,  $\text{HB}(\text{NH}_2)_2\text{NH}_3$ .

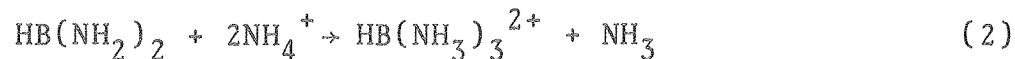
### Introduction

Triamminehydroboron cation,  $\text{HB}(\text{NH}_3)_3^{2+}$ , has been postulated by Parry<sup>1</sup> as a product in ammonia solutions of diaminedihydroboron (+1) hydroborate,  $\text{H}_2\text{B}(\text{NH}_3)_2\text{BH}_4$ , that have been allowed to become warm. Part of the evidence for this cation consisted of measurements of the hydrogen liberated when sodium was added to  $\text{H}_2\text{B}(\text{NH}_3)_2\text{BH}_4$ -ammonia solutions that had aged at  $-40^\circ\text{C}$  for 20 or more hours<sup>1</sup> or to solutions resulting from the rapid addition of diborane to ammonia.<sup>2</sup> Parry and Shore proposed the following equation for the reaction with sodium:



They also found that the molecular weight of aged  $\text{H}_2\text{B}(\text{NH}_3)_2\text{BH}_4$  solutions in ammonia was consistent with  $\text{HB}(\text{NH}_3)_3(\text{BH}_4)_2$ .<sup>3</sup> Relatively unreactive tris(alkylamine or pyridine) hydroboron cations are known,<sup>4,5</sup> but no additional work on  $\text{HB}(\text{NH}_3)_3^{2+}$  has been reported.

Our boron-11 studies of  $\text{HB}(\text{NH}_2)_2$  solutions in ammonia acidified with ammonium ion give strong support for the formation of  $\text{HB}(\text{NH}_3)_3^{2+}$  by the following reaction:



We have detected signals corresponding to  $\text{HB}(\text{NH}_3)_3^{2+}$  and  $\text{HB}(\text{NH}_2)_2$ , and to an additional intermediate boron compound in labile equilibrium. The concentrations of ammon-

ium ion and  $\text{HB}(\text{NH}_2)_2$  were varied in an attempt to determine the formulas of the species involved by measurement of their equilibrium concentrations.

### Experimental

Materials: Reagent grade  $\text{NH}_4\text{I}$  and  $\text{KI}$  were stored in a vacuum desiccator to remove any traces of moisture and iodine. The  $\text{NH}_3\text{BH}_3$  was prepared by a method similar to that of Hu, Van Paasschen, and Geanangle<sup>6</sup> and was recrystallized from ethyl ether. Diaminoborane was prepared and purified as previously described,<sup>7</sup> and was used without delay.

Sample Tubes: Vacuum ball joints were sealed to 10-mm o.d. nmr tubes and the tubes were loaded with carefully weighed solid reagents. About 1 ml of liquid ammonia containing 10% deuterium was condensed in these tubes to dissolve the solid reagents. After a measured volume of  $\text{HB}(\text{NH}_2)_2$  vapor was condensed (frozen with liquid nitrogen) in these tubes, additional ammonia-deuteroammonia was condensed on the contents and the temperature was allowed to rise to  $-35^\circ\text{C}$ . Temperature control was maintained by raising a stirred bath in a clear glass dewar around the vertical tube. The final level in a tube was accurately measured with a cathetometer and compared with volume-to-height ratios previously determined for 7PP 10-mm nmr tubes. The tubes were then sealed with a glass torch,



and the samples were stored at  $-30^{\circ}\text{C}$  until their spectra were obtained. No precipitates were observed in the tubes. When we wished to change the equilibrium concentration in the nmr tubes, they were warmed to room temperature so that some of the  $\text{HB}(\text{NH}_2)_2$  vapor would deposit condensation products on the dry surface of the tube. This was accomplished without the danger of the tubes bursting from ammonia pressure by use of an autoclave. The pressure in the steel autoclave was balanced by first adding 50 ml of liquid ammonia before loading with nmr tubes. If the tubes were not inverted, significant loss of  $\text{HB}(\text{NH}_2)_2$  from solution occurred after 3 days at room temperature.

NMR Spectra: The boron-11 spectra were recorded at 57.78 MHz on a FT spectrometer with a Nicolet 1180 data system. Deuterated ammonia provided the signal for the internal lock. The boron-11 relaxation time was found to be 1-2 seconds for the compounds in these solutions.

Results and Discussion

Our experimental data for samples held at  $-30^{\circ}\text{C}$  are given in Table I. The boron-11 nmr spectra show a doublet at 28.0 ppm downfield of  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$  due to  $\text{HB}(\text{NH}_2)_2$ ,<sup>7</sup> a quartet at 23.0 ppm upfield of  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$  due to the  $\text{NH}_3\text{BH}_3$  reference and one or both of two overlapping doublets centered at 7.1 and 9.0 ppm upfield of  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ . In addition, there was a very broad signal centered 2.0-4.0 ppm upfield of  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ , unresolvable from the base line, due to boron in the Pyrex probe insert. The doublets at -7.1 ppm and -9.0 ppm are within the region corresponding to tetrahedral boron atoms.<sup>9</sup> (A negative chemical shift denotes a resonance at higher field than the reference.<sup>10</sup>) Some of the samples in Table I had the concentration of boron decreased by allowing the nmr tubes to stand at room temperature. This decrease was the result of the deposition of thin films of glassy solid from  $\text{BH}(\text{NH}_2)_2$  vapor<sup>7</sup> on the nmr tube above the solution and, to a lesser extent, the appearance of new boron compounds in the nmr spectra. The principle new species was identified as  $\text{H}_2\text{B}(\text{NH}_3)_2^+$  from its chemical shift of -14.6 ppm and its coupling constant of 120 Hz.<sup>11</sup> Spectra taken at various temperatures showed that none of the compounds resulting from heating the nmr tubes

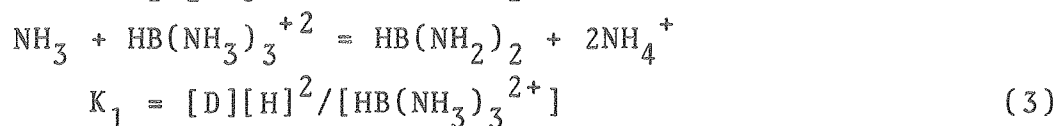
were in labile equilibrium with the compounds originally present at  $-30^{\circ}\text{C}$ .

We obtained the boron concentrations reported in Table I by integration over a range sufficient to count the nuclei present in the  $\text{HB}(\text{NH}_2)_2$  signal, the tetrahedral boron signal, the  $\text{NH}_3\text{BH}_3$  signal, and, if present, the  $\text{H}_2\text{B}(\text{NH}_3)_2^+$  signal. The absolute boron concentrations for these signals were calculated from the integrated spectra using the known concentrations of  $\text{NH}_3\text{BH}_3$ . Repeated spectra taken on an undisturbed sample (#4C) gave a maximum difference in the integration of this data of  $\pm 13\%$ . This large uncertainty may be caused by the broadness of the signals from boron bonded to more than one nitrogen and the need to integrate over a boron background signal. Additional uncertainty existed with some samples because they had only a small concentration of tetrahedral boron. Increasing the signal to noise ratio increased the errors due to the integration of lines of different widths.<sup>12</sup>

The boron-11 nmr spectra of samples #2A and #3A (Table I) were studied at  $-30^{\circ}\text{C}$ ,  $-45^{\circ}\text{C}$  and  $-60^{\circ}\text{C}$  and are shown in Fig. 1. We assign the doublet at  $-9.0$  ppm ( $J = 111$  Hz) to a species  $\text{T}_1$  and the doublet at  $-7.1$  ppm ( $J = 118$  Hz) to a species  $\text{T}_2$ . We observed that the concentration of  $\text{T}_1$  increases at the expense of the

concentrations of  $\text{HB}(\text{NH}_2)_2$  and  $T_2$  when the temperature of the solution is lowered. On returning the samples to  $-30^\circ\text{C}$  the concentrations originally observed at  $-30^\circ\text{C}$  are once again present. This reversible temperature-dependent behavior is evidence for a labile equilibrium involving  $\text{HB}(\text{NH}_2)_2$ ,  $T_1$  and  $T_2$ . The corresponding concentration changes are given in Table II. Because the signal for  $T_1$  overlaps the signal for  $T_2$ , the concentration of tetrahedral boron in Table II is for the sum,  $T_1 + T_2$ .

In order to determine the concentrations of the boron species to permit quantitative study of  $\text{HB}(\text{NH}_2)_2$ ,  $T_1$  and  $T_2$ , it is necessary to select possible formulas for  $T_1$  and  $T_2$ . Then equations can be written for the equilibria observed in the spectra and the integration data from these can be used to obtain concentrations in these equilibria. We assume that one equilibrium ( $K_1$ ) involves  $\text{HB}(\text{NH}_2)_2$ ,  $\text{NH}_4^+$ , and  $T_2$ , and that another ( $K_2$ ) involves  $\text{HB}(\text{NH}_2)_2$ ,  $\text{NH}_4^+$ , and  $T_2$ . For example, if we assume the following equilibria, in which D represents  $\text{HB}(\text{NH}_2)_2$ , H represents  $\text{NH}_4^+$ ;  $\text{HB}(\text{NH}_3)_3^{2+}$  represents  $T_1$ , and  $\text{HB}(\text{NH}_2)_2\text{NH}_3$  represents  $T_2$ , we have:





$$K_2 = [\text{D}]/[\text{HB}(\text{NH}_2)_2\text{NH}_3]. \quad (4)$$

If other possible formulas for  $T_1$  or  $T_2$  are considered, equilibrium equations for  $K_1$  or  $K_2$  can be written in a similar manner, with  $\text{HB}(\text{NH}_2)_2$ , and, if present,  $\text{NH}_4^+$ , being products of the equilibria. For a particular pair or assumed equilibria, it is possible to express the total concentration of tetrahedral boron species,  $T_1 + T_2$ , in terms of the equilibrium constants,  $K_1$  and  $K_2$ ,  $\text{NH}_4^+$  and  $\text{HB}(\text{NH}_2)_2$ . Solving for  $[T_1 + T_2]$  using  $a$ ,  $b$ ,  $m$ , and  $n$  for specific exponents:

$$[T] = [T_1 + T_2] = [\text{D}]^m[\text{H}]^a/K_1^b + [\text{D}]^n[\text{H}]^b/K_2$$

which gives:

$$1 = [\text{D}]^m[\text{H}]^a/[T]K_1 + [\text{D}]^n[\text{H}]^b/[T]K_2 \quad (5)$$

This expression is of the form  $1 = x/K_1 + y/K_2$  when  $[\text{D}]^m[\text{H}]^a/[T]$  and  $[\text{D}]^n[\text{H}]^b/[T]$  are the respective  $x$  and  $y$  variables. The values of  $K_1$  and  $K_2$  are found from computing the least square slopes and intercepts of plots of the above  $x$  and  $y$  variables using the data in Table I (11 points per choice of  $T_1$  and  $T_2$  formula). We made appropriate corrections for the final ammonium ion concentration by deconvoluting the tetrahedral boron signal (Table III) and using the deconvoluted concentrations

for  $T_1$  and  $T_2$  in equation (6):

$$[\text{NH}_4^+]_{\text{final}} = [\text{NH}_4\text{I}] - a[T_1] - b[T_2]. \quad (6)$$

The error in the ammonium ion concentration caused by errors in  $[T_1]$  or  $[T_2]$  is small because the initial  $[\text{NH}_4^+]$  is relatively large. A typical plot of equation 5 in which  $T_1$  is represented by  $\text{HB}(\text{NH}_3)_3^{2+}$  and  $T_2$  is represented by  $\text{HB}(\text{NH}_2)_2\text{NH}_3$  is shown in Fig. 2.

Plots of expression Eq. (5) reveal too great a scatter of points to provide precise values for  $K_1$  and  $K_2$ , probably because of uncertainties in integrated areas of broad boron-11 signals; however, they favor a definite formula for  $T_1$  and narrow the possibilities for  $T_2$ . Certain formulas for  $T_1$  and  $T_2$  are shown to be clearly impossible when equation (5) is applied to the eleven samples in Table I. For  $T_1$ , neutral formulas and formulas having a single positive charge give negative (impossible) least-square intercepts when calculated with any conceivable formulas for  $T_2$ . Consequently,  $T_1$  is taken to be  $\text{HB}(\text{NH}_3)_3^{2+}$ . For  $T_2$  we tried  $\text{HB}(\text{NH}_2)_2\text{NH}_3$ ,  $[\text{HB}(\text{NH}_2)_2]_2$ ,  $[\text{HB}(\text{NH}_2)_2]_3$ ,  $[\text{HB}(\text{NH}_2)_2]_4$ ,  $\text{HB}(\text{NH}_3)_2\text{NH}_2^+$ ,  $[\text{HB}(\text{NH}_2)_2]_2\text{H}^+$ ,  $[\text{HB}(\text{NH}_2)_2]_3\text{H}^+$ ,  $[\text{HB}(\text{NH}_2)_2]_4\text{H}^+$ ,  $[\text{HB}(\text{NH}_2)_2]_2\text{H}_2^{2+}$ , and  $[\text{HB}(\text{NH}_2)_2]_3\text{H}_2^{2+}$ . The best plots were obtained for  $\text{HB}(\text{NH}_2)_2\text{NH}_3$  and  $[\text{HB}(\text{NH}_2)_2]_2$ . The former gave  $K_1 = 0.16$ ,  $K_2 = 1.8$ , correlation coefficient = 0.82, and the latter gave  $K_1 = 0.16$ ,  $K_2 = 0.24$ , and correlation coefficient = 0.84.

Previous studies on electrolyte-free liquid ammonia solutions of  $\text{HB}(\text{NH}_2)_2$ <sup>7</sup> are useful in deducing the formula of  $\text{T}_2$ . The signal for  $\text{T}_2$  is, as precisely as can be determined, identical in chemical shift and coupling constant to the signal observed in liquid ammonia solutions of a glassy solid formed by the decomposition of pure  $\text{HB}(\text{NH}_2)_2$  at  $-78^\circ\text{C}$  (Fig. 3). The tetrahedral signal in these solutions of glassy solid slowly disappears at  $-30^\circ\text{C}$  (after days) and the signal for  $\text{HB}(\text{NH}_2)_2$  grows sufficiently to account for the boron. Since the single tetrahedral signal and the  $\text{HB}(\text{NH}_2)_2$  signal are not accompanied by any other signal that could be attributed to a boron anion, and no electrolytes are initially present, we infer that the tetrahedral boron species in solutions of glassy solid is a neutral molecule that is identical to  $\text{T}_2$ . Substitution of the concentrations of  $\text{T}_2$  obtained by deconvoluting the tetrahedral boron-11 nmr signal from the first ten samples as listed in Table III into the equilibrium equations yielding  $K_2$  gives a mean value of  $K_2$  (1.2) that is in closest agreement with that obtained by the above analysis when  $\text{T}_2$  is assumed to be  $\text{HB}(\text{NH}_2)_2\text{NH}_3$  (1.8). Thus, the mean value of  $K_2$  obtained by assuming that  $\text{T}_2$  is  $\text{HB}(\text{NH}_2)_2\text{NH}_3$  is 1.2 while the mean value of  $K_2$  obtained by assuming that  $\text{T}_2$  is  $[\text{HB}(\text{NH}_2)_2]_2$  is 0.082, a value significantly less than the value of 0.24 obtained from equation (5). However, with two amino groups

capable of donating charge to the boron atom, the coordination to the ammonia should be quite weak. This molecule has not been observed by us in P-V measurements or mass spectral studies on gas phase  $\text{HB}(\text{NH}_2)_2\text{-NH}_3$  mixtures.<sup>7</sup>

Other possible formulas for the species  $\text{T}_2$  include the neutral dimer,  $[\text{HB}(\text{NH}_2)_2]_2$ , which gives a correlation coefficient similar to that of  $\text{HB}(\text{NH}_2)_2\text{NH}_3$ . Some analogous boron molecules include the dimer of  $(\text{C}_6\text{H}_5)_2\text{BNH}_2$ <sup>14</sup> and the dimer of  $(\text{CH}_3)_2\text{NBH}_2$ .<sup>15</sup> However, we have observed in previous work<sup>7</sup> and in this investigation the rapid ammonolysis of one of the most stable boron-nitrogen oligomers, borazine, to give this equilibrium with  $\text{HB}(\text{NH}_2)_2$ . This suggests that species with more than one boron atom are unstable in liquid ammonia, and we suspect that the species  $\text{T}_2$  is  $\text{HB}(\text{NH}_2)_2\text{NH}_3$ .



## References (Part IV)

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Table I  
 Boron concentrations from integration of  
 boron-11 nmr spectra at  $-30^{\circ}\text{C}$

Tube	$\text{NH}_4\text{I}$ (initial)	$\text{NH}_3\text{BH}_3$	Special Treatment	$\text{BH}(\text{NH}_2)_2$	Tetrahedral boron
1A	0.100 <u>M</u>	0.0502 <u>M</u>	a	0.0575 <u>M</u>	0.0285 <u>M</u>
2A	0.259	0.0867		0.0587	0.0759
2B	0.259	0.0867	b	0.0424	0.0311
2C	0.259	0.0867	c	0.0203	0.0187
3A	0.456	0.0921	d	0.0463	0.0807
4A	0.654	0.0938		0.0404	0.0939
4B	0.654	0.0938	b	0.0232	0.0650
4C	0.654	0.0938	c, e	0.0131	0.0531
5A	0.959	0.0963	d	0.0191	0.0804
5B	0.959	0.0963	c, f	0.0142	0.0759
6A	1.00	0.101		0.0180	0.0849

- a) This solution was also 0.400 M in KI.  
 b) The above sample was held for 3 days at  $22^{\circ}\text{C}$ .  
 c) The above sample was held for 3 days at  $22^{\circ}\text{C}$  and 2 weeks at  $-35^{\circ}\text{C}$ . Except for tube 4C, this treatment produced measurable  $\text{H}_2\text{B}(\text{NH}_3)_2^+$  (about 0.005 M).  
 d) Quartz nmr tube.  
 e) Average of 3 runs on this sample.  
 f) Tube inverted after heating at  $22^{\circ}\text{C}$ .

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Table II  
Boron concentrations from integrated spectra of  
samples at lowered temperatures

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Tube	Temperature	$\text{HB}(\text{NH}_2)_2$	Tetrahedral boron
2A	-45°C	0.0412 <u>M</u>	0.0856 <u>M</u>
3A	-45°C	0.0286	0.0898
3A	-60°C	0.0159	0.0991

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Table III  
Deconvoluted boron-11 nmr concentrations for  
boron in T<sub>1</sub> and T<sub>2</sub> at -30°C

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Tube	[B] from T <sub>1</sub>	[B] from T <sub>2</sub>
1A	a	0.029 <u>M</u>
2A	0.002 <u>M</u>	0.074
2B	0.008	0.023
2C	0.006	0.013
3A	0.040 <sup>b</sup>	0.040 <sup>b</sup>
4A	0.056	0.038
4B	0.039	0.026
4C	0.023	0.030
5A	0.067	0.013
5B	0.063	0.013
6A	0.085	c

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a) Less than 0.001 M

b) Estimate from plot

c) Less than 0.01 M

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## FIGURE CAPTIONS (Part IV)

- Fig. 1. Boron-11 nmr spectra of  $\text{HB}(\text{NH}_2)_2\text{-NH}_4\text{I}$  solutions in liquid ammonia showing reversible equilibria. The doublet at 28 ppm is due to  $\text{HB}(\text{NH}_2)_2$  and the quartet at -24 ppm is due to the  $\text{NH}_3\text{BH}_3$  added as an internal reference. The concentrations in samples 2A and 3A are given in Table 2. The doublet at -7 ppm (2A at  $-30^\circ\text{C}$ ) is assigned to a species  $\text{T}_2$  and the doublet at -9 ppm (3A at  $-60^\circ\text{C}$ ) is assigned to the cation  $\text{HB}(\text{NH}_3)_3^{2+}$ .
- Fig. 2. Application of equation (5) to 11 boron-11 nmr spectra (#1A - #6A).  $K_2$  is the constant for the equilibrium  $\text{HB}(\text{NH}_2)_2\text{NH}_3 = \text{HB}(\text{NH}_2)_2 + \text{NH}_3$ .  $K_1$  is the constant for the equilibrium  $\text{NH}_3 + \text{HB}(\text{NH}_3)_3^{2+} = \text{HB}(\text{NH}_2)_2 + 2\text{NH}_4^+$ .
- Fig. 3. Ammonia solution of condensation product formed by allowing  $\text{HB}(\text{NH}_2)_2$  liquid to stand at  $-78^\circ\text{C}$  recorded at  $-30^\circ\text{C}$  by boron-11 nmr. The doublet at 28.0 ppm is due to  $\text{HB}(\text{NH}_2)_2$  and the doublet at -7 ppm may correspond to a species  $\text{T}_2$  found in acidic ammonia solutions of  $\text{HB}(\text{NH}_2)_2$ .

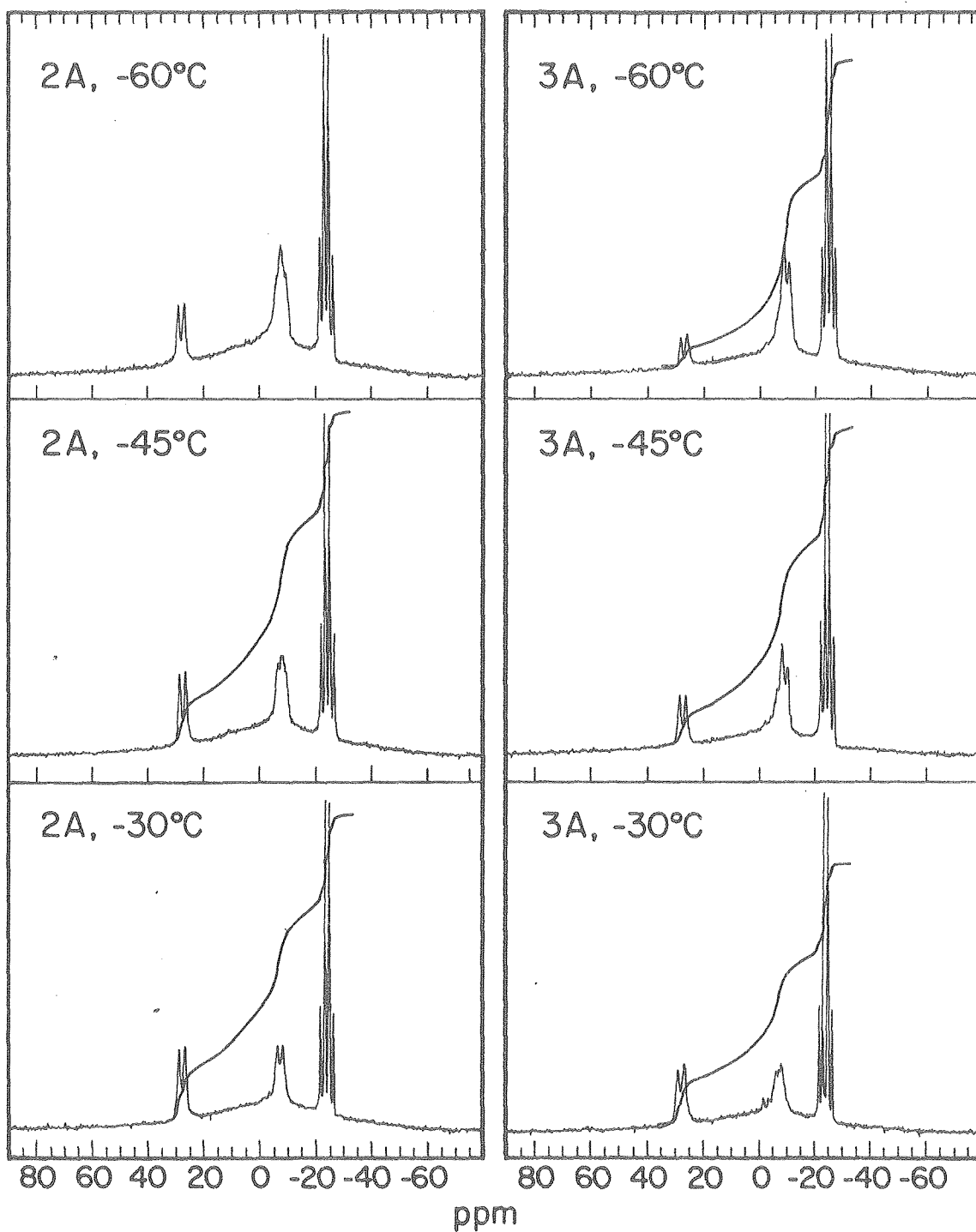


Fig. 1

XBL 8010-12280

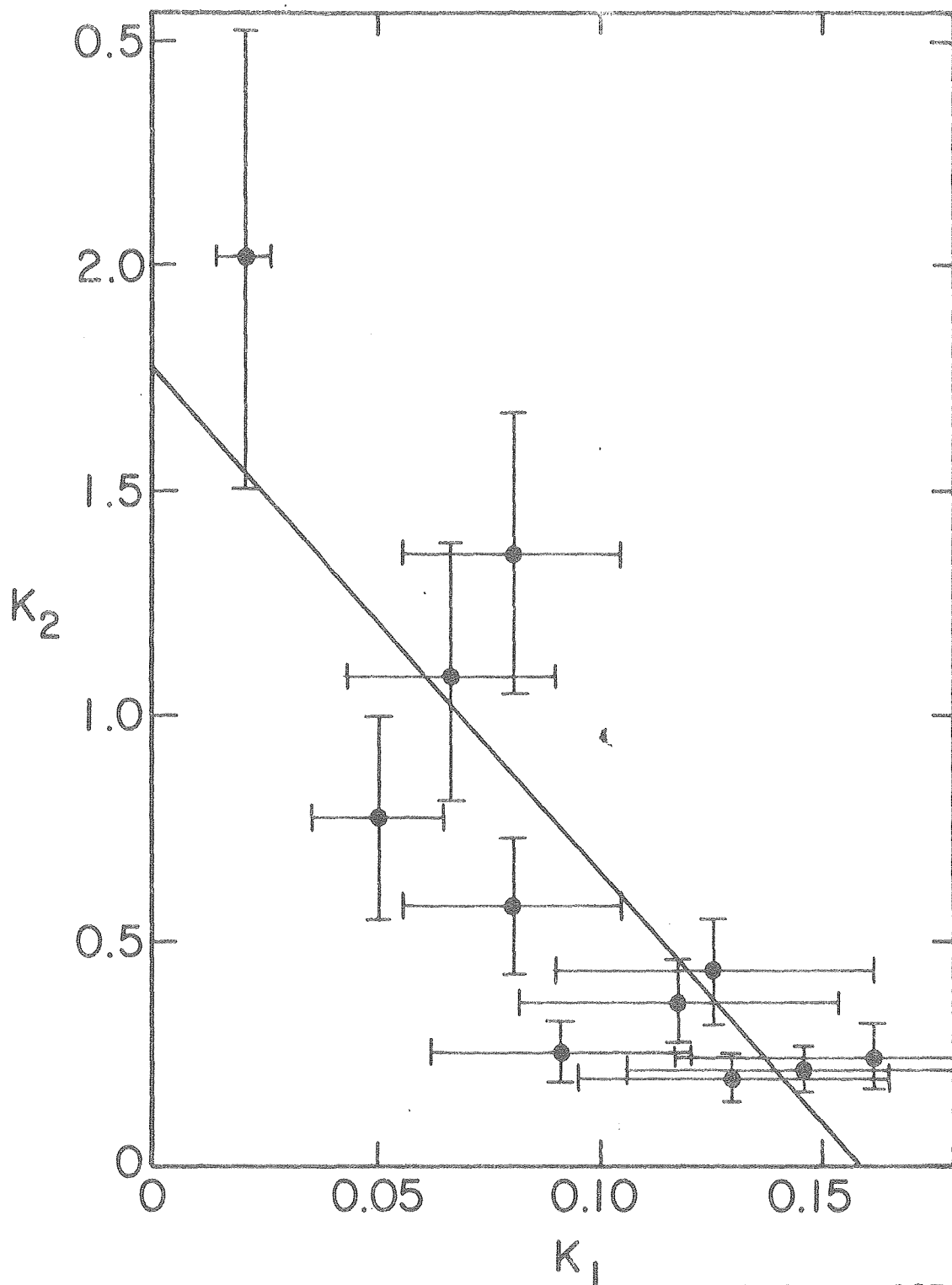


Fig. 2

XBL 8010-12279



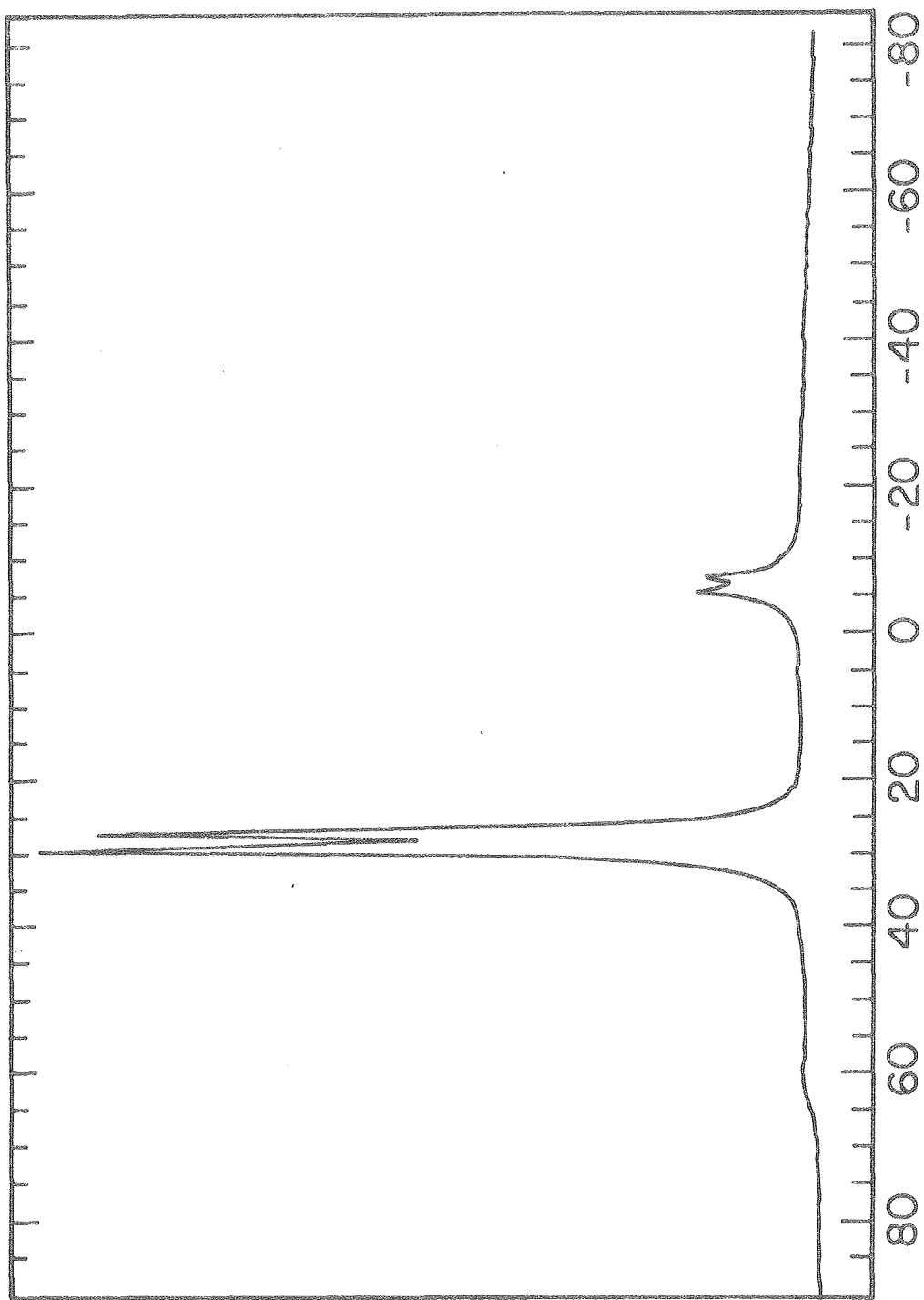


Fig. 3

XBL 8010-12286

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